ELECTROCHEMICALLY INITIATED CYANOMETHYLATIONS

by

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To Angela and my parents
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DECLARATION

I declare that this thesis is of my own composition and describes my own work. Where the work of other authors is referred to this is clearly indicated.

The thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Dr. A.J. Bellamy between 1st October 1975 and 30th September 1978. In conjunction with this work, the following paper has been published:


During the period of this study, I attended the following courses and conferences:

Chemistry of the Atmosphere by Dr. R.J. Donovan and Dr. M.F. Golds, (1 unit).
Nmr Spectroscopy by Dr. Harris, (1 unit).
Electrode Reactions by Dr. W.D. Cooper and Dr. A.J. Bellamy, (1 Unit).
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ABSTRACT

The results of preparative electrolyses in acetonitrile containing tetraalkylammonium salts have confirmed that the hydrodimerisation of cinnamnonitrile, benzaldehyde and acrylonitrile by electro-reduction at low current densities can be used to initiate the nucleophilic cyanomethylation of these compounds. The cyanomethylated adducts, once formed, are capable of regenerating \( \text{CH}_2\text{CN} \) by further proton abstraction. Compounds such as benzophenone and \( \text{3-phenylcinnamnonitrile} \) which have stable radical-anions cannot be cyanomethylated in this way in pure acetonitrile. The effects on the yield of cyanomethylated products of temperature, concentration of the electroactive species, the presence of acids, water and alkali metal cations, and the use of an undivided cell have been investigated.

The results of linear sweep voltammetry (LSV) have shown that the presence of azopyridines in solutions of benzophenone, benzaldehyde or acrylonitrile decreases the peak current of each of these substrates, whereas no significant decrease is obtained for cinnamnonitrile or \( \text{3-phenylcinnamnonitrile} \). Using LSV, it was found that electro-reduced azo compounds in super-dry acetonitrile deprotonate the solvent in a reversible reaction; cyanomethylation of the substrates explains the decreases in peak current.

Computer simulation of the voltammetric experiment revealed that the chemical stability of the radical-anion of the substrate has only a small effect on the peak current while the decrease in the peak current is much larger if regeneration of the nucleophilic species occurs. Working curves were produced from which could be estimated the 2nd-order rate constant, \( k_2 \), for the reaction of an electrochemically generated nucleophilic species with the electroactive
substrate: $k_2$ for cyanomethylation of benzophenone = 600 lmol$^{-1}$s$^{-1}$.

Preparative electrolyses of benzenesulphonylacetonitrile in DMF in the presence of acrylonitrile yielded glutaronitrile, adiponitrile and propionitrile; possible mechanisms have been discussed. Cyanomethylated products were not detected in the electroreduction in DMF of benzenesulphonylacetonitrile in the presence of either acetophenone or 3-methylcinnamonicnitrile. LSV indicated that alkyl aryl ketones undergo nucleophilic addition by a species formed during the electroreduction of benzenesulphonylacetonitrile in DMF.
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CHAPTER 1

General Introduction to Nucleophilic Electro-Orgnic Reaction Mechanisms

Electroreduction of organic molecules

The transfer of an electron to a neutral organic compound produces a radical anion. If a second electron is transferred then a dianion is formed. Both of these species can act as nucleophiles or as bases while the radical anion can also undergo radical reactions. A further possibility is that both of these species can transfer an electron to other species present in the solution.

The initial transfer of electrons can be carried out by a reducing agent or at a cathode. The latter has the advantage that the reduction potential can be varied easily and can be closely controlled while monitoring the current. A great variety of experimental techniques e.g. polarography, cyclic voltammetry, coulometry and potential-step coulometry, enable the electrochemist to obtain much information about reduction (and oxidation) mechanisms. There are several books and review articles which adequately describe these techniques and the information they provide.\(^1,2(a),3,4,5\)

Electrochemistry can therefore be used to prepare radical-anions and dianions, and also to study their reactions. Often the presence of anionic species has been demonstrated by the effect which added acid has on both the product distribution and the electroanalytical results; this illustrates the basicity of these reduced species. There are several early examples of electro-reduced species being trapped with electrophiles and there are also reports of anionic polymerisations being initiated by electro-
Recently there has been an awakening of interest in the potential of these species in organic syntheses, most notably by Baizer and co-workers on hydrodimerisation. Allied with this has been an increase in the number of mechanistic studies of electro-organic coupling reactions. Hydrodimerisation has been shown, generally, to involve radical coupling of two radical anions rather than Baizer's original suggestion of nucleophilic attack by a radical anion on the parent compound. However, in many cases there is still some doubt as to whether a radical or a nucleophilic mechanism is involved, e.g. the crossed hydrocoupling reactions in aqueous sulphuric acid for which Nonaka and Sugino, supported by Suzuki and co-workers, favour a nucleophilic mechanism, while Brown and Lister have advocated an adsorbed radical mechanism.

Since most of the work to be described in the Discussion section involves nucleophilic reaction mechanisms, this chapter will review those electro-organic reactions which have been cited as involving mechanisms of this type. As well as reactions of nucleophilic species produced directly by electroreduction, other examples will be included in which the basicity of a reduced species, such as the azobenzene dianion, has been used to generate other nucleophilic species by deprotonation.

**Electrochemically generated superoxide ion**

In 1970, Dietz and co-workers showed that, in aprotic solvents, the electrochemically generated superoxide ion (I) could be used as a nucleophile. Reduction of oxygen in the presence of primary or secondary alkyl halides yielded the dialkyl peroxides...
by nucleophilic substitution (see Scheme 1). Dibutyl peroxide was formed with 79% current efficiency at a mercury cathode in acetonitrile.

\[
\text{(i)} \quad O_2 \xrightarrow{e} O_2^\cdot
\]

\[
\text{(I)}
\]

\[
\text{(ii)} \quad O_2^\cdot + Bu^\text{nBr} \rightarrow Bu^{\text{n}O_2}^\cdot + Br^-
\]

\[
\text{(iii)} \quad Bu^{\text{n}O_2}^\cdot \xrightarrow{e} Bu^{\text{n}O_2^-} \text{ (electrode)}
\]

\[
\text{(iv)} \quad Bu^{\text{n}O_2}^\cdot + O_2^\cdot \rightarrow Bu^{\text{n}O_2^-} + O_2 \text{ (disproportionation)}
\]

\[
\text{(v)} \quad Bu^{\text{n}O_2^-} + Bu^\text{nBr} \rightarrow Bu^{\text{n}O_2Bu^\text{n} + Br^-}
\]

Scheme 1

Disproportionation (iv) rather than electrode reduction (iii) was shown to be the main reaction pathway. With tertiary alkyl halides elimination was the predominant reaction.

\[
\begin{align*}
\text{H}_3\text{C}\cdots\text{C}^\cdot\text{Br} + O_2^\cdot \xrightarrow{\text{Br}^-} & \quad \text{H}_3\text{C}^\cdot\text{CH}=\text{CH}_2 + \text{HO}_2^- \\
\text{HO}_2^- + O_2^\cdot & \rightarrow \text{HO}_2^- + O_2
\end{align*}
\]

Other nucleophilic reactions which the electro-generated superoxide ion was reported to exhibit included addition to benzylidenefluorenone (II) and epoxidation of cyclohex-2-en-1-one (III).
Epoxidation of $\alpha,\beta$-unsaturated ketones is usually carried out with alkaline hydrogen peroxide in which the reactive, nucleophilic species is $\text{HO}_2^-$. Alkaline hydrogen peroxide is not suitable for the epoxidation of unactivated olefins. Similarly it was found that no epoxide was formed on the addition of cyclohexene to a solution of electrogernated superoxide ion.

Merritt and Sawyer$^1$ studied the kinetics of the nucleophilic displacement of halide from alkyl halides by electro-generated superoxide ion but they did not consider the attack of the alkylperoxide anion on alkyl halide (Scheme 1, v).

**Electrochemical syntheses of sulphones**

Knittel and Kastening investigated the electrochemical synthesis of sulphones by electrolytic reduction of sulphur dioxide in the presence of organic halides$^{19,20}$. Alkyl halides were converted into dialkyl sulphones (IV)
while dihalides led to polymeric sulphones, e.g.

\[
\text{BrCH}_2\text{-CH}_2\text{Br} \quad \text{SO}_2^\cdot \rightarrow (-\text{CH}_2\text{-CH}_2\text{SO}_2^-)_n
\]

or cyclic sulphones e.g.:

\[
\begin{align*}
\text{CH}_2\text{Br} & \quad \text{SO}_2^\cdot \\
\text{CH}_2\text{Br} & \quad \text{SO}_2^\cdot \\
\end{align*}
\]

Asymmetric sulphones were synthesised by using mixtures of alkyl halides

\[
\text{CH}_2:\text{CHCH}_2\text{Br} + \text{CH}_3\text{Br} \quad \text{SO}_2^\cdot \rightarrow \text{CH}_2:\text{CHCH}_2\text{SO}_2\text{CH}_3
\]

Electron spin resonance (e.s.r.) spectroscopy was used to detect the sulphur dioxide radical-anion and to study the kinetics of its reaction with benzyl bromide. Wille and Kastening showed that the mechanism for the electrosynthesis of sulphones from sulphur dioxide in the presence of alkyl halides involves two \( S_N 2 \) reactions (see Scheme 2). Comparison of Schemes 1 and 2 shows that the mechanisms for the reaction of electro-generated superoxide ion and sulphur dioxide radical-anion with alkyl halides are identical.
Electroreduction of tosylate esters, sulphonyls, sulphones and disulphides

In 1968, Yousefzadeh and Mann\textsuperscript{24} isolated substantial yields of ethers from the electrolytic reduction of methyl, ethyl and butyl tosylates (V) at carbon electrodes in acetonitrile. The mechanism involves one-electron uptake by the alkyl tosylate (V) followed by cleavage of the sulphur-alkoxy bond (ii) to form an alkoxide ion and a toluene-\textsubscript{p}-sulphinyl radical (VI) (see Scheme 3).
Nucleophilic attack by the alkoxide ion on a parent molecule results in ether formation with the tosylate ion as the leaving group. The radical VI is probably reduced to the toluene-p-sulphinate ion (VII).

The electroreductive cleavage of sulphonyls, sulphones and disulphides was investigated by several workers. Gourcy, Jeminet and Simonet\textsuperscript{25,26} reported the reduction of arenesulphonyl chlorides in the presence of alkyl halides to form sulphones and sulphides in acetonitrile, but only sulphides in dimethylformamide (DMF) or dimethylsulphoxide (DMSO) (see Scheme 4).

\[ \text{ArSO}_2\text{Cl} \quad \xrightarrow{2e^-} \quad \text{ArSO}_2^- \quad \xrightarrow{\text{RX}} \quad \text{ArSO}_2\text{R} \quad \text{(in MeCN only)} \]

\[ 3 \text{ArSO}_2\text{Cl}^- \quad \xrightarrow{6e^-} \quad \text{ArS}^- + 2\text{ArSO}_2^- + 3\text{Cl}^- \]

\[ \text{ArS}^- + \text{RX} \quad \xrightarrow{\text{-X}^-} \quad \text{ArSR} \]

\textbf{Scheme 4}

\begin{align*}
\text{e.g.} & \\
\text{CH}_3&\text{S-}\text{SO}_2\text{Cl} & \xrightarrow{\text{e}} & \text{CH}_3&\text{S}-\text{CH}_3 & \text{(23\%)} \\
\text{CH}_3&\text{Cl} & \text{DMF} & \text{CH}_3&\text{CN} & \\
\text{CH}_3&\text{S-}\text{SO}_2\text{CH}_3 & + & \text{CH}_3&\text{S}-\text{CH}_3 & \text{(60\%)} & \text{(40\%)}
\end{align*}
Benzyl chloride and methyl iodide were used by Lamm and co-workers to trap the sulphinate ions formed by electroreductive cleavage of a series of cyclic sulphones,\textsuperscript{27}

\[
\begin{align*}
\text{PhSO}_2 \text{CH}_2 \text{Ph} & \xrightarrow{2e; H^+} \text{Ph})_3 \text{SO}_2^- \\
& \xrightarrow{\text{PhCH}_2 \text{Cl}} \text{PhCH}_2 \text{SO}_2 \text{CH}_2 \text{Ph} \\
& \quad (97%)
\end{align*}
\]

and a series of \(\alpha\)-benzenesulphonylnitriles\textsuperscript{28} (VIII).

\[
\begin{align*}
\text{PhSO}_2 \text{CR}_2 \text{CN} & \xrightarrow{2e} \text{PhSO}_2^- + \text{CR}_2 \text{CN} \\
& \quad (\text{VIII}) \\
& \quad \downarrow \text{MeI} \\
& \quad \quad \text{PhSO}_2 \text{Me}
\end{align*}
\]

Iversen and Lund\textsuperscript{29} reported the alkylation and acylation of thioclate anions formed by the electroreductive cleavage of organic disulphides in acetonitrile or DMF.

\[
\begin{align*}
\text{RS-SR} & \xrightarrow{2e} 2\text{RS}^- \\
& \xrightarrow{-2X} 2\text{RSR'}
\end{align*}
\]

A wide variety of disulphides and alkylating and acylating agents were used and, generally, good to excellent yields of isolated product were obtained.

**Electrolytic carboxylations**

In the 1950's and early 1960's, Wawzonek and co-workers\textsuperscript{30,31,32,33,34} used carbon dioxide as a trapping agent for radical-anions. The electroreduction of stilbene (IX) in dimethylformamide (DMF) in the presence of carbon dioxide gave diphenyl-
succinate (X)\textsuperscript{30,35}. The mechanism proposed by Wawzonek and co-workers\textsuperscript{30} in 1955 is given in Scheme 5.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {PhCH\textsubscript{2}CHPh \rightarrow^e \text{PhOHCHPh}};
\node at (2,0) {\text{(IX)}};
\node at (4,0) {\text{(fast)} \downarrow \text{CO}_2};
\node at (2,-1) {\text{PhCH\textsubscript{2}OCHPh} \leftarrow^e \text{PhCH\textsubscript{2}CHPh}};
\node at (4,-1) {\text{-O}_2\text{C} \text{(fast)} \downarrow \text{CO}_2};
\node at (2,-2) {\text{PhCH\textsubscript{2}CHPh} \leftarrow \text{PhCH\textsubscript{2}OCHPh}};
\node at (4,-2) {\text{-O}_2\text{C CO}_2^-}.
\end{tikzpicture}
\end{center}

Scheme 5

In 1968, Dietz and Peover\textsuperscript{35} examined this reaction under controlled electrochemical conditions and showed the proposed mechanism to be correct.

The electrolytic reduction of the related benzalacetophenone (XI) in the presence of carbon dioxide in DMF, was shown by Wawzonek and Gundersen\textsuperscript{34} to give \(\alpha\)-phenyl-\(\beta\)-benzoylpropionic acid (XII).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {PhCH\textsubscript{2}CHCPh \rightarrow^2e \text{PhCH\textsubscript{2}CHCPh}};
\node at (2,0) {\text{(XI)}};
\node at (4,0) {\downarrow \text{CO}_2};
\node at (2,-1) {\text{PhCH\textsubscript{2}CHCPh} \rightarrow 2\text{H}^+ \text{ (work-up)}};
\node at (4,-1) {\downarrow \text{-CO}_2};
\node at (2,-2) {\text{PhCH\textsubscript{2}CHCPh} \rightarrow \text{PhCH\textsubscript{2}CHCPh}};
\node at (4,-2) {\downarrow \text{CO}_2};
\node at (2,-3) {\text{PhCH\textsubscript{2}CHCPh} \rightarrow \text{PhCH\textsubscript{2}CHCPh}};
\node at (4,-3) {\downarrow \text{CO}_2};
\end{tikzpicture}
\end{center}

\text{(XII)}
Wawzonek, Duty and Wagenknecht\textsuperscript{33} also showed that the electrolytic reduction of benzyl chloride (XIII) in DMF under controlled-current conditions in the presence of carbon dioxide yielded phenylacetic acid (XV). They suggested that the reaction proceeded via reductive cleavage of benzyl chloride (XIII).

\[
\text{PhCH}_2\text{Cl} \xrightarrow{2e} \text{PhCH}_2^- + \text{Cl}^-
\]

(XIII)

\[
\text{PhCH}_2\text{CO}^- \xrightarrow{\text{H}^+ \text{ work-up}} \text{PhCH}_2\text{CO}_2\text{H}
\]

(XIV) (XV)

Baizer and Chrama\textsuperscript{36} later reported that in the presence of excess halide, the carboxylate ion (XIV) was converted into the ester, benzyl phenylacetate (XVI).

\[
\text{PhCH}_2\text{Cl} \xrightarrow{2e} \text{PhCH}_2\text{CO}_2^- \xrightarrow{\text{H}^+ \text{ work-up}} \text{PhCH}_2\text{CO}_2\text{CH}_2\text{Ph}
\]

(XIII) (XIV) (XVI)

Similarly, allyl chloride (XVII) was converted into allyl crotonate (XVIII)\textsuperscript{36}.

\[
\text{CH}_3\text{CHCH}_2\text{Cl} \xrightarrow{2e} \text{CH}_3\text{CHCH}_2\text{CO}_2^- \xrightarrow{\text{H}^+ \text{ work-up}} \text{CH}_3\text{CH}:\text{CHCO}_2
\]

(XVII)

\[
\text{CH}_3\text{CH}:\text{CHCO}_2\text{CH}_2\text{CH}:\text{CH}_2
\]

(XVIII)

Phenylacetic acid (XV) was also the major product from the electroreduction of the benzyltriethylammonium ion (XIX) at a platinum electrode in a solution saturated with carbon dioxide\textsuperscript{37}. Ross, Finkelstein and Petersen pointed out that the electrocarboxylation must occur by nucleophilic attack on carbon dioxide rather than by
radical addition since addition of carbon dioxide reduced the yield of toluene without affecting the small yield of bibenzyl (XX), the product formed by radical dimerisation of benzyl radicals (see Scheme 6).

\[
\begin{align*}
\text{PhCH}_2\text{NEt}_3 & \quad \xrightarrow{e, \text{Pt}} \quad \text{PhCH}_2^+ \quad \xrightarrow{e, \text{Pt}} \quad \text{PhCH}_2 \quad \xrightarrow{\text{CO}_2, \text{H}^+} \quad \text{PhCH}_2\text{CO}_2\text{H} \\
\text{(XIX)} & \quad \xrightarrow{\text{PhCH}_2\text{CH}_2\text{Ph}} \quad \text{(XX)} & \quad \xrightarrow{\text{PhCH}_3} \\
\end{align*}
\]

Scheme 6

Weinberg, Hoffmann and Reddy\textsuperscript{38}, in 1971, reported the synthesis of the amino acid dl-N-phenylphenylglycine (XXII) by electroreduction of benzalaniline (XXI) in the presence of carbon dioxide using molten ammonium toluene-\(_2\) sulphonate as the solvent support electrolyte system. The current efficiency was 60\%.

\[
\begin{align*}
\text{PhCH}^+\text{NPh} & \quad \xrightarrow{\text{Hg cathode}, \text{CO}_2} \quad \text{PhCHNHPh} \\
\text{(XXI)} & \quad \xrightarrow{-2.0V (Ag/Ag^+)} \quad \text{PhCHNHPh} \quad \text{CO}_2\text{H} \\
\text{(XXII)} &
\end{align*}
\]

Tyssee and co-workers\textsuperscript{39}, in 1972, reported the reaction of carbon dioxide with a variety of short-lived intermediates formed by the reduction of activated olefins at a mercury cathode in acetonitrile. Mono- and di-carboxylated species as well as dimers of the monocarboxylated species were identified as the methyl esters after work-up using methyl iodide (Scheme 7). They pointed out that carbon dioxide is electroreduced at approximately the same potential as acrylonitrile and therefore the participation of CO\textsubscript{2} must be
considered in cases where high cathodic potentials are involved. This would be the case for electroinactive olefins, such as norbornadiene, and for compounds which are reduced at higher potentials than that of carbon dioxide reduction, e.g. naphthalene. The electroreduction of carbon dioxide itself yields the oxalate dianion (XXIII) which can be reacted with alkyl halides e.g. butyl bromide, to form the dialkyl oxalate ester (XXIV).

\[ 2\text{CO}_2 + 2e^- \rightarrow \text{CO}_2 + (\text{XXIII}) \]

\[ \text{O} \text{O} \]

\[ \text{BuO-C-C-OBu} \]

Wagenknecht found that if the reduction of butyl bromide was performed in the presence of carbon dioxide but at a potential at which only the alkyl halide was reduced, then only dibutyl mercury (XXV) was formed (Scheme 8, i). He proposed that the carboxylation at higher potentials involved a radical mechanism.
Scheme 9
(Scheme 8, iv) with the source of butyl radicals being, presumably, the butylmercury species formed by reduction of the alkyl halide (Scheme 8, i). Once the carboxylate ion XXVI was formed, nucleophilic substitution on the alkyl halide yielded butyl valerate (XXVII). Dibutyl oxalate (XXIV) was also formed.

\[
\begin{align*}
\text{(i)} & \quad \text{BuBr} & \xrightarrow{\text{le}} & \text{Br}^- + \text{BuHg}^+ \xrightarrow{\text{Hg}} \frac{1}{2}\text{Hg} + \frac{3}{2}\text{Bu}_2\text{Hg} \\
\text{(ii)} & \quad \text{CO}_2 & \xrightarrow{\text{le}} & \text{CO}_2^- \\
\text{(iii)} & \quad 2\text{CO}_2^- & \xrightarrow{2\text{BuBr}} & \text{BuO-C-C-OBu}^- \\
\text{(iv)} & \quad \text{CO}_2^- + \text{Bu}^- & \xrightarrow{} & \text{BuCO}_2^- \\
\text{(v)} & \quad \text{BuCO}_2^- + \text{BuBr} & \xrightarrow{} & \text{BuCO}_2\text{Bu} + \text{Br}^- \\
\end{align*}
\]

(XXV)/(XXIV)/(XXVI)/(XXVII)

Scheme 8

A different mechanism was evident at a graphite electrode, for which a nucleophilic butyl anion was proposed as the reactive intermediate (see Scheme 9)\textsuperscript{40}.

Further studies on the electrocarboxylation of activated olefins were reported by Tyssee and Baizer in 1974\textsuperscript{41,42}. Again, nucleophilic attack by electrochemically generated anions on carbon dioxide was proposed for olefins which were more readily reduced than carbon dioxide, e.g. dimethyl maleate (XXVIII) (see Scheme 10).
Hallcher and Baizer\textsuperscript{43} recently studied the utilisation of electrogenerated bases (EGB\textsuperscript{-}) for the carboxylation of weak carbon acids (RH). The general mechanism is given in Scheme 11.

\[
\begin{align*}
\text{PB} & \quad \xrightarrow{e} \quad \text{EGB}^- \\
\text{RH} + \text{EGB}^- & \quad \rightarrow \quad \text{R}^- + \text{EGBH} \\
\text{R}^- + \text{CO}_2 & \quad \rightarrow \quad \text{RCO}_2^- \\
\text{EGBH} & \quad \xrightarrow{[O]} \quad \text{PB}
\end{align*}
\]
The reduction of a protase (PB) produces an anionic species EGB\(^-\) which should ideally be sufficiently basic to deprotonate RH yet be only weakly nucleophilic. To be a commercially viable process, the protase (PB) should be capable of regeneration from EGBH.

The dianion (XXIX) formed by electroreduction of azobenzene was found to be too nucleophilic for this purpose; in DMF containing carbon dioxide and ethyl phenylacetate, only diethyl azodicarboxylate (XXX) was obtained after work-up with ethyl iodide.

\[
\text{PhN:Ph} \quad 2e \quad \rightarrow \quad \text{Ph\bar{N}-Ph} \quad \rightarrow \quad \text{Ph\bar{N}-Ph} \quad \rightarrow \quad \text{Ph\bar{N}-Ph} \\
(XXIX) \quad \text{Ph\bar{N}-Ph} \quad \text{CO}_2 \quad \text{Ph\bar{N}-Ph} \quad \text{CO}_2 \\
\text{Ph\bar{N}-Ph} \quad \text{CO}_2 \quad \text{Ph\bar{N}-Ph} \quad \text{CO}_2 \\
2\text{EtI} \quad \text{CO}_2\text{Et} \\
\text{PhN-NPh} \quad \text{CO}_2\text{Et} \\
(XXX)
\]

The nucleophilic character of the nitrogen atoms was therefore reduced, while maintaining the basicity, by the substitution of a t-butyl group in one ortho-position of each of the phenyl rings. Reduction of 2,2'-azo-t-butylbenzene (XXXI) in the presence of ethyl phenylacetate (XXXII) and carbon dioxide yielded the hydrazo-compound (XXXIII) and, after work-up with ethyl iodide, diethyl phenylmalonate (XXXIV).

\[
\text{PhN-NPh} \quad 2e, \text{CO}_2 \quad \rightarrow \quad \text{PhN-NPh} \quad \rightarrow \quad \text{PhN-NPh} \\
(XXXI) \quad \text{PhN-NPh} \quad \text{CO}_2\text{Et} \\
(XXXII) \quad \text{PhN-NPh} \quad \text{CO}_2\text{Et} \\
(XXXIII) \quad \text{CO}_2\text{Et} \\
\text{2EtI} \quad \text{2PhCH(CO}_2\text{Et)}_2 \\
(XXXIV)
\]
The probase XXXI could be regenerated by air oxidation of XXXIII. Diethyl phenylmalonate (XXXIV) was also prepared by using the sterically hindered tetrabutyl ethenetetracarboxylate (XXXV) as probase, while the corresponding tetraethyl ester XXXVI was used catalytically in the carboxylation of 9-phenylfluorene (XXXVII).

\[
\begin{align*}
\text{RO}_2\text{C}_2\text{O}_2\text{C}_2\text{R} & \quad \text{RO}_2\text{C}_2\text{CO}_2\text{R} \\
\text{Br}_2 & \quad \text{RO}_2\text{C}_2\text{CHCH(CO}_2\text{R)}_2 + 2\text{R'}\text{H} \\
(R = \text{Bu, XXXV}) & \quad (R = \text{Et, XXXVI})
\end{align*}
\]

Electrochemically initiated alkylations

It has been mentioned above that the electrocarboxylation products were in some cases identified and isolated as their methyl\textsuperscript{39, 41, 42}, ethyl\textsuperscript{43} or butyl\textsuperscript{39, 40} esters by trapping the carboxylate anions with alkyl halide. The use of alkyl halides as electrophiles to trap a variety of other electrochemically generated nucleophiles viz. \(\text{O}_2^-, \text{RO}_2^-, \text{SO}_2^-, \text{RSO}_2^-\) and \(\text{RS}^-\), has also been described.

The mechanistic evidence in the case of the carboxylations of organic halides is more ambiguous than that for the reactions
of organic halides with \( \text{O}_2 \) and \( \text{SO}_2 \). The electrocarboxylation of butyl bromide at a mercury cathode\(^{40}\) has been shown to proceed via nucleophilic substitution by electrochemically generated \( \text{CO}_2^- \), analogous to the mechanism for the reaction of alkyl halides with oxygen and sulphur dioxide under electroreductive conditions.

\[
\text{CO}_2^- + R-\text{X} \rightarrow R\text{CO}_2^- + \text{X}^-
\]

However, it has been postulated that the reductive carboxylation of certain organic halides viz. benzyl\(^{33}\) and allyl chloride\(^{36}\), and butyl bromide (at a graphite cathode\(^{40}\)) occurs by reductive cleavage of the organic halide:

\[
R-\text{X} \rightarrow 2e \rightarrow R^- + \text{X}^-
\]

followed by reaction of the nucleophile \( R^- \) with electrophilic carbon dioxide.

\[
R^- + \text{CO}_2 \rightarrow R\text{CO}_2^- 
\]

Baizer and Chruja\(^{36}\) studied the electroreductive cleavage of a variety of organic halides in the presence of activated olefins and postulated nucleophilic addition by the anion formed during the cleavage of the halide. For example, electrolysis of carbon tetrachloride was performed in the presence of the mono-activated olefins acrylonitrile (XXXVIIIA) and ethyl acrylate (XXXVIIIb), and the bis-activated olefin diethyl fumarate (XXXIX).

\[
\begin{align*}
\text{CCl}_4 & \rightarrow 2e \rightarrow \text{Cl}\text{CCl}_3^- \\
\text{CH}_2\text{CHX}, \text{H}^+ & \rightarrow \text{Cl}_3\text{CHCH}_2\text{CH}_2\text{X} \\
\text{CHCO}_2\text{Et} & \rightarrow \text{H}^+ \\
\text{CHCO}_2\text{Et} & (\text{XXXIX}) \\
\text{Cl}_3\text{CCCHCO}_2\text{Et} & + \text{Cl}_3\text{CCCO}_2\text{Et} \\
\text{Cl} & \times \text{CO}_2\text{Et}
\end{align*}
\]
Cyclopropyl derivatives were the major products in the reduction of another polyhalo compound, ethyl trichloroacetate (XL) in the presence of the same mono-activated olefins.

\[
\text{Cl}_3\text{COC}_2\text{Et} + \text{CH}_2:\text{CHX} \rightarrow \text{Cl}\quad\text{CO}_2\text{Et} + \text{Cl}_2\text{CH}_2:\text{CHX}
\]

(XL) (XXXVIII: a, X = CN
b, X = CO\text{2Et})

major product minor product

Karrenbrock and Schäfer\textsuperscript{144} recently reported the use of electrogenerated chlorinated carbanions (XLI a-c) as nucleophiles in the presence of aldehydes and ketones;

\[
\text{Cl}_3\text{CY} \rightarrow \text{Cl}_2\text{CY}^-
\]

(XLI)

a) Y = Cl
b) Y = CO\text{2Et}
c) Y = P(0)(OEt)\text{2}

Thus they prepared trichloromethylcarbinols:

\[
\text{PhCHO} + \text{Cl}_3\rightarrow \text{PhCHClCO}_2\text{Et}
\]

(XLIa) (70%)

ring expanded cyclic ketones:

\[
\text{Cl}_2\text{COC}_2\text{Et} \rightarrow \text{Cl}\quad\text{CO}_2\text{Et}
\]

(XLIb)
and 1,1-dichloro-1-alkenes (via a Wittig-Horner reaction) respectively.

\[
\begin{align*}
\text{Cl}_2\text{C} = \text{O} & \quad \text{R} \quad \text{OEt} \\
\text{OEt} & \quad \text{R} \quad \text{C} = \text{CCl}_2
\end{align*}
\]

(XLIc)

Iwasaki and Harada\textsuperscript{45,46} reported the synthesis of amino acids (XLIV) by the electroreductive cleavage of alkyl halides (XLII) in the presence of Schiff's bases (XLIII), followed by hydrogenolysis of the catholyte.

\[
\begin{align*}
\text{R}^1\text{X} & \quad 2\text{e}^- \quad \text{R}^1^- + \text{PhCH}_2\text{N} = \text{C} - \text{CO}_2\text{R}^3 \\
& \quad \text{H}^+ \quad \text{PhCH}_2\text{NHCO}_2\text{R}^3
\end{align*}
\]

(XLII) (XLIII)

Using this method, \(\alpha\)-methylphenylalanine (XLIVa) and \(\alpha\)-methylaspartic acid (XLIVb) were prepared in very good yields from benzyl chloride (XLIIa) and chloroacetonitrile (XLIIb) respectively.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{PhCH}_2\text{Cl} & + \text{PhCH}_2\text{N} = \text{C} - \text{CO}_2\text{CH}_2\text{Ph} \quad \longrightarrow \quad \text{NH}_2\text{CO}_2\text{H} \\
& \quad \text{PhCH}_2 \\
& \quad \text{Me} \\
\text{R}^1 = \text{PhCH}_2 \quad & \text{R}^2 = \text{Me} \\
& \quad \text{R}^3 = \text{PhCH}_2 \\
& \quad \text{Me} \\
\text{ClCH}_2\text{CN} & + \text{PhCH}_2\text{N} = \text{C} - \text{CO}_2\text{Et} \quad \longrightarrow \quad \text{NH}_2\text{CO}_2\text{H} \\
& \quad \text{CH}_2\text{CO}_2\text{H} \\
& \quad \text{Me} \\
& \quad \text{Me} \\
& \quad \text{R}^1 = \text{NCCH}_2 \quad & \text{R}^2 = \text{Me} \\
& \quad \text{R}^3 = \text{Et} \\
& \quad \text{Me} \\
& \quad \text{Me} \\
& \quad \text{Me} \\
& \quad \text{HO}_2\text{CCH}_2 \quad & \text{R}^2 = \text{Me} \quad \text{76%}
\end{align*}
\]
The use of alkyl halides as electrophiles was exploited by Lund and Simonet in order to mono- and di-methylate some ketones e.g.:

\[
\text{Bu}_4\text{NI} \quad 2e, \text{MeCl}
\]

\[
\begin{array}{c}
\text{Me} \text{O} \\
\text{Me}
\end{array}
\]

(95%)

and their corresponding anils e.g.:

\[
\text{LiClO}_4 \\ 2e, \text{MeCl}
\]

PhNH Me

(100%)

Ph

Lund and his co-workers also studied the alkylation of aromatic anion radicals and proposed that it occurs by indirect reductive cleavage of the alkyl halide followed by a radical coupling reaction rather than a nucleophilic reaction. An abridged reaction scheme is listed in Scheme 12, where A is the aromatic compound and BX is the alkyl halide.

\[
\begin{align*}
A + e^- & \rightarrow A^- \\
A^- + BX & \leftrightarrow A + BX^- \\
BX^- & \rightarrow B^+ + X^- \\
A^- + B^+ & \rightarrow AB^-
\end{align*}
\]

Scheme 12
Their alkylating agent was generally a t-butyl halide. Hess\textsuperscript{53} recently reported that the electroalkylation of quinolines (XLV) with 1-bromo- adamantane (XLVI) yields preferentially 2-adamant-1-ylquinolines via a similar mechanism.

\[
\text{BrC}_{10}H_{15} \xrightarrow{2e, -\text{Br}^-} \text{C}_{10}H_{15}
\]

(XLV: \(R = H\) or Me
\(R' = H\) or Me)

By comparison, Smith and co-workers proposed a nucleophilic substitution mechanism for the electrolytic ethylation of quinoline (XLVa) in anhydrous liquid ammonia\textsuperscript{54}.

\[
\text{EtBr} \xrightarrow{-\text{Br}^-} \text{Et}
\]

and for the electro-methylation and -ethylation of phenazine (XLVII) in acetonitrile\textsuperscript{55}.
In the latter case, the alkylating agents, RX, in decreasing order of reactivity, were dimethyl sulphate, diethyl sulphate and ethyl bromide, but yields of over 90% were obtained with each.

Troll and Baizer\(^{56}\) formed the mono- and di-methylated hydrazobenzenes (XLVIII and XLIX respectively) electrolytically.

Addition of fluorene to a solution of electrochemically reduced azobenzene before the treatment with methyl iodide yielded 9-methylfluorene (L) as the major product, and 9,9-dimethylfluorene (LI). The combined yield was 75%.
In a further report by Troll and Elbe\textsuperscript{57}, it was shown that reduced azobenzene could be either mono- and di-allylated by adding allyl chlorides instead of alkyl chlorides, or converted to cyclic hydrazo compounds in the presence of $a,\omega$-dibromo-alkanes.

Shono\textsuperscript{58} alkylated immonium salts by electroreduction of the salts in the presence of allyl bromide or substituted benzyl bromides e.g.:
He also devised a new route for increasing the number of heterorings in nitrogen heterocycles using bishalides and electrochemistry.

\[
\begin{array}{c}
\text{R}_1^1 N = C H \quad \rightarrow \quad R_1^1 N^+ X^- \quad \rightarrow \quad R_1^1 N \quad R_2^2 X \\
\end{array}
\]

e.g.

He proposed that the electroreduction of immonium salts generates nucleophilic intermediates which can be alkylated by alkyl halides.

Takahashi and co-workers reported the electrochemical syntheses of aliphatic nitriles and nitro compounds from organoboranes using nitromethane (LII) and acetonitrile (LIII), respectively, as solvents. The syntheses were performed in an undivided cell with an iodide, or bromide, salt as the support electrolyte. An alkyl halide was formed in situ at the anode and was subsequently attacked

anode: \[ 3I^- \rightarrow 2^e \rightarrow I_3^- \rightarrow I_2 + I^+ \rightarrow R_2B \rightarrow RI + R_2B' \]

cathode: \[ CH_3Y \rightarrow ^e \rightarrow ^{-}CH_2Y + ^{1/2}H_2 \]

(LII: \( Y = NO_2 \))

(LIII: \( Y = CN \))

in solution: \[ RI + ^{-}CH_2Y \rightarrow RCH_2Y + I^- \text{ (regenerated)} \]

Scheme 13
by the nucleophilic species formed at the cathode as shown in Scheme 13. Yields of up to 150% based on \( R_3B \) were obtained.

Abbot and Bellamy\(^{61} \) recently obtained ethylated carbinols from the reduction of ketones in liquid ammonia in the presence of tetraalkylammonium salts containing ethyl groups.

\[
\begin{align*}
\text{Acyl} & \xrightarrow{2e/2H^+} \text{Akyl} \\
& \xrightarrow{2e} \text{A}^+ \\
& \xrightarrow{\text{Et}_4\text{N}^+} \text{EtOH} + \text{EtOH} \\
& (70 - 75\%) \\
\end{align*}
\]

**Electrochemically initiated acylations**

Another class of electrophile which has been used to trap electrochemically generated nucleophiles includes acid chlorides and anhydrides.

Acetic anhydride was used by Curphey and co-workers in the reductive \( O \)-acylation of 1,3-diketones\(^{62} \).

\[
\begin{align*}
\text{Ketone} & \xrightarrow{2e} \text{Ketone AcAc} \\
& \xrightarrow{2\text{Ac}_2\text{O}} \text{Ketone} \\
& (71\%)
\end{align*}
\]
and of benzophenone$^{63}$,

![Chemical structure image]

and by Hall and co-workers$^{64}$ for the reductive O-acylation of the carotenoid canthaxanthin (LIV).

![Chemical structure image]

Lund and co-workers reported the reductive N-acylation of heteroaromatics$^{65}$

![Chemical structure image]

and reductive N,O-diacylation of nitro and nitroso compounds$^{66}$. 
The reductive acetylation of nitro groups apparently proceeds via the corresponding nitroso compound as shown in Scheme 14.

These workers also reported reductive S-acylation of disulphides and reductive C-acylation of anthracene (LV).

Scheme 14
Scheme 15
and activated olefins 68.

They postulated an intramolecular acylation mechanism to explain their results with $\alpha,\beta$-unsaturated esters and 2-substituted azopyridines 69 (see Scheme 15). Tetrahydropyridazinones and diones were synthesised by Degrand and Lund 69 by electroreduction of aromatic azo compounds in the presence of the acid chlorides, 4-bromobutyril chloride (LVI) and succinyl chloride (LVII) respectively.
In these papers by Lund and co-workers, it was repeatedly pointed out that the electroanalytical results indicate that electroreductive acylation occurs by a different mechanism to that involved in the studies which they had made of electroreductive alkylation (see p 20).

Shono and co-workers reported electrolytic C-acylation of benzyl chlorides (LVIII) and (LIX) with a variety of acid chlorides. The best yields were obtained with butyryl chloride (LX).

\[
\text{PhCH}_2\text{Cl} \quad 2e^- \quad \text{PhCH}_2^- \quad \overset{\text{Cl}^-}{\text{C}_3\text{H}_7\text{CCl}} \quad \overset{\text{O}}{\text{PhCH}_2\text{C}_3\text{H}_7} \quad (69\%)
\]

\[
\text{CH}_3 \quad 2e^- \quad \overset{\text{Cl}^-}{\text{PhCHCl}} \quad \overset{\text{O}}{\text{CH}_3 \quad \text{C}_3\text{H}_7\text{CCl}} \quad \overset{\text{O}}{\text{PhCHC}_3\text{H}_7} \quad (71\%)
\]

They found that acid anhydrides generally provided better yields than acid chlorides in the reductive C-acylation of activated olefins, and that acylation generally occurred exclusively at the \(\beta\)-carbon atom of the \(\alpha,\beta\)-unsaturated ester (LXIA, b) or nitrile (LXIC).

\[
\text{R}_1\text{R}_2\text{C}==\text{CR}_3\text{Y} \quad 2e^- \quad \text{R}_1\text{R}_2\text{C}==\text{CR}_3\text{Y} \quad (\text{R}_4\text{C})_2\text{O} \quad \text{R}_1\text{R}_3\text{C}==\text{CCHY} \quad (\text{R}_4 = \text{Me, Et, n-Pr, i-Pr})
\]

Knittel reported the electrolytic reductive N-acylation of \(\alpha\)-azidostyrene (LXII), which, with 1% water present in the reaction mixture, gave a very good yield of the saturated
amide (LXIII).

\[
\begin{align*}
\text{Ph-C}=\text{CH}_2 & \overset{4\text{e}}{\rightarrow} \text{PhCH-CH}_3 \\
\text{(LXII)} & \overset{\text{Ac}_2\text{O}}{\rightarrow} \text{(LXIII, 85-90\%)}
\end{align*}
\]

The use of electrochemically generated bases

The utilisation of electrogenerated bases for the carboxylation of weak carbon acids and for the methylation of fluorene has already been described (see p14 and 22 respectively). Iversen and Lund were the first to report the use of electrogenerated bases\(^7\). They used them to abstract protons from quaternary phosphonium and ammonium cations in order to form the corresponding ylides. The phosphorus ylide underwent the Wittig reaction with benzaldehyde\(^7\) while the nitrogen ylide underwent a Stevens rearrangement\(^7\).

Baizer, Chruina and White\(^7\), in 1973, reported the use of electrogenerated bases to generate nucleophiles which then attacked activated olefins in a Michael reaction, the product of which regenerated the nucleophilic species as shown in Scheme 16.

\[
\begin{align*}
\text{PB} & \overset{e}{\rightarrow} \text{EGB}^- \\
\text{EGB}^- + \text{CH}_2\text{X}_2 & \leftrightarrow \text{EGBH} + \text{CHX}_2 \\
\text{CHX}_2 + \text{CH=CHZ} & \rightarrow \text{X}_2\text{CHCH}_2\text{CHZ} \\
\text{X}_2\text{CHCH}_2\text{CHZ} + \text{CH}_2\text{X}_2 & \leftrightarrow \text{X}_2\text{CHCH}_2\text{CH}_2\text{Z} + \text{CHX}_2 \\
& \text{(regenerated)}
\end{align*}
\]

Scheme 16
Either azobenzene or the activated olefin itself was used as the probase (PB), reduction of which provided the electrogenerated base (EGB$^-$).

\[
\text{e.g. } \frac{(\text{EtO}_2\text{C})_2\text{C} = \text{C} (\text{CO}_2\text{Et})_2}{\text{XXXVI}} \xrightarrow{0.10\text{F/mol of XXXVI}} \begin{cases} \text{CH(CO}_2\text{Et)}_2 \\ \text{CH}_2(\text{CO}_2\text{Et})_2 \\ \text{CH(CO}_2\text{Et)}_2 \end{cases}
\]

\[97\% \text{ conversion} \quad (93\% \text{ selectivity})\]

of XXXVI

Electrochemically initiated cyanomethylations

A Japanese patent$^{76}$, in the name of Inoue, Takahashi and Ono, described the formation of glutaronitrile (LXV), as well as adiponitrile (LXVI), during the cathodic electrolysis of acrylonitrile (LXIV) in acetonitrile.

\[\begin{array}{c}
\text{CH}_2\text{=CHCN} \\
\text{(LXIV)}
\end{array} \xrightarrow{\text{Pb cathode}} \begin{array}{c}
\text{CH}_2\text{CN} \\
\text{CH}_3\text{CN}
\end{array} \quad \begin{array}{c}
\text{CH}_2\text{CH}_2\text{CN} \\
\text{CH}_2\text{CH}_2\text{CN}
\end{array}
\]

(LXV) (LXVI)

Recently, cyanomethylations arising from electrolyses in acetonitrile were reported by Abbot, Bellamy and Kerr$^{77}$, who proposed that the mechanism involved deprotonation of the acetonitrile by electrogenerated bases.
Other cyanomethylations under similar conditions were reported by van Tilborg, Smit and Scheele\textsuperscript{78},

$\text{CH}_3\text{C}=\text{O} \xrightarrow{e^- } \text{PhS}^- \xrightarrow{-e} \text{PhS}^- \xrightarrow{\text{CH}_2\text{CN}} \text{NCCH}_2\text{C}=\text{OH}$

and by Voss\textsuperscript{79}.

<table>
<thead>
<tr>
<th>PhCOR</th>
<th>$\xrightarrow{e^-} \text{CH}_3\text{CN}$</th>
<th>$\xrightarrow{H^+ / H_2O}$</th>
<th>$\xrightarrow{\text{CH}_3\text{CN}}$</th>
<th>$\xrightarrow{\text{CH}_3\text{I}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\text{PhCCH}(\text{CH}_3)\text{CN}$ (25%)</td>
<td>$\text{PhCC}(\text{CH}_3)_2\text{CN}$ (10%)</td>
</tr>
</tbody>
</table>

Takahashi and co-workers\textsuperscript{59} reported the formation of aliphatic nitriles from organoboranes using acetonitrile and an undivided cell.
They proposed that the mechanism involved the in situ formation of alkyl halides (see p24). Recently, Barnett and Grattan\(^8\) confirmed that the electroreduction of solutions of alkyl halides in acetonitrile yielded the cyanomethylated adducts. Becker and Fritz\(^8\) used isobutyraldehyde (LXVII) to trap the cyanomethyl anion formed during the cathodic decomposition of acetonitrile/potassium hexafluorophosphate.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{CHCHO} & \xrightarrow{\text{Pt}, +e} \text{(CH}_3\text{)}_2\text{CHCHCH}_2\text{CN} \\
\text{(LXVII)} & \xrightarrow{\text{KPF}_6, \text{MeCN}} \text{CH}_2\text{CN}
\end{align*}
\]

Cyanomethylations were also performed by electroreduction of chloroacetonitrile in the presence of ethyl acrylate\(^3\),

\[
\text{ClCH}_2\text{CN} + \text{CH}_2\text{CHO}_2\text{Et} \rightarrow \text{DMF} \rightarrow \text{CO}_2\text{Et}
\]

(43.5% current yield)

and in the presence of Schiff's bases as already described for the synthesis of \(\alpha\)-methylaspartic acid\(^4\),\(^5\) (see p19). Baizer also reported the formation of glutaronitrile (LXV) by the electroreduction of dimethylycyanomethylsulphonium toluene-\(p\)-sulphonate (LXVIII) in acrylonitrile (LXIV)\(^8\).

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{SCH}_2\text{CN} \cdot \text{SO}_3^- + \text{CH}_2\text{CHCN} & \rightarrow \text{CH}_2\text{CN} \\
\text{(LXVIII)} & \rightarrow \text{CH}_2\text{CH}_2\text{CN} \quad \text{(LXV, 20%)}
\end{align*}
\]
CHAPTER 2

Electrochemically Initiated Cyanomethylations

Introduction

There is much literature on the electrochemical reduction of aromatic ketones and $\alpha,\beta$-unsaturated nitriles in aprotic solvents. In both cases, hydrodimerisation is usually identified as the dominant reaction. Thus, the electrolysis of acetophenone (Ia) in N,N-dimethylformamide (DMF) or acetonitrile has been reported as giving the pinacol (II) in almost quantitative yield: \[ \text{Ph} \overset{\text{C}=\text{O}}{\text{CH}_3} \rightarrow 2\text{e} \rightarrow \text{Ph} \overset{\text{C}=\text{C}=\text{C}=\text{C}=\text{C}}{\text{CH}_3 \text{CH}_3} \]

\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{Ph-C—C-Ph} & \\
\text{CH}_3 \text{CH}_3 & \\
\text{(II)} & \\
\end{align*}

By comparison, Abbot has isolated high yields of the nitriles 3-phenylbutyronitrile (Va), 3-methyl-3-phenylglutaronitrile (VIa) and 1-amino-2-cyano-3,4-diphenylcyclopent-1-ene (VIIa), but only traces of the pinacol (II), from controlled-potential electrolyses of acetophenone in dry acetonitrile ($\text{H}_2\text{O} < 100\text{ppm}$). She found that, if the electrolysis was carried out in acetonitrile containing 1% water, then the nitriles were still formed, but that, in the presence of 10% water, only the pinacol was obtained. Traces of 3-methyl-cinnamonicnitrile (IVA) were detected in the product mixtures, and electrolysis of this cinnamonicnitrile was also shown to yield nitriles Va, VIa and VIIa. The proposed mechanism (see Scheme 1) involves attack by the cyanomethyl anion on acetophenone to give
3-hydroxy-3-phenylbutanenitrile (IIIa), with subsequent loss of water giving the cinnamionitrile (IVa) which is susceptible to further cyanomethylation. The formation of the hydroxynitrile intermediate (IIIa) was detected by gas chromatography in a later study.86 The electrolyses of benzaldehyde (Ib), benzophenone (Ic) and cinnnonitrile (IVb) in acetonitrile have also been studied. Examination by infra red (IR) and proton nuclear magnetic resonance (1H NMR) spectroscopy of the crude products indicated the presence of the corresponding propionitriles (V) and glutaronitriles (VI)87.
The cyanomethyl anion is assumed to be generated by deprotonation of the solvent by anionic species produced either directly by electroreduction or by subsequent disproportionation. The electroreduction of the ketone or unsaturated nitrile, although necessary to initiate the formation of cyanomethyl anion, decreases the amount of ketone or unsaturated nitrile available for cyanomethylation. Abbot has shown that acetone and 3,3-dimethylacrylonitrile (VIII) can be cyanomethylated by electroreduction of the more easily reduced azobenzene in acetonitrile containing the ketone or the acrylonitrile. IR and $^1$H nmr spectroscopic analyses of the products indicated a similar range of products to that already described for acetophenone and 3-methylcinnamonnitrile.

Following the initial study by Abbot, Kerr has carried out a detailed investigation of the electroreduction of acetophenone and 3-methylcinnamnnitrile in acetonitrile. He was unable to reproduce the high yields of nitriles obtained in the earlier study and discussed this in terms of the poor design of the original cell, which was an H-type cell with a high internal resistance and a large distance between the reference and the working electrodes. His results showed that the product distribution of nitriles and hydromers was sensitive to the water content of the catholyte, with nitrile formation decreasing with higher concentrations of water.

In order to obtain more information about the kinetics of electrochemically-initiated cyanomethylations, Bellamy devised
the novel electroanalytical technique of measuring the peak currents of acetophenone and other ketones from linear sweep voltammograms run in acetonitrile both before and after the addition of the probe, azobenzene. Linear sweep voltammetry involves the application at a microelectrode of a potential which is varied linearly with time. Cyclic voltammetry is an extension of this technique in which the direction of the sweep is reversed at a predetermined potential. Both techniques provide information about the current, i.e. the amount of material being reduced or oxidised at the microelectrode, as a function of the potential. The hypothesis behind Bellamy’s experiment is that the probe, PB, is reduced to a basic species, normally referred to as the electrogenerated base, EGB⁻, which can deprotonate the solvent to form the cyanomethyl anion. Cyanomethylation of the ketone will then occur thus decreasing the amount of ketone reaching the electrode surface. For each ketone that was studied, a decrease in the peak current of the ketone was observed. The high reduction potential of azobenzene limits the number of ketones that can be studied using azobenzene as the probe. For this reason Niven investigated the cyclic voltammetric behaviour of five azopyridines in acetonitrile. She found that the azopyridines were reduced at less cathodic potentials than azobenzene. Addition of an azopyridine to acetonitrile solutions of benzophenone, acrylonitrile or cinnamonitrile also led to a decrease in the height of the first reduction peak of the ketone or the unsaturated nitrile.

Bellamy has also used cyclic voltammetry and this particular electroanalytical technique to investigate the possibilities of cyanomethylation resulting from the generation of the cyanomethyl anion in DMF solutions by the reductive cleavage of the cyanomethyl-
triphenylphosphonium (IXa) and cyanomethyltriphenylarsonium (IXb) ions. The addition of the bromide salts of either of these ions to a solution of a ketone in DMF again led to a decrease in the peak current of the ketone. These systems, though, are complicated by proton abstraction by the cyanomethyl anion from the parent cation.

\[
\begin{align*}
\text{Ph}_2\text{MCH}_2\text{CN} & + 2e \rightarrow \text{Ph}_3\text{M} + \text{CH}_3\text{CN} \\
\text{(IX)} \quad \text{M} = \text{P} & \quad \text{As} \quad \text{IX} \\
\text{Ph}_2\text{M-CHCN} & + \text{CH}_3\text{CN}
\end{align*}
\]

The aim of the present investigation was to study in greater detail the electrochemically-initiated cyanomethylations of some carbonyl and \(\alpha,\beta\)-unsaturated nitrile compounds in acetonitrile and DMF using both electroanalytical and preparative electrochemical techniques. It was therefore of interest to confirm the identification of the components in the electrolysis product mixtures from ketones and nitriles other than acetophenone and 3-methylcinnamoniitrile, and to determine whether any of the cyanomethylated products could be prepared in high enough yield for the method to be synthetically useful. It was also of interest to study the mechanism of the electrochemically-initiated cyanomethylation and, if possible, to assign rate constants to the various reactions.

It was with this latter objective in mind that Bellamy had run linear sweep voltammograms of ketones both before and after the addition of a cyanomethyl anion precursor. In order to be able to correlate the linear sweep voltammetric data with reaction rate constants it was necessary to analyse the mathematical equations pertaining to the experimental technique and to the reaction.
mechanism. The mathematics are too complicated to be resolved into equations which, in themselves, describe the current, but they are amenable to digital simulation methods. For this reason, work was carried out on the computer simulation of the linear sweep voltammetry experiment. The details of the computer simulation study are given in Chapter 3.

Solvent purification

A major problem which research chemists who study highly reactive species have to face in their attempt to elucidate reaction mechanisms is the purity of the solvent systems in which their reactions are carried out. Electrochemists are no exception.

During the 1960's there was a large number of reports which described methods of removing organic impurities from acetonitrile. The major impurity, though, in both acetonitrile and dimethylformamide (DMF) is water. Various methods were devised to remove the bulk of the water from these solvents. In such "dry" solvents, many compounds were shown to form reasonably stable radical-ions, but highly unstable di-ions. Parker was the first to show that by performing cyclic voltammetry with alumina present in the cell, aromatic dications$^{91}$ and dianions$^{92}$ could be prepared which were stable, at room temperature, on the timescale of slow sweep ($< 0.5\text{Vs}^{-1}$) cyclic voltammetry. The action of the alumina was seen primarily as that of a water scavenger producing super-dry conditions.

Since none of the previous studies of electrochemically initiated cyanomethylation had been carried out in such high purity solvents, it was felt that much valuable information about the cyanomethylation mechanism could be obtained by investigating the effect of solvent purity. But first it was necessary to be able to
prepare high purity DMF and acetonitrile.

DMF has been dried by storing over successive batches of molecular sieve type 4Å and then distilling under reduced pressure and a nitrogen atmosphere. Instead of distilling the solvent, it has also been passed down a column of Woelm alumina (activity grade 1), but this had to be followed by purging the solvent with nitrogen to remove the smell of amines.

McClure and Maricle removed most of the water by heating the DMF over sodium hydroxide for several hours at 90°C, while Bard and his co-workers used anhydrous cupric sulphate to complex both water and dimethylamine. Both procedures entailed subsequent treatment of the DMF with molecular sieve followed by distillation. This final distillation can be carried out directly into an electrochemical cell attached to a vacuum line, with the pressure then being brought to atmospheric with dry helium. Water and alkylamines have also been removed from DMF by azeotropic distillation with benzene, followed by distillation from alumina.

Vacuum distillation of DMF from phosphorus pentoxide has been used by Ritchie and Megerle who pretreated reagent grade DMF with Linde AW500 molecular sieve for 48h, and by Troll and Baizer who followed the distillation with fractionation from calcium hydride under vacuum, and finally stored the solvent over calcium hydride.

Parker and co-workers, by suspending neutral alumina in the cell, were the first to perform electrochemistry in super-dry DMF solutions. Since then, they have reported the development of an apparatus in which the solvent can be passed down an alumina column.
into the cell and then recycled through the column. By recycling the solution several times, they are able to obtain super-dry solutions without alumina being present in the solution. Recently, Hallcher and Baizer obtained super-dry DMF by passing molecular sieve (type 5A)-dried DMF down a column of active neutral alumina in a dry box.

The basic aim of most of these reports on the purification of DMF was the removal of water. The purification of acetonitrile is not as simple. The presence of water in the acetonitrile leads to hydrolysis of the solvent resulting in the formation of acetamide, ammonium acetate and ammonia. Acetonitrile was treated by Wawzonek and Runner with saturated aqueous potassium hydroxide and then dried over anhydrous sodium carbonate before being distilled from phosphorus pentoxide. Kolthoff and co-workers followed a similar procedure, but found that acetic acid formed during the alkaline treatment could be removed by activated alumina, while the drying was carried out with anhydrous calcium chloride and anhydrous magnesium sulphate.

Coetzee and co-workers investigated the impurities present in acetonitrile and recommended a general procedure for purification of the solvent involving stirring with calcium hydride for 48h, fractionation from phosphorus pentoxide, and then refluxing over calcium hydride for several hours before carrying out a final fractional distillation. Calcium hydride was reported as being effective in removing the last traces of acetic acid and water. Other impurities considered in this paper were methyl isocyanide and unsaturated nitriles such as acrylonitrile. The removal of the latter impurities required the acetonitrile to be refluxed with aqueous potassium hydroxide for several hours and then fractionally
distilled before the general purification procedure. Recently, Hofmanova and Angelis\textsuperscript{106} reported a three-step purification of acetonitrile involving treatment with aqueous potassium hydroxide and alumina, with phosphorus pentoxide or molecular sieve, and finally fractional distillation from phosphorus pentoxide.

Instead of the potassium hydroxide and alumina or the initial calcium hydride treatment, Forcier and Olver\textsuperscript{107} preferred to reflux acetonitrile over sodium hydride. This treatment was quicker and removed most of the water as well as the acidic impurities and acrylonitrile. Both methods introduced ammonia or amines which were removed by refluxing the solvent with an acid such as phosphorus pentoxide, sulphuric acid, potassium bisulphate or iodic acid.

O'Donnell, Ayres and Mann\textsuperscript{108} preferred to distil acetonitrile from an anhydrous sodium carbonate and potassium permanganate mixture and then to acidify with concentrated sulphuric acid, decant and distil. Acetonitrile of higher optical purity could be obtained by refluxing the crude acetonitrile with benzoyl chloride before using the above general procedure. McClure and Maricle\textsuperscript{95} used the general procedure but included a final distillation from phosphorus pentoxide.

Sherman and Olson\textsuperscript{109} heated the acetonitrile with dinitrogen tetroxide before adding calcium hydride, and purged with nitrogen at reflux before distillation. Fractional distillation was then carried out from calcium hydride and the final distillate was passed down an alumina column.

In 1972, Walter and Ramaley\textsuperscript{110} reported a detailed comparison of purification methods for acetonitrile. Their results
indicated that their ability to purify acetonitrile was dependent upon
the method used to manufacture the solvent. They concluded that the
best method of purification involved four reflux-distillation stages
with, successively, anhydrous aluminium chloride, alkaline permanganate,
potassium bisulphate, and calcium hydride.

Several workers have used spectrograde quality
acetonitrile. Van Duyne and Reilley\textsuperscript{111} found that this solvent could
be dried as successfully by treatment with activated alumina\textsuperscript{99} as
by repetitive distillations from phosphorus pentoxide on a vacuum
line\textsuperscript{112}.

Acetonitrile can be separated from acrylonitrile by
azeotropic distillation with ethanol for nine days\textsuperscript{94}. Hammerich and
Parker\textsuperscript{91} used this method to purify acetonitrile and then dried the
solvent immediately before use by passing it down a column of neutral
alumina. The suspension of alumina in the cell solution provided
them with super-dry conditions. Compared to their success with other
solvents, they appear to have experienced some difficulty in obtaining
reproducible results with super-dry acetonitrile\textsuperscript{92}.

Burfield, Lee and Smithers\textsuperscript{113} have recently used a
tritiated-water tracer method to measure the effectiveness of various
desiccants on acetonitrile. They found it was an "outstandingly
difficult solvent to completely dry" due to its high affinity for
water. Their findings for static drying were that phosphorus pent-
oxide was the best desiccant but still left a residual water content
of 5 to 10 ppm, 3Å molecular sieve and distillation from boric anhydride
were also good methods, while 4Å molecular sieve was much less efficient
and alumina and calcium hydride, even involving distillation, were
largely ineffective.
Results

a) Dimethylformamide - The standard procedure which was used for drying DMF was to store it over freshly activated 4Å molecular sieve for at least 65h. Cyclic voltammetry revealed the presence of an impurity which was irreversibly reduced at a potential close to the cathodic limit. The results of mass spectrometric analysis of fractionally distilled, dried DMF suggested that the impurity might be ammonia, m/e 17, but this was ruled out by running a cyclic voltammogram of ammonia in DMF, which showed a different electrochemical behaviour from that of the impurity.

The success of further methods to obtain pure and super-dry DMF solutions was measured in terms either of the presence of the electroreducible impurity or by the shape of cyclic voltammograms of benzophenone or azobenzene. In "dry" aprotic solutions, these compounds form stable radical-anions but very reactive di-anions, while, in super-pure conditions, even the di-anions are stable\textsuperscript{43,92}. Furthermore, the potential separation between the reduction peaks for the first and second electron transfers is at its greatest when the di-anion is stable.

Measurements of peak potential separations indicated that the water content of dried DMF could be reduced further by distillation of the DMF from phosphorus pentoxide, and further still by suspending activated neutral alumina in the cell solution. Under these latter conditions, however, it was still necessary to go to greater lengths to keep the benzophenone or azobenzene di-anion stable on the timescale of slow sweep cyclic voltammetry.

The solvent is not the only potential source of contamination; the apparatus, the nitrogen line, the supporting
electrolyte, the electroactive compound and the alumina are all possibilities. Therefore attempts were made to purify each of these, as well as purifying the solvent by treatment with anhydrous cupric sulphate. Pre-electrolysis of the cell solution was also tried. However none of these efforts led to an improvement in the stability of the benzophenone or azobenzene dianion. The only method that was found to be successful in keeping the dianions stable was to cool the cell solution containing suspended alumina to -10°C for azobenzene and to -30°C for benzophenone.

Since there seems to be no reason why the drying techniques used in this work should have been any less effective than those used by others to dry cell solutions of DMF, it is reasonable to assume that the solutions were super dry. Therefore, if the instability of the dianions is due to proton abstraction then a proton source other than water must be responsible. This could have been the irresversibly-reduced impurity, but the continued presence of the impurity peak in cyclic voltammograms of azobenzene indicates that either the electroactive impurity is not the proton source or its deprotonation leads to the formation of another electroactive species of similar reduction potential.

b) Acetonitrile- The acetonitrile was purified originally by a method similar to Coetzee's general procedure in which the solvent was distilled from calcium hydride, then from phosphorus pentoxide, and finally from calcium hydride. Acetonitrile purified by this method still contained acrylonitrile, the reduction of which coincided with the second reduction waves of some of the ketones and \( \alpha,\beta \)-unsaturated nitriles that we hoped to study. Analysis of the untreated solvent by gas chromatography and Karl-Fischer titration showed that acrylo-
nitrile and water were present in concentrations of approximately 100 and 4,000 ppm respectively. If the acetonitrile was distilled from sodium hydride as the first stage, then the acrylonitrile was removed; this was then followed by distillation from phosphorus pentoxide, and from calcium hydride. The water content after this treatment was less than 100 ppm. Freshly activated molecular sieve was added to the final distillate.

During the course of this work it was found that acetonitrile supplied by Fisons was of a much higher electrochemical purity than that supplied by Aldrich, which was found to be unsuitable for the above purification procedures.

Other impurities which were detected by gas chromatography in trace amounts in Fisons SLR grade acetonitrile were propionitrile and benzene. The purification method reduced the concentration of propionitrile, but the sodium hydride distillation increased the benzene concentration; however this was then reduced in the subsequent purification stages to its original value.

Some of the other purification techniques described in the literature were examined. The general purification procedure of O'Donnell, Ayres and Mann using potassium permanganate and concentrated sulphuric acid produced acetonitrile which still contained benzene. The use of benzoyl chloride in the purification led to an increase in the benzene concentration and in the number of impurities. The method recommended by Walter and Ramaley involving the use of anhydrous aluminium chloride did not produce a solvent with a clear background cyclic voltammogram.

Although the addition of activated alumina to purified
acetonitrile solutions increased the separation of the reduction peaks for benzophenone or azobenzene, in neither case was there reoxidation of the dianion even at temperatures below \(-40^\circ\text{C}\). This will be discussed in a later section (see p85). One indication that super-dry conditions were being obtained was that the dianion of perylene was stable at \(5^\circ\text{C}\), in agreement with the results of Jensen and Parker\(^{114}\).

It is therefore believed that by suspending activated alumina in DMF and acetonitrile solutions, super-dry, though not super-pure, conditions can be achieved. However, the presence of alumina in cell solutions when studying the reactions of azo compounds is undesirable since many azo compounds are adsorbed strongly onto the alumina surface. There is also the likelihood of the adsorption of reactive, nucleophilic species such as the cyanomethyl anion. Hence, it was of interest to attempt to obtain super-dry conditions in the absence of alumina in the cell. An apparatus, based on that used by Parker\(^{101}\), was constructed such that the cell solution could be forced, by nitrogen pressure, through an alumina column and back into the cell. Experiments carried out in this apparatus indicated that, although the dryness of the solutions could be improved by this method, the results were not as good as when alumina was actually suspended in the solution.

**Electrolyses in acetonitrile**

Our group was interested in finding out whether the electrochemical reduction of ketones and \(\alpha,\beta\)-unsaturated nitriles in acetonitrile could be a satisfactory method for the preparation of the cyanomethylated products. Authentic samples of the expected products were prepared and used to calibrate analytical equipment, e.g., gas
chromatographs, high pressure liquid chromatographs. Small scale preparative electrolyses were then performed in an attempt to find the optimum conditions for the formation of the nitrile products.

Since Kerr was simultaneously investigating the reduction of acetophenone (Ia) and 3-methylcinnamomnitrile (IVA), it was decided to look at the reduction of benzaldehyde (Ib) and benzophenone (Ic) and the corresponding $\alpha,\beta$-unsaturated nitriles, cinnamonitrile (IVb) and 3-phenylcinnamonitrile (IVc). The electrochemical reduction in acetonitrile of all but the last of these compounds had been shown previously to yield nitrile products, but the analyses had been only qualitative in nature. Also, since the identifications had depended mainly on the analysis of $^1$H nmr spectra of the crude electrolytes products, they were not conclusive. The report by Inoue and co-workers that the electrochemical reduction of acrylonitrile (X) in acetonitrile yields both adiponitrile (XI) and glutaronitrile (XII) suggested that acrylonitrile should also be included in this study.

\[
\text{CH}_2=\text{CHCN} \xrightarrow{\text{cathode}} \text{CH}_2\text{CH}_2\text{CN} + \text{CH}_2\text{CN} \\
(X) \quad \text{(XI)} \quad \text{(XII)}
\]

Preliminary investigations indicated that, while most of the authentics for the benzaldehyde, cinnamonitrile and acrylonitrile electrolyses could be analysed by gas chromatography, this technique was not suitable for the analyses of the products of benzophenone or 3-phenylcinnamonitrile electrolyses, for which high pressure liquid chromatography was required. Cinnamonitrile and acrylonitrile electrolyses were the most amenable to study, since benzaldehyde
gave a larger range of products.

Before carrying out any preparative electrolyses, the electrochemical behaviour of each compound was studied qualitatively by cyclic voltammetry in dry acetonitrile, i.e., acetonitrile which contained less than 100 ppm water but which was later shown to be contaminated with 1-2 mM acrylonitrile. Benzophenone and 3-phenylcinnamionitrile behaved similarly; in each case the cyclic voltammogram showed two reduction peaks of which the first peak had a corresponding oxidation peak while the second peak did not (see Fig. 1a). Such behaviour indicates an initial, reversible electron transfer from the electrode to the neutral molecule to give a radical-anion which is stable during the timescale of the cyclic voltammogram so that, on reversing the sweep, the radical-anion is available for reoxidation. At more negative potentials, the radical-anion is further reduced by the transfer of a second electron to form the dianion, which undergoes a very fast chemical reaction and is therefore not available for reoxidation on the reverse sweep.

The cyclic voltammetric behaviour of benzaldehyde was similar to that of cinnamionitrile (see Fig. 1b). Again there were two reduction peaks, but the height of the second one was much less than the first. Reversal of the sweep beyond the potential of the second peak did not produce an oxidation peak corresponding to the second reduction. If the sweep was reversed before the second peak, there was only a small current corresponding to the reoxidation of the radical-anion to the neutral molecule; this shows that, unlike the radical-anions of benzophenone and 3-phenylcinnamionitrile, the radical-anions of benzaldehyde and cinnamionitrile are reactive, short-lived species.
Cyclic voltammograms of acrylonitrile showed only one reduction peak at \(-2.55\text{V}\) with no corresponding reoxidation peak. The reduction potential and peak shape were the same as those of the impurity which was present in the dry acetonitrile, and which was later confirmed to be acrylonitrile.

**Benzophenone**

Earlier work in this laboratory by Kerr\(^8\) had indicated that benzophenone could be cyanomethylated by electrolysis in acetonitrile. A preliminary study using dry acetonitrile confirmed the presence of cyanomethylated derivatives in the electrolysis products. The results for both a controlled-potential electrolysis and a galvanostatic, or controlled-current, electrolysis are given in Table 1. The former electrolysis was run at a high cathodic potential capable of producing the unstable dianion which, it was hoped, would deprotonate the solvent to yield the cyanomethyl anion and hence lead to cyanomethylated products. The formation of 3-phenylcinnamonicnitrile (IVc) and 3,3-diphenylpropionitrile (Vc) showed that cyanomethylation had occurred, but there was also a relatively large quantity of electro-reduced material, i.e. diphenylmethanol (XIII) and 3,3-diphenylpropionitrile (Vc). Thus, although reduction of the ketone was generating the cyanomethyl anion, it was also decreasing the amount of ketone available to undergo cyanomethylation. The large yields of cyanomethylated products that had been obtained by Abbot indicated that the cyanomethyl anion could be regenerated since otherwise the maximum yield of cyanomethylated products would have been only 50%. Thus the primary products of cyanomethylation are strong enough bases to regenerate the cyanomethyl anion by further deprotonation of the solvent. Taking these factors into account, it was thought possible
that a slower electrolysis might yield more cyanomethylated material vs. the reduced products.

Even carrying out a galvanostatic electrolysis at 20mA (compared to currents of between 100 and 700mA for the controlled-potential electrolysis) still resulted in high yields of the reduced species, but the conversion of benzophenone into cyanomethylated derivatives was higher. At the low potential required for such a small current, the radical-anion rather than the dianion would be the initially formed intermediate. Since cyclic voltammetry indicates that the radical-anion of benzophenone is a stable species, the detection of cyanomethylated species in the electrolysis product was rather surprising. However, when another galvanostatic electrolysis was carried out in purified acetonitrile which contained no acrylonitrile, there was no loss of benzophenone, even at 45°C, and it is therefore most likely that the cyanomethylation in the first galvanostatic electrolysis was initiated by the reduction of the acrylonitrile impurity.

**Cinnamonic Acid**

Cinnamonic acid and 3-phenylcinnamonic acid show different electrochemical behaviour. The radical anion of the latter species is,
like the benzophenone radical-anion, a stable species and hence unlikely to be a suitable cyanomethylation initiator. By comparison, the cinnamoniitrile radical-anion is less stable and undergoes hydrodimerisation during which process protons are abstracted from the surroundings\textsuperscript{115,116}. Because of the instability of the cinnamoniitrile radical-anion, the slow reduction of this $\alpha,\beta$-unsaturated nitrile should initiate the formation of the cyanomethyl anion and lead to cyanomethylation of cinnamoniitrile. Thus, the expected products from galvanostatic electrolyses of cinnamoniitrile in acetonitrile are 3-phenylglutaronitrile (VIIb) and, possibly, the electroreduced product 3-phenylpropionitrile (Vb) as well as various linear and cyclised hydrodimers.

\[
\begin{align*}
\text{PhCH}=\text{CHCN} & \xrightarrow{-\text{CH}_2\text{CN}} \text{PhCHCH}_2\text{CN} \\
(\text{IVb}) & \xrightarrow{\text{H}^+} \text{PhCHCH}_2\text{CN} & \text{CH}_2\text{CN} \\
(\text{VIIb})
\end{align*}
\]

\[
\begin{align*}
\text{PhCH}_2\text{CH}_2\text{CN} & \xrightarrow{2\text{e}^{-}} \text{PhCHCH}_2\text{CN} \\
(Vb)
\end{align*}
\]

The reports by Baizer\textsuperscript{115,117,118} have shown the existence of the three isomers (XIV a–c) of the hydrodimer (neglecting stereoisomers).

\[
\begin{align*}
\text{PhCHCH}_2\text{CN} & \quad \text{PhCH}_2\text{CHCN} & \quad \text{PhCH}_2\text{CHCN} \\
\text{PhCHCH}_2\text{CN} & \quad \text{PhCH}_2\text{CHCN} & \quad \text{PhCHCH}_2\text{CN} \\
(XIVa) & \quad (XIVb) & \quad (XIVc)
\end{align*}
\]

Since they are not detectable by gas chromatography, no attempt was made to analyse for them in the cyanomethylation experiments.

The thermodynamically stable trans isomer of cinnamo-
nitrile was used in all of the preparative electrolyses. Each galvanostatic electrolysis was monitored during the course of the electrolysis by taking samples and analysing by gas chromatography; a standard was added to each before analysis. The disappearance of cinnamonic nitrile and the appearance of 3-phenylglutaronitrile were plotted against time in order to judge when reaction was complete and the maximum yield of the glutaronitrile. A general feature of these electrolyses was the induction period in which the loss of cinnamonic nitrile was negligible (see Graph 1). As an electrolysis proceeded, the concentration of 3-phenylglutaronitrile usually reached a plateau and then decreased slightly. The plateau values are given in Table 2 as % yields. In the following discussion, the Runs described in that Table will be subdivided and summarised in Tables 3-8 for convenience.

The initial experiment was carried out with an electrolyte volume of 150ml (see Run A) but once the experimental method had been finalised, electrolyte volumes of 50ml were used in all subsequent runs. Comparison of Run C with Run A indicates that the decrease in the ratio of catholyte volume to cathode surface area on changing to the smaller cell does not have a major effect on the yield of 3-phenylglutaronitrile.

In the studies by Abbot and Kerr, the initial concentration of ketone or $\alpha,\beta$-unsaturated nitrile was at least 0.1M. Electrolysis of cinnamonic nitrile at such a concentration (see Run C) gave a low yield of the glutaronitrile and no evidence of the propionitrile. Since the major competing reaction was likely to be hydrodimerisation, and the rate equation for the formation of this would involve $[\text{PhCH}=\text{CHCN}]^2$, the effect of decreasing the initial concentration was investigated (see Table 3). As expected, electrolyses
of more dilute solutions reduced the rate of cyanomethylation to a lesser extent than it reduced the rates of the competing reactions, and higher percentage yields of 3-phenyl glutaronitrile were obtained.

The results of Runs D, E and F (see Table 4), in which 20mM solutions of cinnamonic acid were electrolysed at different currents, show that the yield of the glutaronitrile was not sensitive to variations in the current as long as reduction was carried out in the potential range of the first reduction wave. Although the final yields were the same, Graph 2 shows that the rate of loss of cinnamonic acid and the rate of formation of the glutaronitrile increase with the current. In each of these electrolyses, approximately the same quantity of charge, \(1.5 \times 10^{-4}\) F, was passed before the disappearance of cinnamonic acid and the formation of the glutaronitrile had reached their limits (see Table 9, i). Thus the average rate of loss of cinnamonic acid was \(0.3\) mol F\(^{-1}\) while the rate of conversion into 3-phenyl glutaronitrile was only \(2.4\) mol F\(^{-1}\). Since 3-phenylpropionitrile was not formed, this means that \(2.9\) mol F\(^{-1}\) of cinnamonic acid underwent other reactions. Hydrodimerisation involves 1 mol F\(^{-1}\) of the unsaturated nitrile. Therefore hydrodimerisation might account for 34% of the remaining cinnamonic acid, with the rest being involved in other chemical reactions, e.g. attack by the conjugate bases of polymers of acetonitrile such as those studied by Becker and Fritz.\(^8\) It seems more likely though that polymerisation of cinnamonic acid was not being terminated at the hydrodimer stage. Such polymerisation has been reported by Baizer and Anderson for acrylonitrile in the absence of an efficient proton donor.\(^9\) The likely mechanism would involve dimerisation of two cinnamonic acid radical-anions\(^10\), \(^11\) followed by anionic propagation.
Assuming that this is the main mechanism by which the remaining cinnamonitrile was lost, then the average value of 2.9 mol F⁻¹ implies that the average chain length of the polymer was 5.8 cinnamonitrile units.

Re-examination of the results of the effect of concentration (see Graphs 3 and 4, and Table 9, ii) revealed that, for the 20-80 mM electrolyses, 3 mol F⁻¹ of cinnamonitrile were unaccounted for after taking account of cyanomethylation and the lack of formation of 3-phenylpropionitrile. But this value was significantly lower (2 mol F⁻¹) when the concentration was only 10 mM; 2 mol F⁻¹ indicates that the average chain length of the cinnamonitrile polymer was only 4. In such dilute conditions it is not surprising that chain termination by deprotonation of the solvent is occurring earlier.

One consequence of decreasing the initial concentration of cinnamonitrile in the series of experiments described above was that the ratio of cinnamonitrile to supporting electrolyte also decreased. In order to confirm that the higher yields were due to the decrease in the initial cinnamonitrile concentration rather than to the decrease in the ratio of substrate to supporting electrolyte, the concentration of tetraethylammonium fluoroborate was varied (see Table 5). The yield of 3-phenylglutaronitrile and the reaction profile were the same, within experimental error, in each case.

Higher yields of 3-phenylglutaronitrile were obtained.
by increasing the temperature at which the electrolyses were carried out (see Table 6). The effects of higher temperatures on the reaction profiles are illustrated in Graph 5; as well as the increase in the yield of the dinitrile, there was a decrease in the time, $t_c$, required for the reaction to reach completion. The combination of these two effects led to a small decrease in the amount of unaccounted cinnamoni-
trile (mol F$^{-1}$) (see Table 9, iii). A significant decrease in this parameter was obtained with Run Q (see Graph 6) which involved electrolysis of a 10mM cinnaminitrile solution at reflux temperature. In this experiment, the 3-phenylglutaronitrile selectivity was 80% and the average chain length of the cinnaminitrile polymer was 2.6 indicating that much of the polymerisation was being terminated at the hydroidimer.

A comparison of the results for the formation of 3-phenylglutaronitrile (mol F$^{-1}$) (see Table 9 i, ii and iii) emphasises that, in dilute acetonitrile solutions and especially at elevated temperatures, the product of cyanomethylation must regenerate another cyanomethyl anion since, otherwise, at most only 1mol F$^{-1}$ of the dinitrile could be formed.

Since acetonitrile is hygroscopic, it was of interest to determine how sensitive the cyanomethylation reaction is to the presence of water. Neither further drying of the purified acetonitrile by passing it down a column of freshly activated alumina immediately prior to use (Run I), nor the addition of 0.025 vol% water to the
catholyte before electrolysis (Run K) affected either the yield of 3-phenylglutaronitrile (see Table 7) or the reaction profile. These results indicate that cyanomethylation is not sensitive to the presence of trace amounts, i.e. \( \leq 300 \text{ppm} \), of water. There is therefore no danger that small differences in the water content of different batches of acetonitrile, or in a particular batch on standing, will have affected the results of any of the cinnamonic acid electrolyses. The presence in the catholyte of water, which is a much better proton donor than acetonitrile, had been expected to lower the yield of the glutaronitrile by reducing the number of cyanomethyl anions formed by proton abstraction from the solvent. This was found to be the case when higher levels of water were present in the catholyte (Runs M and L). Under such conditions, not only was the yield of the glutaronitrile lower but its rate of formation and the rate of consumption of cinnamonic acid were slower (see Graph 7) and 3-phenylpropionitrile was not formed. These observations are in agreement with more efficient termination of the polymerisation by proton abstraction from the water molecules. Thus the unaccounted loss of cinnamonic acid dropped from 2.9 to 1.7 mol F\(^{-1}\) (see Table 9) with the average chain length of the cinnamonic acid polymer decreasing from 5.8 to 3.4.

As well as using tetraethylammonium fluoroborate as the supporting electrolyte, other supporting electrolytes were tried (see Table 8). Electrolyses carried out with other tetraethylammonium salts showed that the fluoroborate and iodide (Run W) salts gave similar reaction profiles and yields, while the use of the toluene-\(p\)-sulphonate salt (Run T) led to a very long induction period (see Graph 8), a slightly lower yield of 3-phenylglutaronitrile, and the formation of the propionitrile in 3% yield. 3-Phenylpropionitrile is
a reduction product and requires 2 F mol\(^{-1}\). Thus, when tetrathylen-
ammmonium toluene-\(p\)-sulphonate was used as the supporting electrolyte
(see Table 9, Run T), 1.36 mol F\(^{-1}\) of the glutaronitrile were formed,
with 0.2F having been expended in the formation of 0.10 mol of the
propionitrile. Therefore 1.85 mol cinnamtonitrile was unaccounted for
0.8F, i.e. 2.3 mol F\(^{-1}\).

Tetrabutylammonium fluoroborate (Run R) gave similar
results to tetrathylenamonium fluoroborate both in the yield and in
the reaction profile, but with the tetramethylenamonium salt (Run S),
cinnamtonitrile reacted more slowly and 3-phenylglutaronitrile was
obtained in lower yield (see Graph 9). This latter salt is not very
soluble in acetonitrile and the electrolysis was performed with the
electrolyte suspended in the solution.

The use of salts of alkali metals as supporting
electrolytes normally leads to an increase in the yield of propio-
nitriles\(^{118}\). This has been rationalised in terms of the ion-pair
abstracting a proton from water. It was therefore thought that the
electrolysis of cinnamtonitrile in dry acetonitrile containing alkali
metal cations might cause the cinnamtonitrile radical-anion - alkali
metal ion-pair to abstract protons from acetonitrile leading to the
formation of 3-phenylpropionitrile. This would increase the formation
of cyanomethyl anions and hence the yield of 3-phenylglutaronitrile.
A galvanostatic electrolysis of cinnamtonitrile with sodium iodide
as the support electrolyte (Run V) resulted in a very slow rate of
reaction of cinnamtonitrile without any formation of the propionitrile
or the glutaronitrile for 24% conversion. The use of lithium
 perchlorate (Run U) again led to a very slow reaction, but 3-phenyl
propionitrile was formed in 27% selectivity for 18% conversion of
cinnammonitrile; 3-phenylglutaronitrile was not formed. Analysis of the results of Runs U and V (see Table 9 iv) suggests that hydrodimerisation was the major reaction since approximately 1 mol F⁻¹ of cinnammonitrile was unaccounted for. Baizer ¹¹⁸ proposed that alkali metal cations form tight ion-pairs with the radical-anions and that these ion-pairs then have predominantly radical character, while radical-anions in solvent-separated ion-pairs with tetraalkylammonium cations have more anionic character. The present results suggest that the nucleophilic character of all the anionic species was decreased by the presence of alkali metal cations.

Benzaldehyde

The electrochemical behaviour of benzaldehyde is similar to that of cinnammonitrile, i.e. the benzaldehyde radical-anion is unstable and undergoes hydrodimerisation. A slow electrolysis of benzaldehyde in acetonitrile should therefore generate cyanoethyl anions which should react with benzaldehyde (Ib) to form 3-hydroxy-3-phenylpropionitrile (IIIb).

\[
\begin{align*}
\text{Ph} & \quad \overset{\text{CH}_2\text{CN}}{\text{C}=\text{O}} \\
\text{H} & \quad \overset{\text{H}^+}{\underset{\text{H}}{\text{OH}}} \\
(Ib) & \quad \rightarrow \\
\text{Ph} & \quad \overset{\text{OH}}{\text{C}<\text{CH}_2\text{CN}} \\
\text{H} & \quad \underset{\text{H}}{\text{OH}} \\
(IIIb) & 
\end{align*}
\]

Galvanostatic (20mA) electrolysis of a dilute (13.6mM) solution of benzaldehyde in purified acetonitrile confirmed that the hydroxynitrile (IIIb) is the initial product of the addition (see Graph 10 and Table 10). After 10 minutes virtually all of the benzaldehyde had been consumed, a 70% yield of the hydroxynitrile was observed, and the only other identifiable products were the cis- and trans-cinnammonitriles (IVb) in a total yield of 2.7%. Benzyl alcohol was
not formed. Thus on average, per Faraday, 3.81 mol of benzaldehyde had been consumed with the formation of 2.67 mol of 3-hydroxy-3-phenylpropionitrile and 0.10 mol of cinnamonic acid, leaving 1.0 mol of benzaldehyde unaccounted for. This last value and the absence of benzyl alcohol suggest that the other main product is the benzaldehyde hydrodimer, i.e. the pinacol, rather than oligomers. From the high yield of the hydroxynitrile (2.67 mol F⁻¹) it is again evident that the cyanomethyl anion is regenerated by proton abstraction by the adduct.

The electrolysis was continued after all of the benzaldehyde had been consumed. Under the electrolysis conditions, dehydration of the non-electroactive hydroxynitrile (IIIb) occurred to give cinnamonic acid (IVb), which was either reduced to 3-phenylpropionitrile (Vb) or underwent further cyanomethylation to 3-phenylglutarocyanide (VIb). The kinetics of the reactions were such that the concentration of cinnamonic acid was never greater than 12% of the initial benzaldehyde concentration. Trans-cinnamonic acid was always the major isomer (see Table 10).

The formation of 3-phenylpropionitrile is rather surprising since it has already been shown that the electroreduction of cinnamonic acid in acetonitrile in the presence of tetraethylammonium fluoroborate does not yield the saturated nitrile except in the presence of fairly large quantities of water. It is possible that the formation of the propionitrile from benzaldehyde is due to the proximity of water molecules resulting from dehydration of 3-hydroxy-3-phenylpropionitrile.
Although 3-phenylglutaronitrile has been shown to be formed by nucleophilic addition to cinnamionitrile, it is also possible that the glutaronitrile is being formed by nucleophilic substitution of the hydroxynitrile.

Acrylonitrile

Electrolysis of acrylonitrile (X) in acetonitrile was expected to yield the saturated nitrile propionitrile (XV), the \( \beta , \beta \)-coupled hydrodimer adiponitrile (XI), and the cyanomethylated product glutaronitrile (XII), though it was also possible that some of the \( \alpha , \beta \)-coupled hydrodimer 2-methylglutaronitrile (XVI) and the cyclised hydrodimer 1-amino-2-cyanocyclopent-1-ene (XVII) could be formed.
Preliminary galvanostatic (10mA) electrolyses of acrylonitrile (ca. 80mM) in purified acetonitrile containing tetraethylammonium fluoroborate (0.1M) showed that glutaronitrile was initially, i.e. in the first 10min, formed much faster than adiponitrile, but that its production over the next 10 min decreased while production of adiponitrile increased (see Graph 11). The cyclised hydrodimer (XVII) was not detected. Since it was possible that the decrease in the production of glutaronitrile (XII) was due to a very low concentration of acrylonitrile in the bulk of the solution, while the increase in the formation of adiponitrile (XI) was due to a high concentration of acrylonitrile radical-anion adsorbed on the mercury surface, the bulk concentration of acrylonitrile was monitored during an electrolysis. It was found that the acrylonitrile concentration was still 70% of its initial value at the time the rate of production of glutaronitrile slowed down. Thus, the decrease in the production of glutaronitrile occurred even though the bulk concentration of acrylonitrile had hardly changed.

Inspection of Graph 11 shows that the best selectivity of glutaronitrile occurs after approximately 10min electrolysis. Two series of galvanostatic (10mA) electrolyses were carried out involving only partial conversion of the acrylonitrile (see Tables 11 and 12). Electrolysis for 10 min led to approximately 30% conversion of the acrylonitrile. The selectivity for glutaronitrile formation was only 11% and the molar ratio of glutaronitrile to adiponitrile was 18 (Run 3). If the electrolysis was continued for a further 10min (Run 4), it was found that the glutaronitrile selectivity remained the same while the selectivity for adiponitrile formation increased. In a later series of galvanostatic electrolyses, the experiments were generally continued until all of the acrylonitrile had been consumed and the product
distributions were monitored against time; the maximum yields of glutaronitrile and adiponitrile are given in Table 13.

In none of these experiments was there any evidence for the formation of propionitrile (XV), the \(\alpha,\beta\)-coupled hydrodimer 2-methylglutaronitrile (XVI), or the cyclised hydrodimer (XVII). There was evidence (GC/MS) though for the formation of a C\(_6\) olefinic dinitrile such as:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CN} & \quad \text{or} \quad \text{CH} = \text{CHCN} \\
\text{CH} = \text{CHCN} & \quad \text{or} \quad \text{CHCH}_2\text{CN}
\end{align*}
\]

(XVIII) \quad (XIX) \quad (XX)

Mass spectroscopy cannot distinguish between XX, the cis- and trans-isomers of XVIII, and the trans-isomer of XIX; the main m/e peaks being 66, 39 and 106 in each case. The cis-isomer of XIX can be discounted since it does not break down to a fragment with m/e 39\(^{120}\). The olefinic C\(_6\)-dinitrile was obtained in 8.3\% selectivity in Run 9. In Runs 13 to 24, it was found that this species was formed and then consumed as the electrolysis proceeded. The only experiments in which it was not detected were Runs 18 and 20 in which the radical inhibitor \(N,N\)-dimethyl-\(p\)-nitrosoaniline was present in the catholyte; this suggests that the C\(_6\)-dinitrile is formed by a radical reaction.

With the lack of any evidence for the formation of propionitrile, it should be borne in mind that its limit of detection was 7mM. However, it is apparent that, for the 45-90mM acrylonitrile electrolyses, not all of the acrylonitrile could be accounted for even assuming that 7mM propionitrile was present in each case. Comparison with the results of the cinnamoniitrile electrolyses suggests that oligomerisation, resulting from the nucleophilic character of the hydrodimer mono- or di-anion, is a major reaction in the electro-
reduction of α,β-unsaturated nitriles in pure acetonitrile.

The results of Runs 8 to 12 (see Table 12) indicated that the temperature of the catholyte is an important parameter. Increasing the temperature from 13°C to 26°C increased the selectivity for glutaronitrile and the molar ratio of glutaronitrile to adiponitrile without any change in the conversion of acrylonitrile. In subsequent experiments in which the electrolyses products were monitored as a function of time, it was found that, for 90mM solutions, a reaction temperature of 76-81°C gave virtually identical results for the 20min during which the reaction was monitored as a temperature of 22-4°C (see Graph 12), but, for 45mM solutions, improved yields were obtained at 34-7°C vs. 21-4°C (see Graph 13).

Since higher yields had been obtained by using more dilute solutions of cinnamonicnitrile, the effect of reducing the initial concentration of acrylonitrile was investigated in Runs 13, 15, 16 and 17 (see Graph 14). The percentage yield of glutaronitrile increased from 17.5% for a 90mM acrylonitrile solution to 45% for a 23mM acrylonitrile solution. There was no further increase in the yield on further dilution to 12mM. No definite trend was apparent in the yields of adiponitrile (see Table 13). The lack of further improvement in the yield of glutaronitrile with the 12mM solution is rather surprising considering the similarity between the glutaronitrile yields from cinnamonicnitrile and acrylonitrile for the range 20 to 90mM (see Graph 15).

The concentration of the supporting electrolyte was also varied. Electrolyses of 90mM acrylonitrile in the presence of increased concentrations of tetraethylammonium fluoroborate gave improved selectivities for glutaronitrile and adiponitrile, but a lower olefinic C6-dinitrile selectivity (compare Run 9 with Run 10 and Run
11 with Run 8 in Table 12). The increased yields of glutaronitrile and adiponitrile were also observed with a 45 mM acrylonitrile solution when the tetraethylammonium fluoroborate concentration was increased from 0.10 M (Run 24) to 0.30 M (Run 21). When more tetraethylammonium fluoroborate is used, more water is bound in the hydration shells of the supporting electrolyte ions. This means that there are less water molecules available to solvate the electrogenerated anions which should therefore be stronger bases and/or more nucleophilic. The increased yield of adiponitrile can be explained in terms of the increased basicity, rather than increased nucleophilicity, of the dimer mono- and di-anions leading to more deprotonation of the solvent by the dimer rather than to further polymerisation. Thus, more cyanomethyl anions should be formed and they should be more reactive, resulting in a higher yield of glutaronitrile.

The presence in the catholyte of less than 1 vol% water (Run 6) inhibited the formation of glutaronitrile and the olefinic C₆-dinitrile, but increased the yield of adiponitrile while decreasing the conversion of acrylonitrile. In the case of the cinnamonic acid electrolyses in the presence of water, the evidence for an increase in the yield of the hydrodimer was only circumstantial. The present observations support the hypothesis, suggested by the cinnamonic acid results, that the presence of a reasonably high level of water provides a more efficient source of protons for the dimer mono- and di-anions; thus leading to a higher ratio of hydrodimer to oligomer and less formation of cyanomethyl anion and cyanomethylated products. Very similar results were obtained when a trace of acetic acid was added to an otherwise aprotic catholyte (Run 5). The decrease in the yield of the C₆-dinitrile in each case suggests that this
dimeric product is formed by a different mechanism to that of adiponitrile formation.

Another major product which was identified in Run 6 was bis-cyanoethyl ether, which Baizer has shown to be obtained when the pH of a catholyte, containing both water and acrylonitrile, is allowed to rise above 10. The formation of the ether therefore indicates that there is a highly basic region in the catholyte even after the passage of only 60.

The acrylonitrile used by Baizer was stabilised by trace quantities of N,N-dimethyl-2-nitrosoaniline. This compound was prepared and electrolyses (Runs 18 and 20) were performed on solutions of acrylonitrile containing the stabiliser in up to 0.45 mol%. A small but definite increase in the yield of glutaronitrile was observed (see Table 13). N,N-Dimethyl-2-nitrosoaniline is a radical scavenger and should therefore reduce the amount of radical-initiated reactions. Since the yield of glutaronitrile was not reduced by the presence of the nitrosoaniline, an anionic rather than a radical mechanism for cyanomethylation is indicated.

The addition of a catalytic amount (0.45 mol%) of hydroquinone (Run 7) did not affect the conversion of acrylonitrile or the selectivity for adiponitrile but decidedly reduced the selectivity for glutaronitrile. Although hydroquinone can act as a radical scavenger, it would appear that its acidic nature, pKₐ 10.35, is controlling the product distribution.

The use of tetraethylammonium toluene-2-sulphonate instead of the fluoroborate salt as the supporting electrolyte in the electroylysis of cinnamonic acid led to a much longer induction period before consumption of cinnamonic acid and formation of 3-phenyl-
glutaronitrile became apparent. This was also found to be the case when tetraethylammonium toluene-\(\text{p}\)-sulphonate was used in an acrylonitrile electrolysis (Run 22). Graph 16 illustrates that the use of the toluene-\(\text{p}\)-sulphonate salt also led to a decrease in the yield of glutaronitrile and an increase in the yield of adiponitrile. Tetraethylammonium toluene-\(\text{p}\)-sulphonate was used by Baizer in the electrolytic hydrodimerisation of acrylonitrile in an aqueous electrolyte to provide a hydrophobic region at the cathode\(^{122}\). The double layer formed by this supporting electrolyte at the cathode in dry acetonitrile must provide an environment suitable for hydrodimerisation of acrylonitrile and inhibit the increase in the basicity of the bulk of the solution. However, once basic species are released into the solution both cyanomethylation and oligomerisation occur while hydrodimerisation continues at the same rate.

So far all the electrolyses had been carried out in a divided cell and only the catholyte had been examined. The effect of carrying out an electrolysis in an undivided cell in the presence of tetraethylammonium fluoroborate was examined (Run 19). The consumption of acrylonitrile was much slower with only 23% conversion after 50 min (see Graph 17). Glutaronitrile was found initially, but soon reached a maximum yield of 5 to 6% while adiponitrile continued to be found. The selectivities for glutaronitrile and adiponitrile after 50 min were 26% and 36% respectively, while in the 45 mM acrylonitrile electrolyses in divided cells (Runs 15 and 24), only about 30% of the reacted acrylonitrile could be accounted for. Thus it is apparent that not only is the yield of glutaronitrile reduced considerably in an undivided cell, but that the yield of undetected by-products is also reduced, and an increased yield of hydrodimer is obtained. This is probably due to
the maintenance of an approximately neutral, bulk solution by the reaction of basic species produced at or near the cathode with acidic species formed at or near the anode.

All of these results reinforce the hypothesis that the formation of glutaronitrile by the slow electroreduction of acrylonitrile is due to nucleophilic attack by cyanomethyl anions on acrylonitrile and that this reaction of acrylonitrile is in direct competition with its anionic polymerisation. Both of these processes are initiated by the electro-dimerisation of acrylonitrile. Since such a method of initiating deprotonation of the solvent involves loss of acrylonitrile by dimerisation, a preferred process would use an electrogenerated base which could be recycled. A possible source of such an electrogenerated base is azobenzene\textsuperscript{73,75}. Electroreduction of azobenzene to the dianion in acetonitrile should result in proton abstraction by the dianion from acetonitrile\textsuperscript{88}. The expected by-product, hydrazobenzene, could then be oxidised back to azobenzene\textsuperscript{43}.

A controlled-potential electrolysis of azobenzene (99 mM) in the presence of acrylonitrile (51 mM) was therefore carried out at \(-2.0 \text{V (vs Ag/AgNO}_3\text{)}\). The yield of glutaronitrile (26.5\%) was approximately the same as the yield obtained by the slow electrolysis of acrylonitrile (Runs 15 and 24). No adiponitrile was formed although a small amount of the olefinic C\textsubscript{6}-dinitrile was formed and then consumed. Since less than 10\% of the azobenzene had reacted, the results of this experiment are not altogether as expected. The reduction potential for the second electron transfer to azobenzene is about the same as for the first electron transfer to benzophenone. It has already been shown that the presence of acrylonitrile as an impurity in the acetonitrile during the galvanostatic electrolysis of benzophenone resulted
in the generation of cyanomethyl anions, and it is therefore not impossible that variations in the cathode potential over the surface of the mercury pool electrode resulted in the electroreduction of some of the acrylonitrile. However, the lack of formation of adiponitrile argues against the direct electroreduction of acrylonitrile.

Summary

The results of these electrolyses in acetonitrile have confirmed that the hydrodimerisation of cinnamonic acid, benzaldehyde and acrylonitrile by electroreduction at low electrode potentials can be used to initiate the nucleophilic cyanomethylation of these compounds. The cyanomethylated adducts, once formed, are capable of regenerating cyanomethyl anions by further proton abstraction. Compounds such as benzophenone and 3-phenylcinnamonic acid which have stable radical–anions cannot be cyanomethylated in this way in pure acetonitrile. Other probases, such as azobenzene, can also be used to produce electrogenerated bases capable of deprotonating the solvent to form cyanomethyl anions.

The yield of cyanomethylated products can generally be improved by increasing the temperature or by lowering the concentration of the electroactive species. Electrolysis in an undivided cell or the addition of acids, including water, inhibits cyanomethylation by providing a more efficient proton source.

Various supporting electrolytes have been used. Electrolyses in the presence of alkali metal salts do not yield cyanomethylated products. Reasonable yields of cyanomethylated products are obtained when tetraalkylammonium salts are used, although poorer results are obtained with the tetramethylammonium cation or the toluene-p-sulphonate anion.
In parallel with the preparative electrolysis study of electrochemically-initiated cyanomethylations, an electroanalytical investigation was carried out. The purpose of this was 2-fold. Firstly, to obtain additional mechanistic evidence and, secondly, to estimate the rate constants for the cyanomethylation of electroactive species such as aromatic carbonyl compounds and \(^\alpha_\beta\)-unsaturated nitriles. The following compounds, and the effect of probases on them, were examined by linear sweep (LSV) and cyclic (CV) voltammetry: cis- and trans-cinnamionitrile, acrylonitrile, benzophenone and benzaldehyde.

The production of an electrogenerated base (EBG) by the electroreduction of the probe azobenzene is well documented. Iversen and Lund\(^73\) used electroreduced azobenzene to abstract protons from phosphonium cations in order to generate the corresponding ylide; this then reacted with benzaldehyde in a Wittig reaction.

\[
\begin{align*}
\text{PhN=NPh} & \xrightarrow{2e, 2H^+} \text{PhNHNHPh} \\
\text{DMF, LiCl} & \\
\text{Ph}_3\text{POCH}_2\text{Ph} & \xrightarrow{-H^+} \text{Ph}_3\text{P=CHPh} \\
& \downarrow \text{PhCHO} \\
\text{Ph}_3\text{PO} & + \text{PhCH=CHPh} \\
\text{(98%)} & \quad \text{(cis 59%} \\
& \quad \text{trans 39%)}
\end{align*}
\]

A solution of completely reduced azobenzene was used by Baizer, Chruma and White\(^75\) to initiate catalytic Michael reactions; for example see Scheme 2.
The electrochemistry of azobenzene has been investigated by several workers. Aylward, Garnett and Sharp showed that azobenzene is reduced in two, one-electron steps in N,N-dimethylformamide (DMF). The first electron transfer is fast and produces a stable azobenzene radical-anion, while the second electron transfer is slow and produces a diamagnetic species. The electrochemical behaviour of a series of aromatic azo compounds, ArN-NAr, in DMF was investigated by Sadler and Bard, while Boto and Thomas looked at monosubstituted azobenzenes in acetonitrile. In aprotic solvents, each of these compounds is reduced in two, one-electron steps to the radical-anion and the dianion respectively. The radical-anions are stable at a mercury electrode on the timescale of polarography or cyclic voltammetry experiments. On longer timescales the azobenzene radical-anion undergoes a slow disproportionation (k = 0.14 l mol⁻¹ s⁻¹). Cyclic voltammetry showed that for most of the compounds there was no oxidation peak corresponding to re-oxidation of the dianion. This indicates that the dianion is involved in a fast chemical reaction. In both DMF and acetonitrile, the dianion abstracts a proton to form a stable species (XXI) which is oxidised, at approximately the same potential as that corresponding to the re-oxidation of the radical-anion, in a two-electron step to the parent azo compound.
Exceptions were 4,4'-azopyridine and 4-nitroazobenzene which each showed an anodic peak due to re-oxidation of the dianion.

Sadler and Bard\textsuperscript{98} showed that, in the presence of an excess of a proton donor, some of the monoprotonated dianion (XXI) is further protonated to the hydrazo compound, ArNNH\textsubscript{2}Ar. The presence of a proton donor, such as hydroquinone, stops the formation of arylhydrazines, ArNNH\textsubscript{2}, which are otherwise formed on longer timescales by decomposition of the monoprotonated dianions. The arylhydrazines are oxidised at less cathodic potentials than the first redox couple of the corresponding azo compound.

Troll and Baizer\textsuperscript{56} investigated the basic and nucleophilic character of both the azobenzene anion-radical and dianion in hexamethylphosphoric acid triamide and in DMF. The radical-anion is protonated by fluorene (pK\textsubscript{a} 20.5\textsuperscript{56}) but not by triphenylmethane (pK\textsubscript{a} 31) or acetonitrile (pK\textsubscript{a} 25\textsuperscript{56} - 30\textsuperscript{43}). The addition of a 1000-fold excess of water to azobenzene makes the first wave irreversible, while only a 10-fold excess of methyl iodide is required to produce the same effect. The presence of methyl iodide yields mono- and di-methylated hydrazobenzene. Residual water competes with methyl iodide particularly in the reaction with the dianion, leading to higher ratios of mono- to di-methylated species.

There is thus very strong evidence in the literature that the dianions of azobenzene and other azo compounds, with certain exceptions, are strong bases. Bellamy\textsuperscript{88} demonstrated that the addition of azobenzene to acetonitrile solutions of acetophenone or benzophenone led to a decrease in the LSV reduction peak current for
the first electron transfer to the ketone. He proposed that, in the case of benzophenone, this phenomenon was due entirely to cyano-
methylation which was initiated by deprotonation of the solvent by the azobenzene dianion. Although this was also believed to occur to some extent with acetophenone, control experiments in DMF indicated that part of the decrease in peak height in this case could be ascribed to proton abstraction from the ketone by the dianion. Nucleophilic addition of the azobenzene dianion to the carbonyl group was ruled out by the results of control experiments with benzophenone in DMF.

The disadvantage of using azobenzene was that its high reduction potential for the second electron transfer limited the number of ketones or other substrates which could be studied. Even the analysis of the benzophenone results was complicated by the coincidence of the first reduction peak with the second reduction peak of azobenzene. A number of azopyridines and phenylazopyridines were therefore studied by Niven\(^9\)\(^0\). The magnitude of the cathodic potential of the first electron transfer of the azopyridines and the phenylazopyridines increases in the following order:

\[
4,4' < 2,2' < 3,3' < 4 < 2 < 3
\]

azopyridines phenylazopyridines

The radical-anion of each azo compound was stable (for \(v = 227\text{mVs}^{-1}\), \(i_{pa}(1)/i_{pc}(1) \approx 1.0\)). Inspection of the cyclic voltammograms obtained by Niven revealed that those of 4,4'-azopyridine contained an oxidation peak corresponding to the second reduction peak while such an oxidation peak was least evident in voltammograms of 2,2'-azopyridine. Because of the ease of reduction of these two compounds, as well as the different reactivities of their dianions, it was decided to study their electrochemical behaviour in more detail.
The observations of Bellamy and Niven on the decrease in the heights of the first reduction peaks of benzophenone and acetophenone were made using dried acetonitrile which was contaminated with acrylonitrile. The present investigation used acrylonitrile-free acetonitrile (see p45).

The effect of 4,4'-azopyridine on cyclic voltammograms of aromatic carbonyl compounds and \( \alpha,\beta \)-unsaturated nitriles

Cyclic voltammograms of the aromatic carbonyl compounds and \( \alpha,\beta \)-unsaturated nitriles which had been studied by preparative electrolysis in acetonitrile were run in purified acetonitrile both before and after the addition of 4,4'-azopyridine. In each experiment the cathode was a hanging mercury drop electrode (HMDE) and the sweep rate was 0.25Vs\(^{-1}\).

The results for the addition of 4,4'-azopyridine to acetonitrile solutions of carbonyl and nitrile compounds are given in Table 14. In several cases there was a significant decrease in the peak current, \( i_{pc}(1) \). The quoted error limits were obtained from statistical analyses (Student "t" test) of the spread of values of \( i_{pc}(1) \) obtained from a number of voltammograms for the same solution, i.e. they refer to the duplication of the results but not to the replication of a particular decrease for the addition of 4,4'-azopyridine to a particular electroactive substrate. The addition of 4,4'-azopyridine to benzophenone in acetonitrile was repeated but, this time, measurements were made at various sweep rates (see Table 15). With a sweep rate of 0.25Vs\(^{-1}\), the decrease in \( i_{pc}(1) \) was 22% which is in good agreement with the previous result of 19%. However, the present results are much lower than the values of 51% for benzophenone and 17% for trans-cinnamoniitrile which were obtained by Niven\(^90\) using
Since the experimental procedure involved the addition of a solution of the azopyridine in acetonitrile (1.0 ml) to a solution of the electroactive substrate in acetonitrile (21.0 ml), the dilution of the concentration of the electroactive substrate accounts for some of the decrease in the peak height. After correcting for dilution however, it is apparent that the amounts of benzophenone, benzaldehyde and acrylonitrile reaching the cathode were much lower when 4,4'-azopyridine was present. By comparison, the presence of 4,4'-azopyridine did not decrease the heights of the first reduction peaks of 3-phenylcinnamionitrile and cis- and trans-cinnamionitrile.

A further effect which the azo compound had on the cyclic voltammograms of all the electroactive species except those with very unstable radical-anions, i.e. benzaldehyde and acrylonitrile, was to increase the reversibility of the first peak, i.e. to increase the peak current ratio $i_{pa}(1)/i_{pc}(1)$. This phenomenon had already been noted by Bellamy to occur when azobenzene was added to acetophenone and has been explained in terms of the scavenging of traces of proton donors by the azo compound.88

Comparison of the effects of 2,2' and 4,4'-azopyridine and 4-phenylazopyridine on cyclic voltammograms of benzophenone and $\alpha,\beta$-unsaturated nitriles

The effect of adding 4-phenylazopyridine and 2,2'-azopyridine to acetonitrile solutions of benzophenone was also studied. In Table 16 the results for the three azopyridines are compared for a sweep rate of 0.20Vs$^{-1}$. The decrease observed for the addition of
4,4'-azopyridine is much less than the decrease observed with the other two azopyridines.

Several experiments were performed using 2,2'-azopyridine and benzophenone, and $i_{PC}(1)_{_{benzophenone}}$ was measured for various sweep rates both before and after the addition of 2,2'-azopyridine. Although there is a wide spread in the results for the % decrease, it is apparent that the decrease lessens as the sweep rate increases (see Graph 18). The decrease in the peak height at slow sweep rates is much less when the concentrations of both the azopyridine and benzophenone are 1mM compared to 2mM.

Since 2,2'-azopyridine had a much greater effect on the benzophenone peak height than 4,4'-azopyridine, its effects on trans-cinnamonic acid and 3-phenylcinnamonic acid were also examined. However, there was no distinct decrease in peak height in either case.

**Estimation of the rate constants for proton abstraction from acetonitrile by azopyridine dianions**

In Figure 17, a series of computer-simulated cyclic voltammograms ($v = 0.25Vs^{-1}$) are shown for the reduction of a compound involving two successive electron transfers in which the first is chemically reversible and the second is coupled with a 1st order chemical reaction. The four curves describe voltammograms for different rate constants for the following chemical reaction. Comparison of the cyclic voltammogram ($v = 0.25Vs^{-1}$) of 4,4'-azopyridine (see Fig. 2) with the simulated voltammograms indicates that the dianion undergoes a reaction with a pseudo-1st order rate constant of approximately $0.5-2.0s^{-1}$. By similar inspection, the rate constants for the dianions of 4-phenylazopyridine and 2,2'-azopyridine were estimated to be...
approximately 3.9s\(^{-1}\). This value takes into account the difference in the sweep rate of 0.20Vs\(^{-1}\) for the cyclic voltammograms of 4-phenylazopyridine (see Fig. 3) and 2,2′-azopyridine (see Fig. 4) and 0.25Vs\(^{-1}\) for the simulated voltammograms. The shape of the cyclic voltammogram for a reversible electron transfer followed by an irreversible chemical reaction of 1st order rate constant \(k_1\) is dependent upon the ratio \(k_1/a\) where:

\[
a = \frac{nFv}{RT},
\]

and \(n\) is the number of electrons transferred, \(F\) is Faraday’s constant, \(v/\text{Vs}^{-1}\) is the sweep rate, \(R\) is the gas constant, and \(T/\text{K}\) is the temperature. The shapes of the voltammograms in Figure 3 and Figure 4 are similar to the simulated voltammogram with \(k_1/a\) of 0.5, i.e. curve c of Figure 17, which corresponds to a 1st order rate constant of 3.9s\(^{-1}\) \((4.87 \times 0.20/0.25)\) if the sweep rate is 0.20Vs\(^{-1}\).

The rate constants were also calculated from measurements of the ratio of the oxidation to the reduction peak currents for the second electron transfer, \(i_{pa}^{(2)}/i_{pc}^{(2)}\). Using Graph 27, these peak current ratios were correlated with values for \(\log (k_1 \tau)\) and hence with values for the product \(k_1 \tau\), in which \(k_1/\text{s}^{-1}\) is the 1st order rate constant and \(\tau/\text{s}\) is the time interval between the standard potential, \(E^0(2)\), and the switching potential, \(E^\lambda\), at which the direction of the potential sweep is reversed. For values of \(k_1/a\) of 0.05, 0.2 and 0.5, the standard potentials are, respectively, 28, 25 and 21mV less cathodic than the reduction peak potentials, \(E_{pc}^{(2)}\). Switching potentials in the range 35-100mV cathodic of \(E_{pc}^{(2)}\) were used. The rate constants, \(k_1\), were then calculated from the following equation:
Scheme 3: Proposed reaction mechanism for cyanomethylation of an electroactive substrate (B) initiated by electroreduction of an azo compound (Azo)

(see Chapter 3, Scheme 1 for the model mechanism studied by computer simulation)
giving 0.5, 0.7 and 0.8 s\(^{-1}\) for 4,4'- and 2,2'- azopyridine and 4-phenylazopyridine respectively (see Table 17).

A more accurate method of determining the rate constant, while still using fairly slow sweep rates, i.e. 0.2 - 0.25 Vs\(^{-1}\), and a pen recorder, is to obtain a series of values for the current ratio, \(i_{pa}(2)/i_{pc}(2)\), for a series of switching potentials. It should then be possible to plot \(k_1\gamma\) against \(\gamma\) and calculate \(k_1\) from the gradient. This method eliminates any error in the assignment of the standard potential. The use of the two points obtained in the experiment with 4,4'-azopyridine gave a value of 0.3 s\(^{-1}\).

These three estimates of the pseudo-1st order rate constant for the reactivity of the 4,4'-azopyridine dianion are in good agreement and indicate that the value of the rate constant is approximately 0.5 s\(^{-1}\).

The reactivity of the dianions of azo compounds such as azobenzene and the azopyridines has been ascribed to protonation. In pure, dry acetonitrile, as used in these experiments, it is reasonable to assume that proton abstraction occurs from the acetonitrile. It can therefore be assumed that the rate constants obtained for the reactivity of the azopyridine dianions are the same as the pseudo-1st order rate constants for the formation of cyanomethyl anions by deprotonation of acetonitrile by the azopyridine dianions. With this information and the results from the computer simulation (see Chapter 3) of the reaction mechanism given in Scheme 3, it should be possible to correlate the decreases in the peak currents of benzophenone, benzaldehyde and acrylonitrile on addition of azo compounds with 2nd order
rate constants, \( k_2 \), for their cyanomethylation.

**Estimation of the 2nd order rate constants for the cyanomethylation of aromatic carbonyl compounds and \( a,\beta \)-unsaturated nitriles.**

In Graph 29, the effect of the rate constant, \( k_1 \), (see Scheme 3) on the decrease in the peak height of an electroactive substrate at a sweep rate of 0.25Vs\(^{-1}\) is shown for two values of the 2nd order rate constant for cyanomethylation, \( k_2 \). It is apparent that, for \( k_1 \) less than about 15s\(^{-1}\), the decrease in peak height is very much dependent upon the value of \( k_1 \), but for \( k_1 \) greater than approximately 40s\(^{-1}\) the decrease in peak height is independent of the value of \( k_1 \). Thus, in the case of relatively stable dianions for which the value of \( k_1 \) is not known accurately, there will be large errors in the correlation between peak height decrease and \( k_2 \).

Once the value of \( k_1 \) has been estimated, it is necessary to take into account the separation, \( \Delta E_\text{p} \), between the standard potentials of the probase, \( E_\text{p}^0(A) \), and of the electroactive substrate, \( E_\text{p}^0(B) \). This is necessary because, with larger separations of the standard potentials, there is more time for cyanomethylation to occur and hence the decrease in the peak height is larger (see Graph 32). From the results for the addition of \( 4,4' \)-azopyridine to solutions of various aromatic carbonyl compounds and \( a,\beta \)-unsaturated nitriles (see Table 14), it is apparent that the first reduction potentials, \( E_\text{pc}(1) \), of all the substrates except acrylonitrile are within 0.1V of each other. Acrylonitrile, by comparison, is reduced at a much more cathodic potential. The large decrease in peak height which was observed for acrylonitrile may therefore reflect the larger
potential separation rather than a larger rate constant.

The difference between the standard potential and the peak potential in the case of the second reduction peak of 4,4'-azopyridine \( (k_1/a = 0.05 \Rightarrow k_1 = 0.5 \text{s}^{-1} \text{ for } v = 0.25 \text{Vs}^{-1}) \) is 28mV. Since the first electron transfers to benzophenone and 3-phenylcinnamonic acid are chemically reversible on the voltammetric timescale, their standard potentials, \( E^0(1) \), occur 28.4mV less cathodic than their reduction peak potentials, \( E_{pc}(1) \). The difference between the standard potentials of the second electron transfer to 4,4'-azopyridine and the first electron transfer to benzophenone or 3-phenylcinnamonic acid, \( \Delta E^0 \), is therefore the same as the difference between the corresponding peak potentials.

For \( v = 0.25 \text{Vs}^{-1} \), the peak potential of trans-cinnamonic acid is approximately 14mV anodic of the reversible reduction peak potential, i.e. approximately 14mV cathodic of the standard potential (see Graph 19). Since the cyclic voltammograms of the cis- and the trans- isomers of cinnamonic acid are virtually identical, \( \Delta E^0 \) for either of the cinnamonic acid isomers and 4,4'-azopyridine at \( v = 0.25 \text{Vs}^{-1} \) is therefore 14mV more than the difference between the measured peak potentials.

The benzaldehyde radical-anion is less stable than the cinnamonic acid radical-anion. Comparison of a cyclic voltammogram of benzaldehyde (see Fig.5) with the simulated voltammograms in Figure 16 indicates that \( 1 \leq k_1/a < 10 \), i.e. that the standard potential is anodic of the peak potential by 5(±10)mV (see Table 25). Although benzaldehyde is being analysed here in terms of a 1st order chemical reaction of the radical-anion while it is known that dimerisation is the major reaction, it has been shown that the effects on peak potential
and current functions are similar\textsuperscript{126}. The difference between the standard potentials of benzaldehyde and 4,4′-azopyridine is therefore 0.02V larger than the separation between the peak potentials.

Since the reduction peak potential of acrylonitrile is still chemically irreversible at $v = 25\text{Vs}^{-1}$, the peak potential at this sweep rate must be at least 40mV anodic of the reversible peak potential. Decreasing $v$ from 25 to 0.25Vs$^{-1}$ would shift the peak potential approximately a further 40mV anodically, i.e. to 80mV anodic of the reversible peak potential. This means that, at $v = 0.25\text{Vs}^{-1}$, the minimum value of $\Delta E^0'$ for acrylonitrile and 4,4′-azopyridine is 0.08V larger than the separation between the peak potentials.

Simulated cyclic voltammograms were obtained for $v = 0.25\text{Vs}^{-1}$ to cover the range of standard potential separations, $\Delta E^0'$, from 0.25V to 1.00V. Two values of the pseudo-1st order rate constant for the generation of the cyanomethyl anion, $k_1$, were used in order to provide an indication of the error in the 2nd order rate constant for cyanomethylation, $k_2$, caused by the uncertainty in $k_1$. The two values of $k_1$ were 0.487 (see Graph 32) and 4.87s$^{-1}$ (see Graph 33). In both Graphs, curves were drawn for values of $k_2 = 100, 400, 1,600, 10,000$ and 51,200 1 mol$^{-1}$s$^{-1}$. From each Graph, it was possible to read off the percentage decrease in peak height associated with each of these values of $k_2$ for any particular value of $\Delta E^0'$. These percentage decreases, which are associated with a specific $\Delta E^0'$ and a specific $k_1$, were then plotted as a function of log $k_2$ (see Graph 36). By using this Graph, it was possible to correlate, for both estimates of $k_1$, the experimentally determined decrease in peak height for $v = 0.25\text{Vs}^{-1}$ with a value for the rate constant for cyanomethylation, $k_2$. 

This procedure was applied to the results for the addition of 4,4'-azopyridine to various electroactive substrates in purified acetonitrile (see Table 14). Of the electroactive substrates which were studied, all except benzophenone and 3-phenylcinnammonitrile undergo electrohydrodimerisation. It has been shown (p126) however that both 1st and 2nd order chemical reactions following a reversible electron transfer have little effect on the decrease in peak height. The rate constant, $k_1$, for the generation of the cyanomethyl anion by the 4,4'-azopyridine dianion was assumed to be $0.487\text{s}^{-1}$. The evidence that this is a reasonable assumption has been discussed already (see p78). A value of $k_2 = 580 \pm 20 \text{mol}^{-1}\text{s}^{-1}$ was obtained for the rate constant for the cyanomethylation of both benzophenone and acrylonitrile based on the assumptions that $\Delta E^0$ was 0.43V and 0.88V, respectively, for the two substrates. This estimation of $k_2$ for acrylonitrile represents the maximum value of $k_2$ since $\Delta E^0 > 0.88V$. The error in the measurement of the percentage decrease for benzophenone of $\pm 1$ increases the range of $k_2$ to $(6.0 \pm 0.7) \times 10^2$. It was not possible to correlate the 54% decrease obtained for benzaldehyde with a value of $k_2$ since the percentage decrease obtained for $k_1 = 0.487\text{s}^{-1}$ and $\Delta E^0 = 0.52V$ by computer simulation approaches a limit of about 40% (see Graph 36). It has been demonstrated though that, if regeneration of the cyanomethyl anion occurs, then the decrease in peak height is increased dramatically (see p124). The absence of decreases in the peak heights of 3-phenylcinnammonitrile and cis- and trans-cinnamonnitrile indicates that cyanomethylation of these compounds does not occur on the timescale of the voltammetric experiment; if experimental error was obscuring a 5% decrease, then $k_2$ could be as high as $100 \text{mol}^{-1}\text{s}^{-1}$.

In the later experiment with 4,4'-azopyridine and
benzophenone (see Table 15), $\Delta E^{\circ} = 0.48V$ compared to 0.43V in the earlier experiment. Analysis of the result for $\nu = 0.25Vs^{-1}$ gave $k_2 = 630 \text{ l mol}^{-1}\text{s}^{-1}$.

Other results which were obtained at $\nu = 0.25Vs^{-1}$ are those for the addition of 2,2'-azopyridine to benzophenone (see Graph 18). The rate constant for the protonation of the 2,2'-azopyridine dianion was calculated to be 0.7 - 3.9s$^{-1}$. The separation between the standard potentials, $\Delta E^{\circ}$, is therefore approximately the same as the peak potential difference. In the experiment which gave a decrease of 26%, the peak potential difference was 0.37V while a decrease of 31% was obtained when the potential difference was 0.34V. The estimates of $k_2$ which were obtained from these results are given in Table 18. The values of $k_2$ obtained by assuming $k_1 = 4.87s^{-1}$ are slightly lower than the estimates for 4,4'-azopyridine and benzophenone at $\nu = 0.25Vs^{-1}$ assuming $k_1 = 0.487s^{-1}$.

Since several results were obtained with $\nu = 0.20Vs^{-1}$, a further series of simulated cyclic voltammograms were prepared for this sweep rate (see Graphs 34 and 35). From these simulation results, plots of % decrease against log $k_2$ were prepared (see Graph 37). All the experiments at this sweep rate involved benzophenone. The % decrease obtained with 4,4'-azopyridine at $\nu = 0.20Vs^{-1}$ is not in line with the decreases at the other sweep rates (see Table 15). This is emphasised in the low value of $k_2 = 60 \text{ l mol}^{-1}\text{s}^{-1}$ obtained from this result (see Table 18); to obtain $k_2 = 600 \text{ l mol}^{-1}\text{s}^{-1}$ the decrease would have had to be 30%. The estimate of $k_2 = 530 \text{ l mol}^{-1}\text{s}^{-1}$ for 4-phenylazopyridine, assuming $k_1 = 4.87s^{-1}$, is consistent with the estimates which were obtained for 4,4'-azopyridine at 0.25Vs$^{-1}$. The 2,2'-azopyridine result for $\nu = 0.20Vs^{-1}$ led to estimates of $k_2$ of 260 1 mol$^{-1}$s$^{-1}$ and 1800 1 mol$^{-1}$s$^{-1}$, assuming $k_1 = 4.87s^{-1}$ and 0.487s$^{-1}$ respectively.
Thus, the rate constant, $k_2$, for the cyanomethylation of benzophenone in acetonitrile has been estimated as approximately 600 $\text{mol}^{-1}\text{s}^{-1}$ from the voltammetric results for the addition of 4,4'-azopyridine. This figure is based on a rate constant, $k_1$, for the deprotonation of the solvent of 0.487$s^{-1}$. A similar estimate of $k_2$ is obtained with 4-phenylazopyridine if it is assumed that $k_1 = 4.87$s$^{-1}$, which compares reasonably with the value of $k_1 = 3.9$s$^{-1}$ indicated by comparison of cyclic voltammograms of 4-phenylazopyridine with computer simulated cyclic voltammograms. Since the value of $k_1$ for 2,2'-azopyridine was found to be slightly lower than that of 4-phenylazopyridine (see p78), the value of $k_2$ will be greater than the estimates of 260-500 $\text{mol}^{-1}\text{s}^{-1}$ which were obtained for 2,2'-azopyridine assuming $k_1 = 4.87$s$^{-1}$. The results for the addition of the three azo compounds to solutions of benzophenone in purified acetonitrile are therefore consistent.

A more detailed investigation of the cyclic voltammetric behaviour of azo compounds

Although estimates have been obtained for the rate constants for the reactivities of the azopyridine dianions, there were some anomalous results. From the estimated rate constants for the reactivities of the dianions, it was expected that increasing the sweep rate would lead to the cyclic voltammetric peak becoming chemically reversible. Yet, even at $\nu = 20\text{Vs}^{-1}$ there was no peak corresponding to re-oxidation of the dianion of 2,2'-azopyridine. This was also the case for the dianions of benzophenone and azobenzene in either DMF or purified acetonitrile.

It is clear from the reports by Parker and co-workers 92,114,127 that dryness and purity of the electrochemical system are
necessary when attempting to look at stable dianions at room temperature. During the course of this investigation, Hallcher and Baizer reported that the chemical instability of the azobenzene dianion in DMF is due to traces of water, and they obtained a reversible wave for the dianion in DMF which had been dried with active neutral alumina. It was shown that the dianion deprotonates ethyl acetate ($pK_a^{24}$), but not acetonitrile ($pK_a^{25.5-26}$), and leads to the appearance of a peak due to the oxidation of the monoprotonated dianion at a less cathodic potential than that for the oxidation of the radical-anion.

These reports cast some doubt on the hypothesis that the dianions of azo compounds abstract protons directly from acetonitrile, and suggest instead that water molecules are the primary source of protons. If this is the case, then it is improbable that there would be subsequent proton abstraction by the hydroxide ion from acetonitrile, and the observed decrease in the peak height of certain aromatic carbonyl compounds and acrylonitrile on the addition of azo compounds would have to be explained in terms of a different mechanism.

Further experiments were carried out to try to clarify the situation. These included attempts to reproduce the super-pure conditions which had been achieved by both Parker and Baizer with DMF, and which had been reported for acetonitrile by Parker. The results for the purification of both solvents have already been discussed (see p44). Their relevance to the present topic will be examined in this section.

The second electron transfers to benzophenone, azobenzene and $2,2'$-azopyridine in DMF were made chemically-reversible by suspending activated alumina in the electrolyte and cooling the suspensions. DMF which had been cycled twice through a column of
activated alumina was dry enough for the dianion of 4,4'-azopyridine to be stable at room temperature without having alumina present in the cell. The differences between the two reversible reduction peak potentials were 0.76V for benzophenone (-30°C), 0.80V for azobenzene (-10°C), 0.73V for 2,2'-azopyridine (5°C) and 0.73V for 4,4'-azopyridine (20°C). Cooling a suspension of activated alumina in purified acetonitrile containing tetraethylammonium fluoroborate and the electroactive species did not succeed in making the dianions of benzophenone, azobenzene or 2,2'-azopyridine stable.

The addition of ethyl phenylacetate (pK_a 17.43) or ethyl acetate (pK_a 24.43) to super-dry DMF solutions of azobenzene led to a decrease in the separation of the reduction peaks and to the complete disappearance of the peak corresponding to re-oxidation of the dianion (see Figures 6 and 7 respectively) while another oxidation peak appeared at a much less cathodic potential. Lowering the temperature to -60°C led to a cathodic shift for the second reduction peak but it remained chemically-irreversible, even at sweep rates of 50Vs⁻¹. By comparison, the addition of a few drops of water produced a broad oxidation peak at a more cathodic potential (see Figure 8). With the addition of purified acetonitrile to super-dry DMF, the shape of the cyclic voltammogram of azobenzene changed (see Figure 9) and the peak separation appeared to have reached a minimum value with the addition of only 1 vol% acetonitrile. There was no sign of an oxidation peak at less cathodic potentials. Lowering the temperature did not make the dianion more stable.

When dry, rather than super-dry, DMF was used, the azobenzene dianion was unstable. It was surprising to note, however, that decreasing the sweep rate from 1.0Vs⁻¹ to 0.11Vs⁻¹ led to the appearance
of a broad oxidation peak at approximately 0.2V less cathodic than the second reduction peak (see Figure 10). This broad oxidation peak was still present after the addition of alumina (see Figure 11). It was only as the temperature of the super-dry solution was lowered that the shape altered to that of a chemically-reversible peak.

The appearance of this broad oxidation peak between 0.15V and 0.2V less cathodic than the second reduction peak at slow sweep rates is also noticeable in cyclic voltammograms of azobenzene in purified acetonitrile (see Figure 12), or in super-dry DMF to which purified acetonitrile has been added (see Figure 9). The addition of activated alumina to super-dry the acetonitrile led to an increase in the separation of the reduction peaks and to an increase in the size of this oxidation peak.

The cyclic voltammetric behaviour of 2,2'-azopyridine is very similar to that of azobenzene. In Figure 13b, it can be seen that two reversible couples 0.73V apart were obtained for 2,2'-azopyridine in super-dry DMF at 2-5°C. A shoulder is apparent on the peak corresponding to re-oxidation of the radical-anion. At room temperature, the reduction peak potential separation decreased to 0.715V and the height of the peak due to re-oxidation of the dianion decreased while the shoulder developed into an oxidation peak, A, just anodic of the first electron transfer (see Figure 13a). This oxidation peak was only present after sweeping through the second reduction peak. Its height relative to the first reduction peak was increased by the addition of ethyl phenyl-acetate (see Figure 14), which also led to the second reduction peak becoming irreversible and shifting anodically, and to the appearance of another oxidation peak, B, at a less cathodic potential. This last peak, B, is more pronounced at -50°C (see Figure 14). Both oxidation peaks were found to
decrease in height relative to the first reduction peak as the sweep rate was decreased from 1.0Vs$^{-1}$ to 0.05Vs$^{-1}$, though the more cathodic peak, A, decreased less than the other (see Table 19). These two oxidation peaks must be due to the oxidation of the protonated dianion. Since the less cathodic peak is only observed at low temperature and fast sweep rates, it would appear to be due to the oxidation of a relatively unstable species. Unlike azobenzene, the dianions of 2,2'-azopyridine and 4,4'-azopyridine can accommodate the charge on the ring nitrogens as well as on the azo nitrogens. It is therefore possible for protonation to occur at two different sites. Protonation on the ring nitrogen would give an unstable species due to the loss of aromaticity and it is therefore probable that it is the oxidation of this species that is observed in the less cathodic peak.

The addition of acetonitrile (final concentration = 0.9mM) to 2,2'-azopyridine (1mM) in super-dry DMF (see Figure 13c) also led to the emergence of two extra oxidation peaks. This indicates that acetonitrile is protonating the azopyridine dianion. However, the effect of acetonitrile on the peak due to re-oxidation of the dianion was different from the effect of ethyl phenylacetate in that it did not disappear completely but became broader.

The increase in the current ratio, $i_{pa}(2)/i_{pc}(2)$, with decreasing sweep rate which is obtained for 2,2'-azopyridine or azobenzene in either DMF or acetonitrile suggests that the second electron transfer is followed by a reversible chemical reaction$^{127}$. This also explains why the re-oxidation peak is broader than usual, since the dianion will be oxidised as it is re-formed. Since it has been shown that acetonitrile is deprotonated by dianions of azo compounds, it is probable that, in the presence of acetonitrile, such a reversible
reaction could be proton transfer.

\[ R^2- + CH_3CN \rightleftharpoons RH^- + CH_2CN \]

It has already been suggested that the super-dry DMF used in these experiments contained an acidic impurity, which was possibly electroactive (see p45). The present results indicate that the reaction of the impurity with the dianions of azo compounds is reversible. Another possibility is that, in either solvent, traces of water are involved in reversible proton transfer with the dianions of the azo compounds, but since the dianions are still unstable when the system has been super-dried, it is felt that this is not a major pathway.

The presence of a more acidic species such as ethyl acetate or ethyl phenylacetate would mean that the equilibrium

\[ R^2- + AH \rightleftharpoons RH^- + A^- \]

would lie further to the right; cyclic voltammetry (CV) indicates that there is negligible back reaction with these compounds on the time scale of slow sweep CV experiments.

Under the conditions which were used to study the effect of the presence of azo compounds on the cyclic voltammetry of aromatic carbonyl compounds and \( \alpha,\beta \)-unsaturated nitriles, the standard potentials which were estimated for the second electron transfers of the azo compounds were much lower than those obtained for super-dry solvents. Jensen and Parker have attributed this anodic shift in the second peak potential to association of the dianions with hydroxylic compounds\(^{128}\); in this case the hydroxylic compound will be water.
Summary

The presence of azo compounds such as 2,2'-azo-pyridine, 4,4'-azopyridine or 4-phenylazopyridine in solutions of the electroactive substrates benzophenone, benzaldehyde or acrylonitrile in purified acetonitrile caused a decrease in the voltammetric peak height of each of these electroactive substrates, whereas no significant decrease in the peak height was observed for the electroactive substrates cinnamonicnitrile and 3-phenylcinnamonitrile. Electroreduced azo compounds in acetonitrile deprotonate the solvent in a reversible reaction to yield cyanomethyl anions. The decreases in the peak heights are therefore believed to be due to cyanomethylation of the substrates. Using the computer simulation results of Chapter 3, the 2nd order rate constant for the cyanomethylation of benzophenone has been estimated as 600 mol\(^{-1}\)s\(^{-1}\), while the maximum values for the rate constants for the cyanomethylation of acrylonitrile, 3-phenylcinnamonitrile and cinnamonicnitrile have been estimated as 600, 100 and 100 mol\(^{-1}\)s\(^{-1}\) respectively. With benzaldehyde, cyanomethyl anions must also be formed by other methods, e.g. regeneration by proton abstraction by the cyanomethyl adduct, or generation by proton abstraction by the benzaldehyde radical-anion or the pinacol dianion.

Generation of nucleophiles by electrochemical cleavage of substituted acetonitriles

Since the regeneration of the cyanomethyl anion has a major effect on the decrease in the peak height, it would be preferable if cyanomethylation could be studied in a solvent other than acetonitrile, thus eliminating the possibility of regeneration. In order to do this, a mechanism other than proton abstraction would be required for the
formation of the cyanomethyl anion.

There are a number of examples in the literature of the reductive cleavage of substituted acetonitriles in aprotic media yielding the cyanomethyl anion. Wagenknecht and Baizer reported the electroreductive cleavages of the triphenylcyanomethylphosphonium ion $^{129}$ (XXIIa) and the cyanomethyldimethylsulphonium ion $^{130}$ (XXIV). The results were similar in both cases. In macroelectrolyses of these cations in the presence of styrene, acetonitrile was identified but styrene was not cyanomethylated. Microcoulometry indicated that $n_{\text{app}} = 1$, while the addition of acetic acid doubled the height of the polarographic wave. This evidence suggested that the phosphonium (XXIIa) and sulphonium (XXIV) cations undergo 2-electron reductions, yielding cyanomethyl anions which then abstract protons from the parent ions and yield the corresponding ylids (XXIIIa and XXV). This results in pseudo 1-electron reductions. The addition of acetic acid protonates the cyanomethyl anions, and thus inhibits the deprotonation of the parent ions (see Scheme 4).

i) $\text{Ph}_3\text{MCH}_2\text{CN} \xrightarrow{2\text{e}} \text{Ph}_3\text{M} + \text{CH}_2\text{CN} \xrightarrow{\text{H}^+} \text{CH}_3\text{CN}$  

(XXIIa) M = P  

b) M = As

$\text{XXII} + \text{CH}_2\text{CN} \rightarrow \text{Ph}_3\text{M}=\text{CHCN} + \text{CH}_3\text{CN}$  

(XXIII)

ii) $\text{Me}_2\text{SCH}_2\text{CN} \xrightarrow{2\text{e}} \text{Me}_2\text{S} + \text{CH}_2\text{CN} \xrightarrow{\text{H}^+} \text{CH}_3\text{CN}$  

(XXIV)

$\text{XXIV} + \text{CH}_2\text{CN} \rightarrow \text{Me}_2\text{S}=\text{CHCN} + \text{CH}_3\text{CN}$  

(XXV)

Scheme 4
Bellamy has studied the cyanomethyltriphenylarsonium ion (XXIIb) by cyclic voltammetry and found that its behaviour is similar to that of the phosphonium analogue (XXIIa). The heights of the first reduction peaks of electroactive ketones in DMF decreased significantly on the addition of salts of either the phosphonium (XXIIa) or arsonium (XXIIb) ions. This decrease was attributed to reaction of the cyanomethyl anion with the ketones. The disadvantage with these cyanomethyl anion precursors is that ylid formation complicates the quantitative analysis of the system. Another salt that was also prepared and examined was cyanomethyltriethylammonium iodide, but its reduction potential was found to be too cathodic.

Another source of the cyanomethyl anion was suggested by the report by Lamm and Ankner that the 2-electron reduction of benzenesulphonylacetonitrile (XXVI) in DMF yielded the cyanomethyl and benzenesulphinate anions. The proposed mechanism involves cleavage of the radical-anion giving the sulphinate ion and the cyanomethyl radical which is then further reduced to the anion.

\[
\text{PhSO}_2\text{CH}_2\text{CN} \xrightarrow{1e} \left[\text{PhSO}_2\text{CH}_2\text{CN}\right]^\cdot \rightarrow \text{PhSO}_2^- + \cdot\text{CH}_2\text{CN} \xrightarrow{1e} \cdot\text{CH}_2\text{CN}
\]

(XXVI)

The polarographic wave was reported not to be affected by the addition of phenol, indicating that the cyanomethyl anion does not react with the parent molecule. Benzenesulphonylacetonitrile (XXVI) therefore seemed to be admirably suitable as a source of cyanomethyl anion.

**Benzenesulphonylacetonitrile**

Cyclic voltammetry of benzenesulphonylacetonitrile (XXVI) in DMF showed an irreversible reduction peak (\(E_p - E_{p/2} = 70\text{mV}\)) at \(-2.3\text{V}\) (vs. Ag/0.1M Ag\(^+\)). Neither super-dry DMF nor the addition of
When XXVI was added in equimolar amounts to acetophenone and trans-stilbene the peak current of the substituted acetonitrile was observed to be only 60% and 75% of the original peak currents of acetophenone and trans-stilbene respectively. The addition of the nitrile led to a decrease in the peak current of acetophenone but did not affect the peak height of trans-stilbene. The radical-anion of acetophenone is less stable than that of trans-stilbene (for $v = 0.03 \text{Vs}^{-1}$, $i_{pa}(1)/i_{pc}(1)$ is 0.44 for acetophenone and 0.75 for trans-stilbene) and therefore the height of the reduction peak, $i_{pc}(1)$, for acetophenone would be expected to be larger than that for trans-stilbene. Since the peak height of a reversible, 2-electron transfer is $2^{3/2}$, i.e. 2.83, times the height of a reversible 1-electron transfer, the electro-reduction of benzenesulphonylacetonitrile would appear to involve, overall, 1 rather than 2 electrons. Bellamy found that the addition of acetic acid caused the height of the reduction peak of benzenesulphonylacetonitrile to double. These results are in agreement with a 2-electron reduction to the cyanomethyl anion which, in the absence of an alternative proton source, is capable of deprotonating the parent molecule to form a resonance stabilised anion (XXVII).

$$\text{PhSO}_2\text{CH}_2\text{CN} \xrightarrow{2e} \text{PhSO}_2^- + \text{CH}_2\text{CN}$$

(XXVI)

$$\text{XXVI} + \text{CH}_2\text{CN} \xrightarrow{-\text{CH}_2\text{CN}} \begin{bmatrix} 0^- \text{PhS-CHCN} \leftrightarrow \text{PhS-CHCN} \leftrightarrow \text{etc} \end{bmatrix}$$

(XXVII)

The presence of acetic acid may provide an alternative source of protons for the cyanomethyl anion, or regenerate benzenesulphonylacetonitrile from its conjugate base, or both.
Benzenesulphonylacetonitrile is therefore not as ideal a precursor for cyanomethyl anions as Lamm and Ankner's report had suggested. It was nevertheless of interest to study the effect of its addition to ketones and unsaturated nitriles. However, since its reduction potential was highly cathodic, the effect on cinnamonic nitrile, benzaldehyde, 3-phenylcinnamonic nitrile and benzophenone could not be studied easily. The study was limited to substrates with more cathodic reduction potentials.

**Preparative electrolyses using benzenesulphonylacetonitrile**

Preparative electrolyses of mixtures of benzenesulphonylacetonitrile and acetophenone in DMF led to decreases in the concentrations of both species, but no derivatives of acetophenone were identified. The consumption of each compound in the controlled-potential electrolysis was a linear function of the amount of charge passed (see Graph 20). The molar ratio of benzenesulphonylacetonitrile consumed to acetophenone consumed was 2.0, while the total material consumed was 1.0 mol F\(^{-1}\). Similar results were obtained from a galvanostatic electrolysis (see Graph 21), though in this case the molar ratio of the consumed compounds was 1.5. Since hydrodimerisation of acetophenone radical-anions would explain the lack of products detectable by gas chromatography, it is suggested that acetophenone was consumed by electro-reduction rather than by chemical reaction with the electoreduction products of benzenesulphonylacetonitrile. Also, since hydrodimerisation involves 1.0 mol F\(^{-1}\), the reduction of the sulphonylnitrite must also involve 1 mol F\(^{-1}\). This is in agreement with the hypothesis that the electoreduction of benzenesulphonylacetonitrile involves a 2-electron reduction to give

\[
\text{[PhSO}_2\text{CH}_2\text{CN}^-] \xrightarrow{\text{H}^+} \text{PhSO}_2\text{CH}_2\text{CN}
\]

(XXVII) (XXVI)
an electroreduced species which then reacts with the parent molecule.

The reduction potential of 3-methylcinnamionitrile lies between that of benzenesulphonylacetonitrile \( (E_{pc} = -2.3V) \) and that of acetophenone \( (E_{pc} = -2.5V) \). A controlled-potential electrolysis of 3-methylcinnamionitrile and benzenesulphonylacetonitrile was carried out at -1.8V. In the acetophenone electrolysis, this potential had been unable to maintain a significant current for very long and the potential had to be reset at a more cathodic value. By comparison, during the electrolysis of 3-methylcinnamionitrile, the current became so high that the potentiostat was unable to maintain the set potential and the working potential became less cathodic, viz. -1.45V. Once the current had decreased, the product was analysed and found to contain 3-phenylbutanenitrile in 24\% yield along with unreacted starting materials; no cyanomethylated products were detected.

Controlled-potential co-electrolyses of acrylonitrile and benzenesulphonylacetonitrile were also carried out at both -2.1V and -1.8V. These electrolyses were similar to that of 3-methylcinnamionitrile in that, after an initial period, the current increased while the working potential became less cathodic, but unlike the case of 3-methylcinnamionitrile, there was no subsequent decrease in the current even after the passage of \( 17 \times 10^{-3} \)F and the consumption of \( 5.75 \times 10^{-3} \)mol of starting materials. The products of the electrolyses included the hydrodimer, adiponitrile, and the cyanomethylated product, glutaronitrile, as well as acetonitrile which was formed in 50\% yield. Once there was no more acrylonitrile in the solution, the formation of adiponitrile stopped, but glutaronitrile continued to be formed (see Graphs 22 and 23). Propionitrile (17\%) was only identified in the -1.8V electrolysis product.
Scheme 5

PhSO₂CH₂CN \rightarrow \text{XXVI} \quad \text{XXVI} + \text{CH}_2\text{CN} \rightarrow \text{PhSO}_2\text{HCN} + \text{CH}_3\text{CN} \quad \text{XXVII}

\begin{align*}
\text{XXVII} & \quad \text{(i)} \\
\text{H}^+ & \quad \text{(X)} \\
\text{PhSO}_2\text{HCN} & \quad \text{PhSO}_2\text{CH}_2\text{CN} \quad \text{XXIX}
\end{align*}

\begin{align*}
\text{XXVII} & \quad \text{(ii)} \\
\text{H}^+ & \quad \text{PhSO}_2^- \quad \text{XXIX}
\end{align*}

\begin{align*}
\text{PhSO}_2^- & \quad \text{CH}_2\text{CN} \\
\text{CH}_2\text{CH}_2\text{CN} & \quad \text{PhSO}_2^- \\
\text{XXIX} & \quad \text{CH}_3\text{CH}_2\text{CN} \quad \text{(XI)}
\end{align*}

\begin{align*}
\text{CH}_2\text{CN} & \quad \text{CH}_3\text{CH}_2\text{CN} \\
\text{CH}_2\text{CH}_2\text{CN} & \quad \text{CH}_3\text{CH}_2\text{CN} \\
\text{XXIX} & \quad \text{(XII)}
\end{align*}

\begin{align*}
\text{PhSO}_2^- & \quad \text{CH}_2\text{CN} \\
\text{CH}_2\text{CH}_2\text{CN} & \quad \text{PhSO}_2^- \\
\text{XXIX} & \quad \text{CH}_3\text{CH}_2\text{CN}
\end{align*}
Although glutaronitrile is formed by co-electrolysing acrylonitrile and benzenesulphonylacetonitrile, this does not necessarily imply that the cyanomethyl anion is reacting with acrylonitrile. This would not explain the high current, the decrease in the cathodic working potential, and the large quantity of charge passed. Cyclic voltammetry indicates that the cyanomethyl anion rapidly deprotonates benzenesulphonylacetonitrile (XXVI) to form the resonance-stabilised anion (XXVII). It is then possible for this anion to add to acrylonitrile to form the \( \alpha \)-propionitrilebenzenesulphonylacetonitrile anion which, after protonation to its conjugate acid (XXVIII) would undergo electroreductive cleavage to yield the benzenesulphinate and glutaronitrile anions (see Scheme 5, i).

However, such a mechanism does not account for the formation of propionitrile or adiponitrile. Ogata, Sawaki and Isono have shown that the benzenesulphinate anion attacks \( \alpha, \beta \)-unsaturated systems in general and acrylonitrile in particular\(^{133}\). A possible mechanism for the formation of propionitrile and adiponitrile is shown in Scheme 5, ii. Nucleophilic addition of the benzenesulphinate anion on acrylonitrile (X) would give the anion of benzenesulphonylpropionitrile which by proton abstraction would yield its conjugate acid (XXIX). XXIX would then undergo further electroreductive cleavage to form the propionitrile anion and regenerate the benzenesulphinate anion. Nucleophilic attack by the \( \beta \)-anion of propionitrile on acrylonitrile would yield the adiponitrile anion.

The presence of acrylonitrile in such a basic solution as would result from either mechanism shown in Scheme 5 would be likely to lead to its polymerisation initiated by any of the anions of the nitriles or of XXVIII or XXIX.
The high currents and the large amount of charge that was passed can only be explained if electroactive products were formed which had reduction potentials that were less negative than the reduction potential of benzenesulphonylacetonitrile. This is likely to be the case for XXVIII but the reduction potential of XXIX will lie between that of benzenesulphonylacetonitrile and methyl phenyl sulphone which is much more negative.

Similar mechanisms may be suggested for the co-electrolysis of benzenesulphonylacetonitrile and 3-methylcinnamonic nitrile, but this co-electrolysis differs from that of acrylonitrile in two major respects:

1) the current falls off before all of either starting material is consumed, and
2) only 2F per mol of consumed benzenesulphonylacetonitrile were passed.

Nucleophilic addition by the benzenesulphinate anion on 3-methylcinnamonic nitrile could occur at the less hindered C atom which is adjacent to the nitrile group. Protonation would be followed by reductive cleavage and further protonation to give 3-phenylbutanenitrile with regeneration of the benzenesulphinate anion. Nucleophilic addition by the benzenesulphonylacetonitrile anion (XXVII) to 3-methylcinnamonic nitrile is less likely for steric reasons. The recovery of 60% of the 3-methylcinnamonic nitrile suggests that the formation of the initial adduct is an equilibrium reaction.

If the proposed mechanisms are correct than it should be possible to electroreduce a solution of benzenesulphonylacetonitrile (1M mol\(^{-1}\)) and then add an \(\alpha,\beta\)-unsaturated nitrile before acidifying the solution. Cyclic voltammetry of the solution should then reveal
additional, irreversible reduction peaks at less cathodic potentials than that of benzenesulphonylacetonitrile.

The proposed mechanisms must also be considered for the co-electrolysis of benzenesulphonylacetonitrile with acetophenone. Nucleophilic addition on an alkyl aryl ketone by the deprotonated benzenesulphonylacetonitrile, XXVII, is less likely for steric reasons than nucleophilic addition by the benzenesulphinate anion. Proton abstraction from the ketone (pK_a \approx 20) by XXVII is also unlikely because of the resonance-stabilised nature of the sulphonylacetonitrile anion.

Effect of benzenesulphonylacetonitrile on cyclic voltammograms of aromatic carbonyl compounds and \(\alpha,\beta\)-unsaturated nitriles

The additions of benzenesulphonylacetonitrile to solutions of a series of alkyl aryl ketones and to acrylonitrile and trans-stilbene were studied by cyclic voltammetry. In all cases except trans-stilbene, the presence of benzenesulphonylacetonitrile caused a greater decrease in the height of the first reduction peak of the electroactive substrate than could be accounted for by dilution. For each electroactive species, the peak height of the first reduction peak was measured at various sweep rates both before and after addition of the sulphonylacetonitrile, and the percentage decreases in the peak current were calculated. Results for sweep rates up to 1.0Vs^{-1} were obtained and are listed in Table 20 and illustrated in Graph 24 for a molar ratio of the sulphonylacetonitrile to electroactive substrate of 0.004:0.002. Generally the decrease in peak height appears to increase with slower sweep rates.

Examination of the cyclic voltammograms of the various electroactive substrates for \(v = 0.25\text{Vs}^{-1}\) indicated that the radical-
anions of all but acrylonitrile are reasonably stable, with the
standard potential of the first reduction of each substrate, except
acrylonitrile, being 20-28mV less cathodic than the peak potential.
The standard potential of benzenesulphonylacetonitrile will be at
least 70mV cathodic of its peak potential. This estimate is based
on the evidence that the peak is still totally irreversible at 25Vs⁻¹;
in the case of a 1st-order cleavage reaction the peak potential shift
is 30mV per decade, and a totally irreversible peak is still at least
10mV anodic of the standard potential. The standard potential
separations between benzenesulphonylacetonitrile and the alkyl aryl
ketones will therefore be at least 90mV less than the peak potential
separations at 0.25Vs⁻¹ (see Table 21). The standard potential
separation in the case of acrylonitrile was assumed to be the same as
the peak potential separation.

i) trans-Stilbene

The lack of a definite decrease in the height of the
first reduction peak for trans-stilbene reflects the lack of activation
of the double bond towards nucleophilic attack.

ii) Acrylonitrile

The decrease in the voltammetric peak height of
acrylonitrile on the addition of benzenesulphonylacetonitrile is
believed to be due to attack by the benzenesulphinate anion and by the
benzenesulphonylacetonitrile anion, rather than by the cyanomethyl
anion, on acrylonitrile. Cyclic voltammograms of DMF solutions of
acrylonitrile and benzenesulphonylacetonitrile reveal an oxidation
peak approximately 0.1V less cathodic than the reduction peak of
acrylonitrile (see Figure 15). The oxidation potential of this
peak does not vary with sweep rate while the reduction peak potential
shifts cathodically with increasing sweep rate. This behaviour suggests that there is a reversible reaction between acrylonitrile and an electrogenerated species. Since the electroreduction of 2mol of benzenesulphonylacetonitrile yields 1mol of benzenesulphinate anion and 1mol of the conjugate base of the sulphonylacetonitrile, an average rate constant for the reaction of both of these anions with acrylonitrile can be estimated from the decreases in the voltammetric peak heights on the addition of benzenesulphonylacetonitrile (2mM) to acrylonitrile (2mM). The results are given in Table 22 and are compared in Graph 25 with working curves obtained from simulation studies. The working curves apply to the generation of reactive species by a very fast chemical reaction following a reversible electron transfer. This is a reasonable model for the present system. It can be seen that, unlike the working curves, the experimental values unexpectedly increase as the elapsed time, $\tau$, decreases. Thus, the estimates obtained for the second order rate constant, $k_2$, increase from 100 to 1000 mol$^{-1}$s$^{-1}$ as the sweep rate increases from 0.1 to 10Vs$^{-1}$. There is an added uncertainty in the estimates obtained from the lower values of $\tau$, since these estimates have been made by extrapolation of the working curves. It should be noted, though, that the assumption that $\Delta E^\circ$ is the same as the peak potential separation of 0.28V is weak and an error in the estimation of this parameter would lead to errors in the estimation of $k_2$.

iii) Alkyl and aryl ketones

The alkyl phenyl ketones form a definite series. The percentage decreases are large and increase in the order:

$t$-butyl $< i$-propyl $< ethyl $< methyl

There is a small decrease in the standard potential separation along
this series which means that the difference in the relative reactivities are even larger than indicated by the percentage decrease values. This order of reactivity is consistent with nucleophilic attack at the carbonyl carbon atom being inhibited sterically by the increased bulk of the alkyl groups and by the increasing inductive effect of the larger alkyl groups reducing the polarity of the carbonyl carbon atom.

The decrease in the peak height of acetyl mesitylene is much smaller than for the alkyl phenyl ketone series even though its reduction potential is much more cathodic. This means that acetyl mesitylene is much less reactive. Again, this is consistent with nucleophilic attack since there would be steric hindrance in the transition state.

The effect of varying the sweep rate from 0.03Vs\(^{-1}\) to 100Vs\(^{-1}\) was studied for the addition of benzenesulphonylacetonitrile to acetyl mesitylene and to propiophenone (see Graph 26). In each case, the decrease in peak height on addition of the sulphonylacetonitrile is greater at slower sweep rates. This would be expected to occur if a species formed during the reduction of benzenesulphonylacetonitrile was reacting with the ketone; with a slower sweep rate more time is available for the intermediate to react with the substrate, thus decreasing the concentration of the substrate in the vicinity of the electrode. While the decrease in peak height for acetyl mesitylene changes from 19% to 3% between 0.03Vs\(^{-1}\) and 30Vs\(^{-1}\), the corresponding decreases in peak height for propiophenone are 68% and 62% i.e. propiophenone is undergoing a very fast reaction which is not affected much by the sweep rate.

So far these results for the alkyl aryl ketones have been treated qualitatively. In order to attempt a quantitative analysis
of the results it is necessary to propose a likely reaction mechanism. The original aim of this work was to study the rate of reaction of electrochemically generated cyanomethyl anions with electroactive substrates. This mechanism is complicated by proton abstraction from the parent molecule by the cyanomethyl anion, since cyanomethylation and proton abstraction would be occurring simultaneously. If cyanomethylation was the dominant reaction, then comparison of the experimental results with the computer simulation would provide a reasonable first approximation for the rate constant for cyanomethylation. The voltammetric behaviour of benzenesulphonylacetonitrile indicates that proton abstraction by the cyanomethyl anion from a parent molecule is very fast. The large decrease in peak height for acetophenone would indicate that a high degree of cyanomethylation was occurring, yet preparative electrolyses have not shown any evidence of this. It therefore seems unlikely that cyanomethylation is the main reason for the decrease in peak height.

However, the order of reactivity of the alkyl aryl ketones, as measured by the decrease in peak height, is consistent with nucleophilic addition. The most likely nucleophile had appeared to be the benzenesulphinate anion. Further evidence for this mechanism could be found in the larger value for the decrease in peak height obtained for propiophenone in the presence of water (see Table 20); more efficient protonation of the cyanomethyl anion and/or the conjugate base of benzenesulphonylacetonitrile would result in greater conversion of XXVI to benzenesulphinate anion. It has been shown, though, that the addition of tetraethylammonium benzenesulphinate to a solution of indan-1-one and tetraethylammonium fluoroborate in DMF does not result in a decrease in the peak height of indan-1-one. Hence, it is apparent that more detailed analyses of the products from preparative
electrolyses, combined with further experiments, are required to elucidate the reactions that occur when benzenesulphonylacetonitrile is electrolysed in the presence of alkyl aryl ketones.

**Summary**

Preparative electrolyses of benzenesulphonylacetonitrile in DMF in the presence of acrylonitrile yielded glutaronitrile, adiponitrile and propionitrile. It is likely that glutaronitrile is formed by nucleophilic addition of the conjugate base of benzenesulphonylacetonitrile to acrylonitrile followed by electroreductive cleavage of the adduct, while adiponitrile and propionitrile result from addition of the benzenesulphinate anion to acrylonitrile. The average rate constant for the addition of these nucleophiles to acrylonitrile has been estimated by linear sweep voltammetry (LSV) as 100 to 1200 \text{mol}^{-1}\text{s}^{-1}.

Cyanomethylated products were not detected in the electroreduction in DMF of benzenesulphonylacetonitrile in the presence of either acetophenone or 3-methylcinnamonnitrile; 3-phenylbutanenitrile was formed in the latter case.

LSV indicated that, while stilbene is unreactive, alkyl aryl ketones undergo nucleophilic addition by a species formed during the electroreduction of benzenesulphonylacetonitrile.
CHAPTER 3

Computer Simulation of the Electroanalytical Experiments

Introduction

Much effort has been devoted to obtaining complete analytical solutions to many of the systems studied by electroanalytical methods (see publications by R.S. Nicholson and co-workers in 'Analytical Chemistry' and J.M. Saveant and co-workers in 'J. Electroanalytical Chemistry'). Recently, however, a less sophisticated technique has become popular in which finite-difference approximations are applied directly to the equations which describe the changes in concentration of species over time and distance. This method was applied originally to electroanalysitcal experiments by Feldberg. The advantage of this technique over the analytical solution approach is that it is easy to adapt to complex reaction mechanisms, but it has drawbacks in that the number of parameters is large and the effect of each parameter must be investigated individually by performing several simulations.

We adopted this latter general approach in order to simulate the cyclic voltammetric behaviour for the addition of electrochemically generated cyanomethyl anions to electroactive substrates. The main objective was to produce data from the computer simulation which would enable the estimation of the rate constant for cyanomethylatation of various electroactive substrates using linear sweep voltammetry (LSV).

The model mechanism which was studied is given in Scheme 1.

\[
\begin{align*}
A + e & \underset{k_1}{\overset{\longrightarrow}{\rightleftharpoons}} A^- , E^0(A) \\
A^- & \longrightarrow Z \\
B + e & \underset{k_2}{\overset{\longrightarrow}{\rightleftharpoons}} B^- , E^0(B) \\
B + Z & \longrightarrow Y \\
\end{align*}
\]

Scheme 1
Species A and B undergo reversible 1-electron transfers to $A^-$ and $B^-$; the standard potentials are $E^0(A)$ and $E^0(B)$ respectively. Species $A^-$ then undergoes a chemical reaction of 1st order rate constant $k_1$ to form species Z which can then react with B in a 2nd order reaction of rate constant $k_2$. The results of the computer simulation will be applicable to any reaction mechanism which is similar to the model, and can be applied to electrooxidations as well as electroreductions. Of particular interest, though, are cases where the reactive species Z is the cyanornethyl anion and B is a suitable substrate for cyanomethylation, e.g. a ketone or an $\alpha,\beta$-unsaturated nitrile.

The mathematical equations and boundary conditions which define the model system are set out in Appendix 1; definitions of the symbols used in this chapter are listed in Appendix 2. Equations 1-5 describe the changes in the concentrations of the various species as functions of time and distance due to diffusion and to chemical reaction. The effects of the applied potential on the concentrations of the electroactive species at the electrode surface are described by Equations 6 and 7. In Equations 8-10 the law of mass balance is applied to the flux of material at the solution/electrode interface. The other boundary conditions are the concentrations in the bulk solution, i.e. where $x \to \infty$, which are assumed as constant during the timescale of the experiment, and the initial concentrations, i.e. when $t=0$.

It is also necessary to know how the potential varies as a function of time for the two electroanalytical techniques, LSV and CV, of interest. CV is an extension of LSV in which, at time $\lambda$, the direction of the potential sweep is reversed. Equation 11a therefore applies to a potential sweep towards more cathodic potentials in LSV, and in CV before the switching time, $\lambda$, while Equation 11b
applies to the reverse sweep in CV.

(11a) ... \[ E_t = E_i - vt \quad , \quad 0 < t \leq \lambda \]

(11b) ... \[ E_t = E_i - 2v \lambda + vt \quad , \quad \lambda \leq t \]

The approach to the simulation is to consider the problem as 2-dimensional viz. distance (from the electrode surface) and time (from the initiation of the experiment). The distance and time dimensions are divided into suitable intervals denoted by \( \Delta x \) and \( \Delta t \) respectively. For a particular value of \( t \), the concentration of each species at each distance is calculated. The current can then be calculated from the concentration gradients at the electrode surface. The concentrations are recalculated for \( t + \Delta t \) and then the current at \( t + \Delta t \) is determined. This process is carried out for each time increment.

The present approach differs from Feldberg's in that the emphasis is on the digital simulation of the appropriate mathematical equations rather than simulation of the chemical system.

**Digital simulation using finite-difference methods**

In order to calculate the concentration of each species at each distance for a particular time increment, it is necessary to apply a finite-difference method to Equations 1-5.

The general finite-difference approximation to the self diffusion equation:

(12) ... \[ \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \]

is given in Equation 13 where \( 0 \leq \theta \leq 1 \). The usual values assigned to \( \theta \) are 0, \( \frac{1}{2} \) and 1 and these are known respectively as the explicit,
\[
\frac{c_i(x, t + \Delta t) - c_i(x, t)}{\Delta t} = \frac{D_i}{(\Delta x)^2} \left\{ \theta \left[ c_i(x + \Delta x, t + \Delta t) - 2c_i(x, t + \Delta t) + c_i(x - \Delta x, t + \Delta t) \right] + (1 - \theta) \left[ c_i(x + \Delta x, t) - 2c_i(x, t) + c_i(x - \Delta x, t) \right] \right\}
\]
Crank-Nicolson implicit, and fully implicit methods.

With \( \theta = 0 \), i.e. the explicit method, Equation 13 reduces to:

\[
\frac{c_i(x, t + \Delta t) - c_i(x, t)}{\Delta t} = \frac{D_i}{(\Delta x)^2} \left[ c_i(x + \Delta x, t) - 2c_i(x, t) + c_i(x - \Delta x, t) \right]
\]
which can be rewritten as:

\[
\frac{D_i \Delta t}{(\Delta x)^2} \left[ c_i(x + \Delta x, t) - 2c_i(x, t) + c_i(x - \Delta x, t) \right] + c_i(x, t)
\]

Since the concentrations at \((x, t + \Delta t)\) are given solely in terms of known concentrations at time \(t\) and do not require knowledge of any concentrations at time \(t + \Delta t\), it is possible to calculate the concentrations at each value of \(x\) (except \(x = 0\)) independently.

By comparison, setting \( \theta = \frac{1}{2} \) in Equation 13 gives:

\[
\frac{D_i \Delta t}{(\Delta x)^2} \left[ c_i(x - \Delta x, t + \Delta t) + (2 + 2P_i)c_i(x, t + \Delta t) - P_i c_i(x + \Delta x, t + \Delta t) \right] + P_i c_i(x - \Delta x, t) + (2 - 2P_i)c_i(x, t) + P_i c_i(x + \Delta x, t)
\]
where \( P_i = \frac{D_i \Delta t}{(\Delta x)^2} \),

while if \( \theta = 1 \):
(17) \[ -P_1 c_1(x - \Delta x, t + \Delta t) + (1 + 2P_1) c_1(x, t + \Delta t) - P_1 c_1(x + \Delta x, t + \Delta t) = c_1(x, t) \]

Since both Equations 16 and 17 include more than one \( t + \Delta t \) term, it is necessary to solve the equations simultaneously. Because of the simpler procedure required for handling the explicit method rather than the simultaneous equations of the implicit methods, the explicit method was used in the original program.

If Equation 15 is used in Equation 2 then a simple algorithm for the calculation of concentrations of \( A^- \) is obtained:

(18) \[ c_{A^-(x, t + \Delta t)} = \]
\[ D_{A^-} \cdot \Delta t \left[ c_{A^-}(x + \Delta x, t) - 2c_{A^-}(x, t) + c_{A^-}(x - \Delta x, t) \right] / (\Delta x)^2 \]
\[ + (1 - k_{1.} \cdot \Delta t) c_{A^-}(x, t) \]

The explicit finite-difference equation for the 2nd order Equation 3 is:

(19) \[ c_B(x, t + \Delta t) = \]
\[ D_{B^-} \cdot \Delta t \left[ c_B(x + \Delta x, t) - 2c_B(x, t) + c_B(x - \Delta x, t) \right] / (\Delta x)^2 \]
\[ + \left[ 1 - k_{2.} \cdot \Delta t \cdot c_B(x, t) \right] c_B(x, t) \]

The drawback of the explicit method compared to the implicit methods is that the explicit method when applied to Equations 1 and 4 is stable only when \(^{136}\):

(20) \[ \frac{D_i \cdot \Delta t}{(\Delta x)^2} \leq \frac{1}{2} \]

and when applied to Equation 2 is stable only when \(^{137}\):

(21) \[ \frac{D_{A^-} \cdot \Delta t}{(\Delta x)^2} \leq \frac{1}{4} - \frac{k_{1.} \cdot \Delta t}{4} \]
Scheme 2: Flow diagram for computer simulation program using explicit finite-difference methods

A feed in data

B calculate parameters

D set up boundary conditions for $t=0$

Do $t=1, NT$

calculate the potential $E$

impose the boundary conditions for $x \to \infty (t=0)$ at $X=NR$

Do $X=NR-1$ to 1

calculate the concentrations of each species at $X=X-1$

NO $x = \Delta x$?

YES

impose the boundary conditions at the electrode surface;

$x = 0, t > 0$

I calculate the current

NO $E_t = E_f$?

YES END

G output data and parameters for reference

J output potential and currents
The equations obtained by the application of the implicit methods are always stable. Thus, the use of the explicit method restricts the choice of $\Delta t$ and $\Delta x$ to values which satisfy Equations 20 and 21.

**The computer program**

The procedure for the computer simulation is set out in Scheme 2 and the basic program, EGBL, is included in Appendix 3. This program is designed to simulate linear sweep voltammograms; extension to cyclic voltammograms is possible by making the modifications listed in Appendix 4 which change the sign of the potential increment once the switching potential, $E_A$, has been reached. The programming language which is used throughout the investigation is Fortran. The variables which are used in the computer programs are defined in Appendix 5.

Steps A-F (see Scheme 2 and Appendix 3) are straightforward. The use of the finite-difference methods occurs in Step G. The change, due to diffusion, in the concentration of each species at each distance, $x$, is calculated by the function "DELBl": $c_i(x,t+\Delta t)$ is then calculated by correcting $c_i(x,t)$ for this change, e.g. Appendix 3 lines 96 and 101, as well as for any change in concentration due to kinetic terms, e.g. Appendix 3 lines 98-100.

It was stated earlier that the concentrations at each value of $x$, except $x = 0$, could be solved by the application of the explicit method to Equations 1-5. The concentrations at the electrode surface are obtained by imposing boundary conditions 6-10. This is carried out in Step H (see Scheme 2 and Appendix 3). Most workers have used the simple, two-point finite-difference approximation to the partial derivative in Equations 8-10:
but from pilot calculations, a six-point Lagrangian formula was found to give more accurate results for a given $\Delta x$:

$$\frac{\partial c_i}{\partial x} \bigg|_{x=0} \approx \frac{c_i(x=\Delta x) - c_i(x=0)}{\Delta x}$$

(22) ... \[ \frac{1}{120} \frac{1}{\Delta x} \left\{ -274c_i(x=0) + 600 \left[ c_i(x=\Delta x) - c_i(x=2\Delta x) \right] \\
+ 400c_i(x=3\Delta x) - 150c_i(x=4\Delta x) + 24c_i(x=5\Delta x) \right\} \]

In order to simplify Equations 8 and 9, the assumptions are made that

$$D_A = D_{A^-} \quad \text{and} \quad D_B = D_{B^-}$$

These assumptions are reasonable since the sizes of anions $A^-$ and $B^-$ will be very similar to the sizes of molecules $A$ and $B$ respectively. But since these species are in a strong electric field, the diffusion coefficients of the ionic species will be superimposed upon by the force on the ions due to the field strength. No correction is made in this program to account for this latter aspect. $D_z$ is also set equal to $D_A$; the strength of this assumption depends on the real system which is being studied, i.e. on the size of $Z$ relative to $A$, and on the ionic or non-ionic nature of $Z$ since, again, an ionic species will be affected by the electric field.

The six-point Lagrangian formula is also used in Step I to calculate the flux of species $A$ and $B$ at the electrode surface; from which the currents due to each of these species can be determined:

$$i(i) = nFAD_i \frac{\partial c_i}{\partial x} \bigg|_{x=0}$$

(23) ...
Choice of parameters

The simulation results apply to 1-electron charge transfers, and to voltammograms run at room temperature, i.e. 298°K was incorporated in the program (see Appendix 3, line 7) and was used in the Nernst Equations 6 and 7 (see Appendix 3, lines 109 and 110). All the simulations were performed with $D_A = D_B$ ($= D_{A^-} = D_{B^-} = D_z$) = $2 \times 10^{-5}$ cm$^2$ s$^{-1}$. The results of Bacon and Adams$^{138}$ indicated that this was a reasonable estimate.

The separation in the standard potentials of the A/A$^-$ and B/B$^-$ redox couples, $\Delta E^\circ$, was in the range 0.25-1.00V. Concentrations of 2mM were experimentally convenient and so in the initial simulations: $c_A = c_B = 0.00214$. Since the chart recorder used in the early experimental work was limited to a maximum sweep rate of 0.25Vs$^{-1}$, this value was used in the initial simulation studies. For $v = 0.25$Vs$^{-1}$, a grid of 1200 time points and 93 distance points was used for a potential range of 1.0V (i.e. time range = 4.0s) and a diffusion layer thickness of 0.039cm, i.e. the grid intervals were $\Delta x = 4.24 \times 10^{-4}$ cm and $\Delta t = 3.34 \times 10^{-3}$ s. This grid had been shown by Howat$^{139}$ to reproduce the analytical results of Nicholson and Sham$^{127}$ for a reversible electron transfer followed by a 1st-order chemical reaction in which $k_1/a = 10$ ($a = nFv/RT$). The values of $k_1$ which are used in the simulations are calculated from the values of $k_1/a$ (for $v = 0.25$Vs$^{-1}$) which were used by Nicholson and Sham$^{127}$ (see Figure 16).

The information available from each simulation

The output from the simulation tabulates, for each value of the potential, the values of the current due to each species and the total current. Usually, the output was searched manually for the potential range in which the current reached a maximum. An interpolation...
program was then used to tabulate the results for this potential range in potential increments of 0.1mV; the peak current and the potential at which this peak current occurred were then read from the table. A computer program was developed to draw the simulated voltammogram in the usual current vs. potential form or in a current vs. time form.

From simulated cyclic voltammograms, the anodic peak current, $i_{pa}'$, was measured by the method of Polcyn and Shain$^{131}$, i.e. from the extension of the cathodic current as shown in Figure 20.

The effect of the various parameters on the shape of the voltammogram will be examined in terms of the peak current, $i_{pc}(B)$, and potential, $E_{pc}(B)$, for species B rather than on the peak potential, $E_{pc}(\text{total})$, and the current, $i(B)$, due to species B at the total current peak, although the latter are, experimentally, more readily measured. The reason the former were selected for analysis was that they are not affected by the shape of the voltammogram due to the reduction of species A, while the latter are. $E_{pc}(B)$ is slightly cathodic of $E_{pc}(\text{total})$ and $i_{pc}(B)$ is slightly larger than $i(B)$; the differences increase with the value of $k_2$, e.g. for $k_1 = 97.36s^{-1}$, $k_2 = 51200 \text{ mol}^{-1}\text{s}^{-1}$, $\nu = 0.25\text{V}\text{s}^{-1}$ and $\Delta E^o' = 0.252V$, $i_{pc}(B) = 0.225\text{Acm}^{-2}$ while $i(B) = 0.220\text{Acm}^{-2}$ (the decreases in peak height compared to the value for $k_2 = 0$ ($i_{pc} = 1.2018\text{Acm}^{-2}$) are 81.3% and 81.7% respectively).

The results for $i_{pc}(B)$ will often be discussed in terms of the decrease in peak height since, in the voltammetric experiment, rather than the absolute magnitude of the current, its magnitude relative to the initial peak current is measured.
Results and discussion

Simulation of known systems

Setting $k_2 = 0$ in Scheme 1 effectively decouples the two systems, with species B being involved in a reversible charge transfer while species A is involved in a reversible charge transfer followed by an irreversible chemical reaction, i.e. an EC process. Nicholson and Shain\textsuperscript{127} have previously published results for both of these systems using analytical solutions.

Digital simulation of a reversible electron transfer in the absence of any chemical reactions (see Table 23) gave peak current ratios, $i_{pa}/i_{pc}$, to within 0.1% of the theoretical value of 1.0 if the switching potential, $E_A$, was $>\, 100$ mV cathodic of the standard potential, $E^0$. The position of the anodic peak, $E_{pa}$, was within 0.5 mV of Nicholson and Shain's results\textsuperscript{127} while the cathodic peak, $E_{pc}$, was within 0.2 mV [$E_{pc} - E^0 = -28.35$ mV (simulation); $-28.50$ mV (Nicholson and Shain\textsuperscript{127})]. The height of the reduction peak, $i_{pc}$, was directly proportional to the concentration (see Table 24) in agreement with Nicholson and Shain's results\textsuperscript{127}.

Comparison of the simulation results for an EC process involving a reversible electron transfer and an irreversible chemical reaction with Nicholson and Shain's results\textsuperscript{127} showed that the peak potentials were within 1.3 mV while the peak currents were within 0.5% (see Table 25). Graph 27 of $i_{pa}/i_{pc}$ versus $\log(k_{pc})$, where $\gamma$ is the time taken between $E^0$ and $E_A$, shows that the simulation results (see Table 26) and Nicholson and Shain's results\textsuperscript{127} fit the same working curve. Simulated cyclic voltammograms for an EC process are shown in Figure 16.
Figure 17 illustrates simulated cyclic voltammograms for an EEC process for which an additional program had been prepared. The effect of the irreversible chemical reaction on the second reversible electron transfer for $\Delta E^0' = 0.45V$ was identical to that for an isolated EC process. This is in agreement with the results of Polcyn and Shain. 131

Investigation of the accuracy of the simulation

The simulation has been shown to be reliable when species A and B are decoupled, i.e. $k_2 = 0$. In the simulation studies for $k_2 \neq 0$ it was intended to study as wide a range of rate constants as possible. Initial studies showed that, using the grid parameters quoted above, the simulation was unstable at $k_1 = 200s^{-1}$ or $k_2 = 10^5$ $\text{mol}^{-1}\text{s}^{-1}$. It was also of interest to investigate the effect of varying the sweep rate in the simulations since sweep rate is a major experimental variable. In order to be certain that the simulations would represent the system adequately, it was necessary to check that suitable time and distance grids were being used over the range of sweep rates and the range of rate constants.

i) Sweep rate. - The simulation is based on the assumption that at a given distance from the electrode surface known as the diffusion layer thickness, $x = \delta$, the boundary conditions for an "infinite" distance will be applicable, i.e. that $c_a(\delta, t) = c_b$. The diffusion layer thickness, $\delta$, is so called because it represents the limit of the diffusion of species towards and away from the electrode.

The diffusion of each species is defined by Fick's second law, i.e. by Equation 12.
The solution to Equation 12 in terms of $c_i(\delta,t)$ can be expressed as:

$$c_i(\delta,t) = c_i^b 2\pi^{-\frac{1}{2}} \int_0^\delta \frac{\delta e^{-y^2}}{2D_1^i t^\frac{3}{2}} dy$$

which can be rewritten as:

$$c_i(\delta,t) = c_i^b 2\pi^{-\frac{1}{2}} \int_0^Z e^{-y^2} dy$$

where

$$Z = \frac{\delta}{2D_1^i t^\frac{3}{2}}$$

The integral $\int_0^Z e^{-y^2} dy$ is called the error function of $Z$, erf$Z$, i.e. Equation 25 can be written as:

$$c_i(\delta,t) = c_i^b \text{erf}Z$$

Table 27 gives values of erf$Z$ for several values of $Z$. The closer erf$Z$ is to 1.0, the more precise is the assumption that $c_i(\delta,t) = c_i^b$; thus the value of $Z$ determines the degree of accuracy being placed on this assumption. Table 28 shows how the value of the diffusion layer thickness, $\delta$, depends on the choice of $Z$.

In the simulations which were compared with Nicholson and Shain's results for the reversible charge transfer and the EC process, the diffusion layer thickness was 0.039 cm and the sweep time was 4.0 s. It is apparent from Tables 27 and 28 that a value of erf$Z$ between 0.9953 and 0.9996 ($Z = 2.0 - 2.5$) gave results which were in good agreement with the published results. However if simulations using sweep rates $< 0.2 \text{Vs}^{-1}$ and hence sweep times $> 5$ s were required, then either larger diffusion layer thicknesses must be used or lower accuracy must be accepted since if $\delta$ is kept constant erf$Z$ will
For simulations using slower sweep rates it was desirable to maintain the optimum value (as found by Howat\(^{139}\)) of \(D \Delta t / (\Delta x)^2 = 0.37\) yet allow for a larger diffusion thickness and a longer sweep time. To fulfill these requirements, the values of \(\Delta x\) and \(\Delta t\) were not changed but the number of distance and time points was increased. The simulation then required much more computer space and time.

Joslin and Pletcher\(^{141}\) have described ways in which computer time can be reduced. Using one of their methods, program EGS4 (see Appendix 4b) was developed which calculated the necessary diffusion layer thickness at each time increment. The sweep time and hence the maximum diffusion layer thickness for a chosen value of \(Z\) were calculated manually. The maximum diffusion layer thickness was then fed into the program with the other data. The number of distance increments which was to be used was calculated in the program at each time increment.

The results show that the use of values of \(erfZ\) less than 0.9953 did not lead to any loss in accuracy (see Table 29). The results for \(v = 0.075 Vs^{-1}\) are the most telling; a diffusion layer thickness of 0.039cm, which is only 75% of that required for \(Z = 2.0\) for the sweep time of 8.67s to \(E_{pc}(B)\), did not cause any loss in the accuracy of the simulation.

ii) Rate constants \(k_1\) and \(k_2\). It is obvious that the faster a chemical reaction is then the smaller are the time and distance over which the reaction occurs. The distance is known as the kinetic layer. Joslin and Pletcher\(^{141}\) require that the simulation of chemical reactions must be performed over several time and distance increments and specifically
require that for a first order reaction, Equations 27 and 28 are satisfied.

\begin{equation}
\Delta x < \frac{\sqrt{D}}{k}
\end{equation}

\begin{equation}
\Delta t < k^{-1}
\end{equation}

Table 30 shows the maximum grid intervals as defined by Equations 27 and 28 for a range of values of first order rate constants.

Using EGB1 with $\Delta t = 3.34 \times 10^{-3}$ s and $\Delta x = 4.24 \times 10^{-4}$ cm should restrict the first order rate constant to $k \leq 100$ s$^{-1}$, which is the case. Using program EGB4, values of $\Delta t$ and $\Delta x$ of as low as $1 \times 10^{-3}$ s and $2.5 \times 10^{-4}$ cm respectively can be used conveniently, but these would still restrict the maximum rate constant to $< 1,000$ s$^{-1}$.

Equations 27 and 28 were produced for a first order chemical reaction, but the present study involves a second order chemical reaction and although the simulation had been found to be stable for values of $k_2 = 5.12 \times 10^4$ lmol$^{-1}$ s$^{-1}$, there was concern as to whether the results for such high values of $k_2$ were accurate. It was therefore decided to modify the program so that smaller grids could be used.

Although a finer grid is necessary in the region in which the reactive species are produced and react, i.e. close to the electrode surface, it is not essential further away from the electrode surface. Joslin and Pletcher used a distance grid in which the size of the distance increments increased smoothly with the distance from the electrode surface. A suitable function which achieves this is

\begin{equation}
y = f(\bar{x}) = \frac{l}{m} - \frac{l}{m + \bar{x}}
\end{equation}

where $\bar{x}$ is the dimensionless parameter $\bar{x} = x/\delta$ and $l$ and $m$ are constants. This function transforms a non-linear $\bar{x}$-distance grid into a uniform $y$-distance grid. The form of the explicit finite-difference equation used with such a grid was reported by Joslin and Pletcher for:
\[ \frac{\partial c_i}{\partial t} = \frac{D_i}{\delta^2} \frac{\partial^2 c_i}{\partial x^2} \]

as:

\[
(30) \quad c_1(y,t + \Delta t) - c_1(y,t) = \\
\frac{\Delta t D_i}{\delta^2(\Delta y)^2} \left[ \frac{\partial f(\bar{x})}{\partial \bar{x}} \right]_{y,t} \left\{ \frac{\partial f(\bar{x})}{\partial \bar{x}} \right\}_{y + \Delta y/2, t} \left[ c_1(y + \Delta y, t) - c_1(y, t) \right] - \\
\frac{\partial f(\bar{x})}{\partial \bar{x}} \left\{ c_1(y, t) - c_1(y - \Delta y, t) \right\} 
\]

Kinetic terms are treated in exactly the same way as before but \( c_1(y,t) \) replaces \( c_i(x,t) \).

Since the derivatives \( \partial c_i / \partial x \) and \( \partial c_i / \partial \bar{x} \) can be written as

\[
\frac{\partial c_i}{\partial x} = \frac{1}{\delta} \frac{\partial c_i}{\partial \bar{x}} \quad \text{and} \quad \frac{\partial c_i}{\partial \bar{x}} = \frac{\partial c_i}{\partial \bar{x}} \cdot \frac{\partial f(\bar{x})}{\partial \bar{x}}
\]

then the concentration gradient at the electrode surface in the x-grid,

\[
\left. \frac{\partial c_i}{\partial x} \right|_{x = 0}
\]

, can be written in terms of the concentration gradient at the electrode surface in the transformed grid, \( \left. \frac{\partial c_i}{\partial \bar{x}} \right|_{\bar{x} = 0} \):

\[
(31) \quad \left. \frac{\partial c_i}{\partial x} \right|_{x = 0} = \frac{1}{\delta} \left. \frac{\partial c_i}{\partial y} \right|_{y = 0} \cdot \left. \frac{\partial f(\bar{x})}{\partial \bar{x}} \right|_{\bar{x} = 0} = \frac{1}{\delta} \cdot \frac{1}{m^2} \left. \frac{\partial c_i}{\partial y} \right|_{y = 0}
\]

The current is therefore calculated as

\[
i(i) = \frac{nFAD_i}{\delta m^2} \left. \frac{\partial c_i}{\partial y} \right|_{y = 0}
\]
When Equation 31 is used in boundary conditions 8, 9 and 10, the differential 
\( \frac{\partial f(x)}{\partial x} \) disappears to leave, respectively:

\[
\begin{align*}
\frac{\partial c_A}{\partial y} \bigg|_{y=0} &= -\frac{\partial c_A}{\partial y} \bigg|_{y=0} \\
\frac{\partial c_B}{\partial y} \bigg|_{y=0} &= -\frac{\partial c_B}{\partial y} \bigg|_{y=0} \\
\frac{\partial c_Z}{\partial y} \bigg|_{y=0} &= 0
\end{align*}
\]

(assuming \( D_A = D_A^- \) and \( D_B = D_B^- \)).

These equations were incorporated into a program, EGB6 (see Appendix 6), to perform simulation of Scheme 1. Before the program could be run, values for \( t \) and \( m \) had to be selected. Table 31 illustrates how the optimum number of simulation points, \( NY \), is affected by the choice of \( \Delta t \) and constants \( l \) and \( m \). The table was prepared by calculating \( y_{\text{max}} \) from:

\[
(32) \quad y_{\text{max}} = f(x = 1) = \frac{l}{m} - \frac{l}{m+1}
\]

and then calculating \( \Delta y \) for several values of \( \Delta t \) from:

\[
(33) \quad \Delta y = \frac{(D_{11} \Delta t)^{\frac{1}{2}}}{0.6 \delta} \frac{l}{m^2}
\]

Equation 33 arises from the choice of

\[
\frac{D_1 \Delta t}{\delta^2 (\Delta y)^2} \left( \frac{\partial f(x)}{\partial x} \right)^2_{\text{max}} = 0.36
\]

The optimum number of simulation points, \( NY \), was obtained by dividing \( y_{\text{max}} \) by \( \Delta y \) and rounding up to the next integer. After determining from the rate constant what size of time interval was necessary, the
choice of $\Delta y$ and of $l$ and $m$ was limited by $NY$, i.e. by the computer
time and space which was available for the simulation. Graph 28 shows
how $x$ varies over a uniform $y(y/y_{\text{max}})$ scale for two values of the
constant, $l = m$.

The major modifications which have been introduced in
program EGB6 come in lines 24 - 47 and in lines 111 - 125 (see Appendix
6). The former modification carries out the calculation of $\Delta y(DRY)$,
y_{\text{max}}(YMAX) and $NY$ (NYMAX) as described above. Because $NY$ (NYMAX) is
rounded up to the next integer, the actual value of $DRY$ to be used in the
simulation is recalculated in line 30 as $YMAX/NYMAX$. For each value of
$0.5\Delta y$, the values of $x(XBAR)$ are calculated using:

$$ x = \frac{ym^2}{l - my} $$

which is the rearranged form of Equation 29, and the values of the 1st
derivative of Equation 29, $dy/dx$ (PP), are also calculated using:

$$ \frac{dy}{dx} = \frac{1}{(m + x)^2} $$

The latter modification involves the application of Equation 30 to
Equations 1-5. Again, it was found necessary to use a six-point Lagrangian
formula rather than the two-point finite-difference method for the deter-
mination of $\frac{\partial c_i}{\partial y}$. 

If very small values of $\Delta t$ were used, then the output
was too large to store in a file. The program was therefore modified
(to EGB7) to write the current for every twentieth time increment.

Table 32 shows that the use of a finer grid for a fast
second order rate constant does not lead to a change in the peak
current, $i_{PC}(B)$, from that which had been obtained using $\Delta t = 3.34 \times 10^{-3}s$
and $\Delta x = 4.24 \times 10^{-4}$ cm. It should be noted that the peak potential values for species A which is involved in an EC process attain the same accuracy as Nicholson and Shain's published results.

Effect of variations in $k_1$ and $k_2$

Graph 29 illustrates that for a particular value of the 2nd order rate constant, $k_2$, the peak height of species B, $i_{pc}(B)$, decreases dramatically as the 1st order rate constant, $k_1$, increases to approximately 15s$^{-1}$ but thereafter there is little further change. Using program BFB6, simulations using values of $k_1$ as large as 800s$^{-1}$ were run. These results (see Table 33) show that for application to experimental data, the results for $k_1 = 97s^{-1}$ can be accepted as the limit of the decrease in the peak height. Indeed, as long as the experimental 1st order rate constant is greater than approximately 40s$^{-1}$, then the results for $k_1 = 97s^{-1}$ can be accepted as accurate enough by comparison with the accuracy of the experimental data.

Similarly, for a particular value of $k_1$, the peak height of species B is sensitive to the second order rate constant for values of $k_2 < 1 \times 10^4$ 1mol$^{-1}$s$^{-1}$, but relatively insensitive above this value (see Graph 30). It is possible, by plotting the decrease in $i_{pc}(B)$ vs. $\log_{10} k_2$, to expand the plot of the region of interest, i.e. where $i_{pc}(B)$ is sensitive to $k_2$ (see Graph 31).

Effect of varying concentration

The concentrations of species A and B were varied and it was found that the decrease in $i_{pc}(B)$ depended on the actual molarity of each species rather than the relative molarities (see Table 34).

Simulations were performed to tie in with experiments
in which the concentration of one or other of the species was varied. No simple relationship was found between the decrease in $i_{pO}(B)$ and the concentration of species B (see Table 35).

**Effect of varying $\Delta E^{0'}$ and $v$.**

The time which elapses between the reduction of species A and the subsequent reduction of species B will affect the extent of the decrease in $i_{pO}(B)$. Thus, if $\Delta E^{0'}$ is large or the sweep rate, $v$, slow, then there is more time for species Z to be formed and to react with species B leading to a larger decrease in $i_{pO}(B)$.

The effect of $\Delta E^{0'}$ on the decrease in $i_{pO}(B)$ is illustrated for $v = 0.25Vs^{-1}$ in Graphs 32 ($k_1 = 0.487s^{-1}$) and 33 ($k_1 = 4.87s^{-1}$) and for $v = 0.20Vs^{-1}$ in Graphs 34 ($k_1 = 0.487s^{-1}$) and 35 ($k_1 = 4.87s^{-1}$). From these graphs, working curves for the two values of $v$ were prepared (see Graphs 36 and 37) for the two values of $k_1$ and several values of $\Delta E^{0'}$. These particular working curves were used for the estimation of the rate constants for cyanomethylation, initiated by proton abstraction from the solvent by azopyridine dianions, of various electroactive substrates in acetonitrile (see Chapter 2, p79 "Estimation of 2nd order rate constants for the cyanomethylation of aromatic carbonyl compounds and $\alpha,\beta$-unsaturated nitriles").

The effect of $v$ on the decrease in $i_{pO}(B)$ is illustrated for $\Delta E^{0'} = 0.40V$ and $k_1 = 97.36s^{-1}$ in Graph 38. As already stated, it is a major drawback in a simulation study such as this to have too many variables. It has been shown that $i_{pO}(B)$ is insensitive to variations in $k_1$ when $k_1 > 40s^{-1}$; hence, setting $k_1$ equal to, say, 97s$^{-1}$ will provide data applicable to $k_1 > 40s^{-1}$. Since both $\Delta E^{0'}$ and $v$ affect the elapsed time, it was thought possible that these two variables could
be combined into a single parameter \( \Gamma \) defined as:

\[
\frac{\Gamma}{s} = \frac{\Delta E^{o'}}{v} \frac{v}{Vs^{-1}}
\]

It is apparent from Table 36 that the use of different pairs of \( \Delta E^{o'} \)
and \( v \) for particular values of \( \Gamma \) and \( k_2 \) does not give identical results
for the decrease in peak height. The differences are most noticeable
at low values of \( k_2 \) where the decrease in \( i_{pc}(B) \) is of the order of
20 \( \pm \) 1\%. But it is in this range that a small change in \( k_2 \) produces a
large change in the peak height so that the loss in accuracy is unimportant.
The accuracy of the simulation is still better than that achievable experimentally.

A series of working curves of decrease in \( i_{pc}(B) \) vs. \( \Gamma \)
using \( k_1 = 97s^{-1} \) can therefore be prepared (see Graph 39) from which \( k_2 \)
can be estimated as long as \( k_1 > 40s^{-1} \).

**Peak potential data**

The peak potential, \( E_{pc}(B) \), was usually obtained from the
simulation output, but for several reasons it was of secondary interest.
Experimentally, the obvious effect had been the decrease in the peak
height, while there had been no noticeable change in the peak potential.
Due to the lack of precision in the measurement of peak potentials from
cyclic voltammograms, variations of less than 10mV would probably be
undetectable. In addition, the investigation of the accuracy of the
simulations had shown that the peak potential values were not as accurate
as the peak current values though any error in the simulation was
negligible when compared with the experimental uncertainty.

The effect of the reaction of species Z with species B is to shift the potential cathodically; the shift increases as \( k_2 \)
increases (see Graph 40). The effect of \( v \) on \( \mathbf{B}_p \) is illustrated in Graph 41 for several values of \( k_2 \); this graph is similar to Graph 38 of decrease in \( \mathbf{B}_p \) vs. \( v \) for the same set of parameters.

So far, these results have been shown to apply to the model system described by Scheme 1. It was of interest to look at more complex systems.

**Regeneration of species Z**

Another chemical reaction was added to those in Scheme 1:

\[
\begin{align*}
\quad & k_3 \\
Y & \rightarrow Z
\end{align*}
\]

This represents the regeneration of the nucleophilic species Z. For the case of cyanomethylation in acetonitrile, such a process could be envisaged as proton abstraction from the solvent by the cyanomethyl adduct Y.

It is necessary to modify Equation 5 to:

\[
\frac{\partial c_Y}{\partial t} = D_Y \frac{\partial^2 c_Y}{\partial x^2} + k_2 c_B c_Z + k_1 c_A - k_3 c_Y
\]

and to include:

\[
\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - k_2 c_B c_Z + k_3 c_Y
\]

Additional boundary conditions are also required:

\[
\begin{align*}
t = 0; & \quad c_Y(x,0) = 0 \\
t > 0; & \quad x \rightarrow \infty; \quad c_Y(x,t) = 0 \\
x = 0; & \quad D_Y \frac{\partial c_Y}{\partial x} \bigg|_{x=0} = 0
\end{align*}
\]

The modifications to Program EGB1 which were necessary to give a program
which could include regeneration of species Z are listed in Appendix 4c. When writing this program, it was assumed that $D_Y = D_B$.

The effect of $k_3$ on the decrease in $i_{pc}(B)$ is shown in Table 37. It is apparent that the regeneration of species Z has a very dramatic effect on the amount of species B reaching the electrode.

Further reaction of species B^-

So far species B^- has been considered as a stable species on the electroanalytical timescale. The simulation results could therefore be applied to benzophenone and 3-phenylcinnamalonitrile but not to systems such as cinnamaldehyde or acetophenone.

i) 1st-order reaction.- Simulations were performed of a system consisting of the reactions in Scheme 1 but in which species B^- was involved in an irreversible 1st-order chemical reaction:

$$\text{B}^- \xrightarrow{k_4} \text{YY}$$

The only modification required to the equations in Appendix 1 was that Equation 4 was amended to:

$$\frac{\partial c_{B^-}}{\partial t} = D_B^- \frac{\partial^2 c_{B^-}}{\partial x^2} - k_4 c_{B^-}$$

Program EGB4, in which the diffusion thickness is increased as a function of time, was modified as described in Appendix 4d to take account of the 1st-order reaction of species B^- . Using this modified program, the effect of $k_4$ on the decrease in $i_{pc}(B)$ was examined; the decrease for a particular value of $k_4$ was calculated from $i_{pc}(B)$ for that value of $k_4$ and $k_2 = 0$. As $k_4$ is increased, the decrease in $i_{pc}(B)$ is reduced slightly (see Table 38). The extent of the reduction is affected by the value of $k_1$ (see Table 39) and by the value of $k_2$. 
The largest reductions occur in regions where they would lead to only a small error in $k_2$.

These results indicate that experimental data for a system in which species $B^-$ undergoes an irreversible 1st-order chemical reaction can be analysed using the results from the simulation of Scheme 1, but that the estimated value of $k_2$ will be slightly high.

ii) 2nd-order reaction. - Most of the electroactive species investigated in this work undergo dimerisation processes. The model system in Scheme 1 was modified to include the dimerisation reaction of species $B^-$:

\[
2B^- \xrightarrow{k_5} B_2
\]

Equation 4 was amended to:

\[
\frac{\partial c_{B^-}}{\partial t} = \frac{D_{B^-}}{\partial x^2} \frac{\partial^2 c_{B^-}}{\partial x^2} - k_5 c_{B^-}^2
\]

while the program modifications are listed in Appendix 4e.

The dimerisation of an electroreduced species has been previously investigated by Olmstead, Hamilton and Nicholson\(^{126}\); the simulation results for the decoupled system, i.e. $k_2 = 0$, were virtually identical to their results.

It is apparent from the results in Table 41 that the dimerisation of species $B^-$ has negligible effect upon the % decrease in $i_{pc}(B)$.

Summary

Computer simulation of the linear sweep voltammetry of the system described by the reactions in Scheme 1 was used to investigate the effects of various parameters, e.g. separation of the formal potentials, $\Delta E^{0'}$, sweep rate, $v$, concentration of both species, $c_A^b$ and $c_B^b$, and the
1st and 2nd order rate constants, $k_1$ and $k_2$, on the peak current for species B, $i_{pc}(B)$. The results for $k_1 = 97.36 \text{s}^{-1}$ were found to be applicable to experimental systems where the 1st-order rate constant is greater than $40 \text{s}^{-1}$. It was discovered that $\Delta E^{\circ'}$ and $\gamma$ could be incorporated into a single parameter $\Gamma (= \Delta E^{\circ'}/\gamma)$. A graph of the decrease in $i_{pc}(B)$ versus $\Gamma$ was produced containing working curves for values of $k_2$ in the range 100 to $51200 \text{ lmol}^{-1}\text{s}^{-1}$. These results were also shown to be applicable to cases where species B is involved in an irreversible chemical reaction, but if species Z is regenerated then the decrease in $i_{pc}(B)$ is much larger. Unfortunately, these working curves still rely on a good knowledge of $\Delta E^{\circ'}$ and while $E^{\circ}(B)$ may be known, the determination of $E^{\circ}(A)$ is not always possible. LSV is therefore not the best electroanalytical technique to obtain quantitative kinetic information from such a system; potential step methods are likely to be more suitable.

The original program was modified to perform simulations using very small time and distance increments over the required diffusion layer thickness. These simulations have shown that the results obtained with $\Delta t = 3.34 \times 10^{-3} \text{s}$ and $\Delta x = 4.24 \times 10^{-4} \text{cm}$ are accurate. It has also been shown that in the calculation of the diffusion layer thickness a value of $Z = 1.6$ ($\text{erf}Z = 0.9764$) is sufficient.
CHAPTER 4

Experimental

$^1$H Nuclear magnetic resonance (nmr) spectroscopy was performed on a Varian Anaspect EM360 (60MHz) or on a Varian Associates H.A. 100 (100MHz) spectrometer. $^{13}$C nmr spectroscopy was performed on a Varian CFT-20 spectrometer system. Tetramethysilane was used as internal reference. In the description of nmr data the following abbreviations are used: singlet(s), doublet(d), triplet(t), quartet(q) and multiplet(m).

Infrared spectra were recorded on a Perkin-Elmer 157 G spectrophotometer. The abbreviations used to describe the infrared bands are weak(w), medium(m) and strong(s). A Unicam SP 800A spectrophotometer was used to record ultraviolet and visible spectra.

Mass spectra were run on an A.E.I. MS 902 double focusing instrument. Fragmentation patterns are quoted in terms of the m/e values with the relative intensity of each peak quoted afterwards in brackets.

Gas liquid chromatography was performed on a Perkin-Elmer F11 or on a Pye 'Series 104' instrument with flame ionisation detection. The columns used were either 6' x $\frac{1}{4}$" O.D. glass columns packed with either 10% ApL on Chromosorb G (80-100 mesh) or 5% Carbowax 20M on Chromosorb W, or a 6' x $\frac{1}{8}$" O.D. stainless steel column packed with 15% PEG (MW 20,000) on Chromosorb P (acid washed, 80-100 mesh). Determination of the peak areas was initially performed by a Kent Chromalogue 3 digital integrator connected to the detector output, but most of the data was obtained by measurement of the dimensions of each peak on the recorder traces. Quantitative analysis results were obtained
from gas chromatography by calculating response factors for each component using a mixture of known weights of authentic samples and standards.

Gas liquid chromatography/mass spectrometry (GC/MS) was carried out on a V.G. Micromass 12 connected to a Pye 'Series 104' gas chromatograph.

High pressure liquid chromatography was carried out on a modified Du Pont 820 or a Chromatronix Model 3100 Liquid Chromatograph. The 100mm x 5mm stainless steel columns were packed with either Spherisorb Alumina (7μ) or Partisil-10 silica. Ultraviolet detectors operating at 254nm were used and integration of the peak areas was carried out by triangulation or by use of an Autolab 6300 Digital Integrator.

Elemental analysis was performed on a Perkin-Elmer 240 Elemental Analyser.

Melting points were determined on a Reichert hot stage microscope and are uncorrected.

Preparative electrolyses were carried out in the cell illustrated in Figure 18 using either a Chemical Electronics TR70/2A Potentiostat or a Hermes Controls Series 50 100V/0.5A Potentiostat. Electrode potentials were measured with a Philips Digital Multimeter P4.2421. The cracked-glass reference electrode contained a silver wire in a 0.1M silver nitrate solution in acetonitrile. The mercury was measured out by volume (3.0ml) and had an approximate surface area of 11cm² when unstirred. A carbon rod was usually used as the secondary electrode. In controlled-potential electrolyses, the amount of charge passed was measured using a hydrogen-nitrogen gas coulometer.
employing 0.1M aqueous hydrazine sulphate. Calibration of the
coulometer was carried out by applying a constant current through the
coulometer for a measured time interval and measuring the volume of
gas evolved. During most of the galvanostatic electrolyses the
reference electrode was omitted and a thermometer inserted in its place.

Cyclic voltammetry was performed either with a "Three
Electrode Polarograph" unit (design from V.D. Parker) or with a
Chemical Electronics TR70/2A Potentiostat driven by a Chemical
Electronics Waveform Generator Type R.B.I.. Current vs. potential (i/V)
curves and current vs. time (i/t) curves were recorded on either a
Bryans X-Y/t Plotter Model 21005 (maximum sweep rate = 300mVs⁻¹), a
Bryans X-Y/t Model 26000 A4 (maximum sweep rate = 1Vs⁻¹), or a Tektronix
5103N storage oscilloscope. Cyclic voltammetry was carried out in the
analytical cell illustrated in Figure 19. The working electrode was
either a platinum disc or a hanging mercury drop. The electrode was made
by heating a platinum wire (0.635mm diameter) to red heat for a short
period (heating for too long increased the size of gas bubbles on the
surface of the wire), forming a drop of soft glass around the wire and
sealing it into a soft glass tube. The tip was then ground down and
polished until a smooth glass-platinum surface was obtained. The
platinum electrode was then ready for use. Before each experiment the
disc surface was immersed in boiling aqua regia, rinsed with distilled
water and then polished with fine grade 'wet and dry' paper. The electrode
was rinsed with distilled water and then acetone and allowed to dry.

To prepare a hanging mercury drop electrode \( \text{H}^+ \text{(HMDE)} \),
the platinum disc electrode (PDE) was immersed in an aqueous 1M
perchloric acid solution with a mercury pool in the bottom of the flask.
A 3V battery was connected across the PDE and a platinum counter electrode,
which was also immersed in the solution. The PDE was connected to the negative terminal of the battery. Hydrogen gas was evolved at the PDE for 10min and then the PDE was dipped into the mercury pool several times without disconnecting from the battery until a mercury drop adhered to the platinum and covered the complete surface. The HMDE was disconnected from the battery and rinsed with distilled water and then acetone. It was stored with the tip of the electrode immersed in clean mercury.

Preparation for cyclic voltammetry involved weighing the supporting electrolyte (2.5mmol) into a 25ml volumetric flask and making up to the mark with solvent. 20ml of this supporting electrolyte solution was pipetted into the cell and nitrogen, which had previously passed through a molecular sieve tower and then a solvent presaturator, was bubbled into the solution for 15min to remove oxygen. The electroactive species was weighed into a 5.0ml volumetric flask, made up to the mark with solvent, and a sample (0.50ml or 1.00ml) was added to the electrolyte solution by pipette. The solution was stirred with a magnetic stirrer bar and deoxygenated for a further 15min. In cases where a second electroactive species, e.g. azopyridines or benzene-sulphonylacetonitrile, had to be added to the electrolyte, it was also pipetted as a 1.0ml solution. Between each cyclic voltammetry run the solution was magnetically stirred and nitrogen was bubbled into the solution and onto the working electrode. When recording cyclic voltammograms, a slight nitrogen pressure was maintained above the solution.

In cases where there are two successive reduction (or oxidation) peaks, or where a cyclic sweep is being used to study a reduction-oxidation couple, it is necessary to obtain a baseline from which the height of the second peak can be measured. The method
used in this study is based on the findings of Polcyn and Shain\textsuperscript{131} that, at potentials beyond the peak potential, the decay curve with increasing potential is identical to the decay curve at constant potential. This is because the decay current is diffusion controlled and independent of potential. Thus the potentiostat can be used to generate the linear or cyclic sweep as usual, but instead of recording the current against a potential axis, the current is recorded as a function of time. The superposition of a baseline is illustrated in Figure 20 for the determination of the ratio $i_{pa}(1)/i_{pc}(1)$ for the first electron transfer of benzophenone, and in Figure 21 for the measurement of the height of the first reduction peak, $i_{pc}(1)$, for benzophenone after the addition of 4,4'-azopyridine.

Tetraethylammonium fluoroborate was usually used as the supporting electrolyte. It was prepared\textsuperscript{145} by neutralising 20-25% aqueous tetraethylammonium hydroxide with 40% fluoroboric acid, evaporating the water on a rotary evaporator and recrystallising two or three times from absolute ethanol. After the final recrystallisation, the crystals were washed with diethyl ether and stored in a vacuum desiccator over calcium chloride or phosphorus pentoxide.

Lithium toluene-$p$-sulphonate was prepared by neutralising aqueous toluene-$p$-sulphonic acid with lithium hydroxide. The salt solution was concentrated and recrystallised twice from glacial acetic acid.

Tetraethylammonium toluene-$p$-sulphonate\textsuperscript{122} was prepared by adding triethylamine (66g, 0.65mol) to an ethanolic solution of ethyl toluene-$p$-sulphonate (132g, 0.66mol) which had been recrystallised from ethyl acetate. The reaction mixture was magnetically stirred and
the flask was fitted with a reflux condenser. The mixture was heated to 80°C where-upon the reaction became exothermic. The source of heat was removed until the mixture began to cool and then the mixture was heated at reflux for 5h. The mixture was allowed to cool, concentrated, recrystallised from ethanol, washed three times with sodium-dried ether and stored in a vacuum desiccator over phosphorus pentoxide.

Tetrabutylammonium fluoroborate, tetramethylammonium fluoroborate, tetraethylammonium iodide and sodium iodide were available in the laboratory.

Before being used as an electrolyte each of the above salts was transferred to a drying pistol and heated at 100°C under vacuum in the presence of phosphorus pentoxide for at least 24h.

Lithium perchlorate was available in the laboratory and was dried at room temperature in a vacuum desiccator in the presence of phosphorus pentoxide.

4-Phenylazopyridine was obtained from C. Niven. 90

o-Nitroaniline (Fisons) was recrystallised from water, then dissolved in diethyl ether, dried over magnesium sulphate, and concentrated. The crystals which separated were isolated and stored in a vacuum desiccator over phosphorus pentoxide.

**Solvent purification**

i) **Acetonitrile** - The usual method that was used to purify acetonitrile was that of Forcier and Olver. 107 This method gave a clear potential range from 0 to -3.2v if Fisons SLR grade acetonitrile was used while acetonitrile purchased from Aldrich Chemical Company was unable to be satisfactorily purified. The method involved three distillation stages, each time through a 2 fractionation column into dried flasks
protected from atmospheric moisture by a calcium chloride drying tube. The middle 80% of the distillate was collected in each distillation.

Stage 1: Acetonitrile was heated under reflux for 15 min with sodium hydride (1 g l⁻¹ prepared by washing an 80% dispersion of sodium hydride in oil with sodium-dried benzene, filtering under nitrogen and weighing quickly). Distillation was then carried out and excess sodium hydride in the residue was destroyed by adding glacial acetic acid.

Stage 2: Acetonitrile was heated under reflux for 10 min with phosphorus pentoxide (2 g l⁻¹) and then distilled.

Stage 3: Acetonitrile was heated under reflux for 15 min with calcium hydride (3 g l⁻¹) and then distilled. Excess calcium hydride was destroyed by pouring the residue onto cold water in a well-ventilated hood.

Molecular sieve (Linde Type 3A or 4A) which had been freshly activated by heating under vacuum at 325 °C for several hours was added to the final distillate, and the container was stoppered and sealed with "Parafilm" to reduce the absorption of water from the atmosphere.

The water content of the purified acetonitrile was determined by titration with Karl-Fischer reagent and found to be less than 100 ppm (0.01%) compared with a value of 4 x 10⁻³ ppm (0.4%) for the untreated Fisons SLR grade acetonitrile.

Originally acetonitrile had been distilled from calcium hydride, then from phosphorus pentoxide, and finally from calcium hydride. Cyclic voltammograms of tetraethylammonium fluoroborate in acetonitrile purified by this method contained an irreversible
reduction wave at approximately -2.5V. Changing the initial treatment with calcium hydride to treatment with sodium hydride removed the impurity which was causing the reduction wave at -2.5V.

Acetonitrile was analysed by gas chromatography on 15% PEG at 50°C. Untreated acetonitrile (Fisons) was found to be contaminated with traces of benzene (confirmed by mass spectrometry), acrylonitrile, propionitrile and a fourth component. Distillation from sodium hydride removed acrylonitrile but increased the concentration of benzene. Phosphorus pentoxide treatment removed the fourth component, reduced the concentration of propionitrile but introduced another impurity. The final stage of purification reduced the concentration of benzene to its original level and reduced further the concentration of propionitrile. Benzene was the major trace impurity with its concentration being approximately five times that of acrylonitrile in untreated solvent.

Other methods of purifying acetonitrile were investigated. Acetonitrile (800ml) was heated under reflux with benzoyl chloride (10ml) for 1h and then distilled into water (10ml). The solution was heated under reflux with anhydrous sodium carbonate (20g) and then distilled. The concentration of benzene and the number of impurities were greater after this treatment.

Acetonitrile which had been heated under reflux for 4h with potassium permanganate (15g) and anhydrous sodium carbonate (10g), filtered, acidified with concentrated sulphuric acid, distilled and then fractionally distilled, still contained benzene.

Anhydrous aluminium chloride (7.5g) was added to acetonitrile (500ml) and heated under reflux for 1h and then distilled. Potassium permanganate (4.0g) and lithium carbonate (4.0g) were added
to the distillate (380ml) and the mixture was heated under reflux for 15min and then distilled, discarding the first 20ml. This distillate (290ml) was heated under reflux for 1h with potassium bisulphate (3.75g) and then distilled. Freshly activated molecular sieve was added to the treated acetonitrile. Cyclic voltammetry showed the presence of an impurity which was reduced just before the cathodic limit.

ii) N,N-Dimethylformamide (DMF).- DMF was dried by adding freshly activated molecular sieve (Linde type 3A or 4A) (225g l\(^{-1}\)) and storing for at least 65h before use. Its cyclic voltammogram contained a broad, irreversible peak at approximately -2.9V.

A sample of dried DMF was distilled into five fractions which were then analysed by mass spectrometry. The spectra of the fractions indicated that the only mass fragment which changed in its abundance relative to the other fragments was m/e 17. This fragment became more abundant as the distillation temperature was increased to 80\(^{\circ}\)C. The cyclic voltammogram of DMF to which ammonia had been added showed a reduction-oxidation couple close to the cathodic limit. Both waves were sharp with \(i_{pa}/i_{po} = 1.5\), in contrast to the irreversible nature of the reduction peak of the impurity.

**Attempted preparation of "super pure" solutions**

Considerable care had to be taken when trying to obtain "super dry" solutions for analytical electrochemistry. Basically this involved adding alumina (ICN Pharmaceuticals, W200 neutral Grade Super 1) to the cell solution. The best results were obtained if the alumina was freshly activated by heating in a vacuum at 325\(^{\circ}\)C for several hours, allowed to cool and then dried nitrogen introduced into the vacuum before adding the activated alumina (5g) to the cell solution (20ml).
The effectiveness of this treatment was judged by adding an electroactive species to the cell and measuring the separation between the reduction peak potentials ($\Delta E_{pc}$) of the first and second electron transfers in the cyclic voltammogram of the species. The ratio $i_{pc(2)}/i_{pc(1)}$ and the degree of reversibility of the second electron transfer were also examined closely.

Usually cyclic voltammetry was carried out at a sweep rate of 227mVs$^{-1}$ in a 0.1M solution of tetraethylammonium fluoroborate. In most cases tetraethylammonium fluoroborate (0.434g, 2.00mmol) was weighed into a sample tube and stored in a drying pistol until it was required. It was then tipped directly into the cell and solvent (20.0ml) was pipetted into the cell immediately afterwards. Cyclic voltammograms were run 10s after the nitrogen bubbler and the magnetic stirrer had been switched off. In all these experiments a silver wire was used as the reference electrode to exclude the possibility of leakage of a reference solution into the cell.

Methods of purifying not only the solvents but also other parameters such as the supporting electrolyte, the electroactive species, and the nitrogen supply, as well as the variation of the temperature, were investigated.

i) **DMF**- Dried DMF (200ml) was stirred overnight with anhydrous cupric sulphate, decanted and distilled under vacuum (37-39°C, 2.5-3mm). Cyclic voltammetry in the presence of activated alumina showed that there was still an impurity which was reduced at approximately 400mV before the cathodic limit. This impurity peak coincided with the second reduction peak of benzophenone.

Phosphorus pentoxide (20g) was added to magnetically stirred, dried DMF (200ml). The solvent was distilled under vacuum.
(28-35°C, 2-6mm) through a fractionation column (14cm) from the phosphorus pentoxide with the pressure being adjusted by means of a nitrogen-leak in one of the receiving flasks. This distillation was always carried out immediately before the solvent was required.

Cyclic voltammograms of 0.1M tetraethylammonium fluoroborate in DMF distilled from phosphorus pentoxide still contained reduction waves close to the cathodic limit. Neither the addition of activated alumina, nor pre-electrolysis using a platinum foil cathode at a potential 200mV anodic of the cathodic limit removed the impurities causing these waves; the latter in fact led to a deterioration in the background cyclic voltammogram.

A series of experiments was carried out on the behaviour of benzophenone in DMF containing tetraethylammonium fluoroborate and on the effect of adding alumina to such a solution. In experiments carried out early in the series, the peak separation, ΔEpc, for benzophenone before the addition of alumina ranged from 425 to 515mV for dried DMF and from 490 to 540mV for DMF distilled from P2O5, while experiments performed later in the series gave a value of 590mV for dried DMF and a range of 610 to 650mV for DMF distilled from P2O5. The most likely reason for this improvement appeared to be the use of an improved nitrogen line; the molecular sieve tower which was used to dry the nitrogen in the earlier experiments had been in use for some time. In the latter part of the series, the nitrogen was treated by a series of towers of which the final one contained freshly activated molecular sieve.

Originally the alumina was used either without any treatment or after heating at 325°C under a vacuum maintained by a
water pump. These methods gave peak separations for benzophenone of up to 640mV on the addition of the alumina to the cell. In all experiments in which alumina was activated by heating at 325°C under a vacuum maintained by an oil pump, the peak separations were greater than 715mV. With the improvement of the nitrogen line the peak separations at room temperature in the presence of alumina increased from 715-730mV to 730-760mV, but the second electron transfer remained totally irreversible. With DMF distilled from phosphorus pentoxide and using properly activated alumina it was possible to make the second electron transfer reversible ($\Delta E'_{pc} = 760-775mV$) by working at low temperatures (-30 to -60°C). If the temperature was then allowed to rise to -10°C, the second oxidation peak decreased in height and broadened. At 0°C, the oxidation peak was no longer noticeable.

Various modifications were made in the preparation of the materials: the alumina was initially washed with dried DMF before activation; the alumina was purchased from a different supplier (Woelm N-Super I type W200); repeated recrystallisations of tetraethylammonium fluoroborate from ethanol were carried out with final washings with pentane or dried ether and one batch was further recrystallised from dried methanol and hexane and washed with hexane; the nitrogen was passed through a line of towers of alkaline pyrogallol, concentrated sulphuric acid, and potassium hydroxide pellets before the activated molecular sieve tower; the molecular sieve tower on the nitrogen line was freshly activated and then used at -78°C; benzophenone was recrystallised from pentane and stored in a vacuum desiccator. However none of these modifications made any significant change to the form of the cyclic voltammogram of benzophenone in DMF.

The reduction peak of the impurity was still present in cyclic voltammograms of azobenzene in DMF but the second electron transfer
to azobenzene occurred at a less cathodic potential than the reduction of the impurity. Various attempts to obtain purer DMF were judged on the behaviour of azobenzene.

Dried DMF (Fisons SLR) was stored over 3A molecular sieve, Fisons AR grade DMF was stored over 4A molecular sieve, Fluka puriss grade DMF was dried over 4A molecular sieve, and some of the dried Fluka DMF was distilled from phosphorus pentoxide, but none of these procedures improved on the performance of dried DMF (Fisons SLR) distilled from phosphorus pentoxide. A peak separation for 1mM azobenzene in DMF at room temperature of 620-640mV in the absence of alumina could be increased to 800mV by the addition of activated alumina. At -10°C the second electron transfer was reversible ($\Delta E_{pc} = 800^{+10} mV$).

ii) Acetonitrile. Cyclic voltammograms were run of 1.0mM benzophenone in 0.1mM tetraethylammonium fluoroborate in purified acetonitrile using a PDE. At room temperature the peak separation increased from 450mV to 540mV on addition of activated alumina. Lowering the temperature to -47°C increased the peak separation to 620mV. The second peak was totally irreversible.

The peak separation for 1mM azobenzene at a HMDE could be improved from 400-450mV to 510mV by adding activated alumina, but at a PDE the separation was 600mV in the absence of alumina, 675mV in the presence of alumina at room temperature, and 730mV in the presence of alumina at -45°C.

The cyclic voltammogram of perylene in the presence of alumina showed two successive reversible electron transfers with $\Delta E = 510 mV$ at 5°C.

iii) Using an alumina column. The apparatus shown in Figure 22 allowed
the electrolyte solution to be passed down an alumina column several times. Various experiments were run to ascertain whether solutions could be "super dried" without a suspension of alumina actually being present in the solution.

The cell was filled with 1mM benzophenone in 0.1M tetra-ethylammonium fluoroborate in DMF (25ml) which had been dried and distilled from phosphorus pentoxide. The peak separation was 610mV. This increased to 690mV and 715mV after the solution had been passed down the column of activated alumina (approximately 5g) once and twice respectively.

Tetraethylammonium fluoroborate was dissolved in dried DMF, the solution passed down the column of activated alumina, and azo-benzene was added to the solution; $\Delta E_{pc} = 700\text{mV}$.

The peak separation in cyclic voltammograms run at a HMDE of 1mM benzophenone in purified acetonitrile improved after passing the solution down a column of non-activated alumina from 300mV to 450-465mV. Peak separations at a HMDE of up to 420mV could be obtained without any alumina treatment.

**Preparative electrolyses in acetonitrile**

The supporting electrolyte was either dissolved in purified acetonitrile and the solution poured into both anodic and cathodic compartments or the salt was added separately to each compartment and the purified acetonitrile poured into each.

Nitrogen (B.O.C.'s O.F.N.) which had been passed through a molecular sieve (Linde type 4A) tower and then through a solvent presaturator was bubbled into the cell solution for 45min to remove oxygen.
The substrate was weighed into a sample flask and transferred to the cathodic compartment by pipetting some catholyte solution into the flask and then pipetting the solution back into the cathodic compartment; this procedure was repeated two or three times. Deoxygenation was then continued for 15 min.

The products of electrolyses were obtained by either (a) work-up or (b) sampling techniques.

(a) The electrolysis was stopped by switching off the current and adding ammonium chloride in water (a few ml) to the catholyte solution. The catholyte solution was then decanted from the mercury, the mercury was washed with purified acetonitrile and the washings were combined with the decanted catholyte solution. The solvent was then evaporated off in vacuo and the residue was taken up in water and chloroform. The two layers were separated and the aqueous phase was extracted with chloroform. The chloroform layers were combined, washed with water and saturated sodium chloride solution, and then concentrated before analysis.

(b) A sample (0.50 ml) of the catholyte solution was removed before the electrolysis was started and then samples (0.50 ml) were taken during the electrolysis; the time or the quantity of gas evolved in the coulometer since the beginning of the electrolysis was noted for each sample. Each sample was added to solid ammonium chloride. Analysis was performed by injecting the crude samples directly into the gas chromatograph.

Benzophenone

Product analyses were obtained by HPLC on Partisil-10 silica developed with 20% ethyl acetate (containing 0.3% w/w water) in n-hexane. HPLC on alumina (7 μ) using the same solvent and 1H nmr
spectroscopy were used to confirm the identities of the products.

The galvanostatic (20mA) electrolysis of benzophenone (0.62g, 3.4mmol) in 0.1M tetraethylammonium fluoroborate in purified acetonitrile (50ml) was monitored by taking samples (0.5ml) of the catholyte solution, adding the standard solution of o-nitroaniline in purified acetonitrile and analysing the samples by HPLC. The initial temperature was 21°C, but during the electrolysis (3.25h) the temperature was increased to 45°C. However there was no indication of any loss of benzophenone.

Benzophenone (1.82g, 10mmol) was dissolved in 0.1M tetraethylammonium fluoroborate in dried acetonitrile (CaH₂/P₂O₅/CaH₂ treatment) (150ml) which had been pre-electrolysed at -2.0V for 15min. Galvanostatic (20mA) electrolysis was performed for 24h during which time more supporting electrolyte was added to the anodic compartment. When the electrolysis was finished ammonium chloride (1.07g, 0.02mol) in water (100ml) was added to the catholyte solution, which was then concentrated to half its volume and extracted with diethyl ether and then methylene chloride. Both extracts were dried and concentrated. HPLC and ¹H nmr spectroscopy indicated that the methylene chloride extract (0.35g) contained trace amounts of benzophenone but none of the other products. The results of analysis of the ether extract are given in Table 1.

0.1M Tetraethylammonium fluoroborate in dried acetonitrile (100ml) was pre-electrolysed at -3.0V until the current was less than 3mA. Benzophenones (1.21g, 7.5mmol) was dissolved in the catholyte solution, and controlled-potential electrolysis was carried out. The potential was initially set at -3.0V, producing a current of 700mA and
within 10 min the solution was boiling. The potential was therefore reset at -2.55 V and the current dropped to 100–300 mA. After 2.5 h the electrolysis was stopped and ammonium chloride (1.0 g) in water (50 ml) was added to the catholyte solution, which was evaporated to half its volume and extracted into diethyl ether. The extract was dried, concentrated (yield 2.38 g) and analysed (see Table 1).

Galvanostatic electrolyses of trans-cinnamtonitrile using the sampling technique (see Table 2)

The basic conditions were a galvanostatic (20 mA) electrolysis of cinnamtonitrile (20 mM) in 0.1 M tetraethylammonium fluoroborate in purified acetonitrile (50 ml) at 22–24 °C. To each of the samples (0.50 ml) collected during an electrolysis was added a standard solution of o-nitroaniline solution (usually 0.50 ml, in either toluene or purified acetonitrile). Gas chromatographic analysis was then carried out using 10% ApL at 195 °C; gas chromatography of authentic samples showed that the order of elution of expected components was 3-aminocrotononitrile, 4-amino-2,6-dimethyl-pyrimidine, 3-phenylpropionitrile, cis-cinnamtonitrile, trans-cinnamtonitrile, o-nitroaniline and 3-phenylglutaronitrile. The product assignments were confirmed by GC/MS on 10% ApL and 5% Carbowax 20M.

Run L, in which water (0.25% of the catholyte volume) was added to the catholyte solution, was not followed to completion (see Graph 7).

In Run U, lithium perchlorate was used as the supporting electrolyte and electrolysis was carried out for 16 min, by which time 18% of the cinnamtonitrile had been consumed, no dinitrile had been formed but 3-phenylpropionitrile (5%) was detected. In Run V, the supporting electrolyte was sodium iodide and the electrolysis was carried out for
20min, during which time 24% of the cinnamonitrile was consumed but no products were detected.

Galvanostatic electrolysis of benzaldehyde using the sampling technique (see Table 10 and Graph 10)

Benzaldehyde was purified by decanting from solid impurities, washing free of acid with aqueous sodium carbonate solution, drying over anhydrous sodium carbonate and distilling from a pinch of zinc dust under reduced pressure using a nitrogen leak. It was stored under nitrogen in a refrigerator.

Benzaldehyde (50.3mg, 0.475mmol) was dissolved in the catholyte solution in a cell containing 0.1M tetraethylammonium fluoroborate in purified acetonitrile (50ml). Galvanostatic (20mA) electrolysis was performed at 23-4°C. Diethyl phthalate solution (0.2ml, of known concentration in toluene) was added to each of the samples (0.5ml) taken during the electrolysis and analyses were performed by gas chromatography using 10% ApL at 196°C.

Gas chromatography (GC) of authentic samples showed that the order of elution of expected components was 3-aminocrotononitrile, benzaldehyde, benzyl alcohol, 4-amino-2,6-dimethylpyrimidine, 3-phenylpropionitrile, cis-cinnamonitrile, trans-cinnamonitrile, 3-hydroxy-3-phenylpropionitrile, diethyl phthalate and 3-phenylglutaronitrile. The 3-hydroxy-3-phenylpropionitrile peak tailed badly.

The remainder of the catholyte solution was worked-up and analysed by GC/MS on 10% ApL; this confirmed the assignment of the product peaks.
Acrylonitrile

i) Preliminary electrolysis (Run 1).—(see Graph 11) Galvanostatic electrolysis of acrylonitrile (0.109g, 2.0mmol) in 0.1M tetraethylammonium fluoroborate in purified acetonitrile (30ml) was monitored by taking samples of the catholyte solution. To each of the samples was added a standard solution of cinnamionitrile in purified acetonitrile as a GC standard, and the samples were analysed for glutaronitrile, adiponitrile, and the cyclised hydrodimer, 1-amino-2-cyanocyclopent-1-ene, by GC using 10% ApL at 174°C. Both glutaronitrile and adiponitrile were detected, but the cyclised hydrodimer was not. The yields of glutaronitrile were calculated assuming that its GC peak did not obscure any other peaks.

ii) Using the work-up technique (Runs 2-12).—(see Tables 11 and 12) Galvanostatic (10mA) electrolyses of 10min duration were performed on acrylonitrile (0.09M) in 0.1M tetraethylammonium fluoroborate in purified acetonitrile; in Runs 2-7, 10mmol acrylonitrile and 150ml acetonitrile were used, while in Runs 8-12, 6.9mmol acrylonitrile and 100ml acetonitrile were used.

After each electrolysis, the decanted catholyte solution was distilled under vacuum at room temperature and the distillate was collected in a trap cooled to -80°C. The volume of distillate was measured or made up to a known volume with purified acetonitrile and the amount of acrylonitrile present in the distillate was determined by the method of Beesing and co-workers. This involved adding an excess of dodecanethiol to a sample of the distillate and back titrating with iodine solution. The amount of acrylonitrile present was calculated from the amount of dodecanethiol consumed. The method involved adding
a sample (10ml) of the distillate to 0.125M ethanolic dodecanethiol solution (10ml), and then adding 1M ethanolic potassium hydroxide solution (1.0ml), swirling the reaction mixture and stoppering the flask. After 2.0min, glacial acetic acid (1-2ml) was added to stop the reaction and the volume was made up to 75ml with ethanol. The solution was then titrated with 0.1N iodine solution.

A blank run in which no distillate was added was also performed. All titrations with iodine solution were carried out using starch indicator to determine the end point. Each analysis was performed in duplicate. The exact molarity of the iodine solution was determined by titration with B.D.H. 0.1N standard sodium thiosulphate solution.

Control determinations were carried out on known concentrations of acrylonitrile solutions in purified acetonitrile, on acrylonitrile solutions containing water (10%), and on the distillate from a known quantity of acrylonitrile in acetonitrile containing water (11%) and 0.115M tetraethylammonium fluoroborate. The accuracy of the determinations was within ±3%. A control experiment carried out on propionitrile in acetonitrile showed that propionitrile did not interfere with the method.

The residue left after distillation of each catholyte solution was extracted with chloroform, the extract was concentrated, and then the concentrate was dissolved in chloroform (a few mls) and analysed by GC using 10% ApL at 175°C and using 5% Carbowax at 180°C. A weighed quantity of cinnamoniitrile was added to each electrolysis product as a standard; in Runs 9-12, cinnamoniitrile was added to the catholyte solution before distillation, in Run 8 it was added to the residue before work-up, and in Runs 2-7 it was added to the concentrated chloroform extract.
Gas chromatography of authentic samples on 10% ApL at 174°C showed that succinonitrile was eluted first followed by 3-amino-crotononitrile, glutaronitrile and 2-methylglutaronitrile which were unresolved. Adiponitrile, 4-amino-2,6-dimethylpyrimidine, 1-amino-2-cyanocyclopent-l-ene and trans-cinnamonnitrile were then eluted in that order. Diethyl phthalate had a retention time of over 30min.

Gas chromatography of authentic samples on Carbowax 20M at 180°C showed that the order of elution was 2-methylglutaronitrile, glutaronitrile, succinonitrile, 3-aminocrotononitrile, then adiponitrile and 4-amino-2,6-dimethylpyrimidine which were unresolved, diethyl phthalate and 1-amino-2-cyanocyclopent-l-ene. Trans-cinnamonnitrile had the same retention time as glutaronitrile.

Gas chromatography of the products of Runs 2-12 on 10% ApL usually showed four peaks which were assigned as an unknown, glutaronitrile, adiponitrile and cinnamonnitrile. GC/MS confirmed the identification of the latter three components but indicated that there was another component (m/e 106 and 66) unresolved from the glutaronitrile. Further gas chromatography of the product mixtures on 5% Carbowax 20M at 180°C showed that all of the mixtures contained an unknown compound (A) with the same retention time as 2-methylglutaronitrile, but GC/MS indicated that this was not 2-methylglutaronitrile (see Table 42). The mass fragmentation pattern of this component indicated that it was an unsaturated C₆-dinitrile. None of the product mixtures contained 3-aminocrotononitrile.

In the GC analysis of the products from Run 6 using 10% ApL, there was an additional peak due to an unknown compound (B) eluted between adiponitrile and 4-amino-2,6-dimethylpyrimidine, with a fragmentation pattern of m/e 97(5), 84(38) and 54(100). GC/MS analysis
of this product mixture on 5% Carbowax 20M showed that unknown compound (B) was eluted as a major peak after 1-amino-2-cyanocyclopent-1-ene. This unknown compound (B) seemed to be present in all the other product mixtures, but in only trace amounts; its identity was assigned as bis-(cyanoethyl) ether (see Table 42).

iii) Using the sampling technique (Runs 13-24). - (see Table 13) The acrylonitrile was purified by washing successively with 10% aqueous sulphuric acid, 10% aqueous sodium carbonate and a saturated aqueous solution of sodium sulphate, then drying over calcium chloride and fractionating. I.r. spectroscopy showed no difference between the distilled and the original material. Neither material showed any impurities on GC using 1% PEG.

In each Run, acrylonitrile was galvanostatically (10mA) electrolysed in purified acetonitrile (50ml) and samples were taken during the course of the electrolysis. The acrylonitrile concentration during an electrolysis was monitored by GC of the samples using 15% PEG at 50°C. This allowed resolution of the acrylonitrile peak from the following acetonitrile (solvent) peak. Propionitrile would be eluted on the tail of the acetonitrile peak and would be detectable if present in concentrations of 7mM or greater, but there was no evidence for its formation in any of the electrolyses.

After analysis on 15% PEG, each sample had diethyl phthalate solution (usually 0.50ml, of known concentration in toluene) added to it. Further analysis was then carried out by GC using 5% Carbowax 20M at 180°C. Four peaks were observed and were assigned to the unsaturated C₆-dinitrile, glutaronitrile, adiponitrile and diethyl phthalate. GC using 10% ApL at 174°C confirmed the identification of adiponitrile and the absence of 4-amino-2,6-dimethylpyrimidine. The
final catholyte solution in Run 24 was worked-up and GC/MS performed on 5% Carbowax 20M. This confirmed the assignment of glutaronitrile and adiponitrile. The unsaturated C₆-dinitrile was formed and then consumed during each electrolysis; its maximum yield was less than 5%.

In order to obtain quantitative analyses it was necessary to know the catholyte volume in the divided cell. This was calculated as 38ml from data obtained from the cinnammonitrile electrolysces.

In Run 14, the electrolysis of acrylonitrile (90mM) in purified acetonitrile containing 0.1M tetraethylammonium fluoroborate was carried out as in Run 13 but at reflux temperature. Over the 20min for which the reaction was monitored, the results were identical to those obtained for Run 13 in which a temperature of 22-4°C was used (see Graph 12).

Run 19 was performed in an undivided cell with 0.1M tetraethylammonium fluoroborate as the supporting electrolyte; after 50min only 23% conversion of acrylonitrile had occurred. In Graph 17 the product profile for Run 19 is compared with that of a similar electrolysis in a divided cell, Run 24.

iv) Controlled-potential electrolysis of azobenzene in the presence of acrylonitrile. Tetraethylammonium fluoroborate (2.5g, 11.5mmol) was dissolved in purified acetonitrile (50ml). Azobenzene (0.688g, 3.78mmol) and acrylonitrile (0.103g, 1.94mmol) were added to the catholyte solution giving concentrations of 99mM and 51mM respectively. The electrolysis was monitored by removing samples (0.5ml) of the catholyte solution. Reduction was carried out at -2.0V; the initial current (70mA) dropped to approximately 10mA after 1min. During the electrolysis the temperature increased from 25 to 31°C. The acrylonitrile concentration was monitored by gas chromatography on 15% PEG. A standard solution of
o-nitroaniline in toluene was added to each sample and further analysis was carried out by gas chromatography on 5% Carbowax 20M at 180°C.

An unsaturated C₆-dinitrile was formed and consumed during the electrolysis but adiponitrile was not formed. The maximum yield of glutaronitrile (26.5%) was reached simultaneously with the complete disappearance of the acrylonitrile (after only 20°C had passed). The electrolysis was stopped after a total of 100°C had passed. Only 9.3% of the azobenzene had been consumed.

Preparative electrolyses of benzenesulphonylacetonitrile in DMF in the presence of ketones or α,β-unsaturated nitriles

Tetraethylammonium fluoroborate was added to the cathodic and the anodic compartments (0.80g, 3.7mmol and 1.7g, 7.8mmol respectively) and then dried DMF was added to the cell. Benzenesulphonylacetonitrile (3.8mmol) and ketone or nitrile (1.9mmol) were added to the catholyte. The electrolyses were performed in the controlled-potential mode.

In the presence of acetophenone

The electrolysis was monitored by sampling the catholyte solution and adding to the samples a standard solution of cinnamonic acid in dimethylformamide. Gas chromatographic analysis was performed on 10% ApL at 195°C.

The applied potential was set at -1.8V for the first 30min, -2.0V for the next 32min and -2.1V for the final 66min. The current was never more than 100mA. The electrolysis was stopped, and the solution stirred for 14h before adding ammonium chloride. The concentration of benzenesulphonylacetonitrile was 5.3% lower in the final sample than in the sample taken at the end of the electrolysis.
A galvanostatic (50mA) electrolysis was also performed on a solution containing equimolar amounts of benzenesulphonylacetonitrile and acetophenone. This electrolysis was monitored by adding a standard solution of o-nitroaniline to samples (0.5ml) which were taken every 5min from the catholyte solution.

In both experiments, acetophenone and benzenesulphonylacetonitrile were consumed without the formation of identifiable products. The results are shown in Graphs 20 and 21.

In the presence of 3-methylcinnammonitrile

A voltage of -1.80V was applied to the cell. During the first 0.5h the current was less than 60mA, but thereafter it increased and the measured potential dropped to approximately -1.45V. After 50min of electrolysis the current had dropped to approximately 20mA and the electrolysis was stopped at 55min after 463 coulombs had passed.

The catholyte solution was worked-up and the standard, o-nitroaniline, was added. GC using 10% ApL at 195°C showed the recovery of 3-methylcinnammonitrile (60%) and the formation of 3-phenylbutanenitrile (24%), while 63% of the benzenesulphonylacetonitrile had been consumed. The identity of the products was confirmed by GC/MS.

In the presence of acrylonitrile

The electrolyses were monitored by taking samples (0.5ml) of the catholyte solution. Acrylonitrile, acetonitrile and propionitrile were analysed by GC using 15% PEG at 70°C. The concentrations of each were calculated from their peak heights relative to the peak height of the initial acrylonitrile concentration. This involved making a correction for their relative response factors; these were determined by carrying out gas chromatographic analysis of DMF solutions containing known
amounts of each. The standard solution of diethyl phthalate in DMF was added to each of the samples and GC analysis was carried out using 5% Carbowax at 180°C. This allowed the analysis of glutaronitrile, adiponitrile and benzenesulphonylacetonitrile. The assignments of glutaronitrile and adiponitrile were confirmed by working-up an electrolysis and carrying out GC/MS using 5% Carbowax 20M and 10% ApL on the product.

The experiment was carried out twice, at -2.1V and at -1.8V. In both cases the current was initially very small (approximately 20mA) but then increased to the maximum available from the potentiostat (approximately 750mA) and remained at this level. The results are given in Graphs 22 and 23.

Cyanomethylations using lithium amide/liquid ammonia solutions

The method of Ivanov and Anghelova\textsuperscript{149} was used involving lithium amide prepared as described by Dunnavant and Hauser\textsuperscript{150}.

Lithium pellets were washed with petroleum ether (b.p. 30–40°C) under a nitrogen atmosphere. A few pellets were added to liquid ammonia in a 3-necked, round-bottom flask fitted with a sealed, mechanical stirrer and a condenser filled with dry ice and fitted with a calcium oxide drying tube. When a blue colour appeared a few crystals of ferric nitrate were added and then the remainder of the lithium was added slowly.

After the blue colour had been discharged (30–60min), acetonitrile (1mol per 1.5mol of lithium) in an equivalent volume of diethyl ether was added, followed after 5min by an equimolar quantity of the ketone, aldehyde or $\alpha,\beta$-unsaturated nitrile in diethyl ether. More diethyl ether was added to wash in any remaining reactant.
The reaction mixture was stirred for 1h, neutralised with solid ammonium chloride (1mol per mol of lithium), the ammonia was allowed to evaporate and water was added.

**Preparation of 3-hydroxy-3,3-diphenylpropionitrile**

Benzophenone (27.3g, 0.15mol) was added to acetonitrile (6.25g, 0.15mol) and lithium amide (1.6g lithium, 0.23mol) in liquid ammonia (200ml).

The work-up yielded a grey precipitate which was filtered off and washed with water. The precipitate was taken up in a minimum quantity of boiling benzene, the organic phase was decanted while hot from the aqueous phase which had separated, and was filtered while still hot. On cooling, white crystals separated (27.7g, 81%), which were pure by HPLC, m.p. 139.5-140.5°C (lit. m.p. 139-140°C); \(^1\)H nmr spectrum (60MHz, CDCl\(_3\)): \(\delta\) 2.76 (s, 1H, OH), 3.23 (s, 2H, CH\(_2\)), 7.30 (s, 10H, 2C\(_6\)H\(_5\)); ir spectrum: \(\nu_{\text{max}}\) 3360cm\(^{-1}\) (s, OH) and 2260cm\(^{-1}\) (m, CN).

**Preparation of 3-hydroxy-3-phenylpropionitrile**

Benzaldehyde (7.42g, 0.07mol) was added to acetonitrile (2.875g, 0.07mol) and lithium amide (0.65g lithium, 0.10mol) in liquid ammonia (80ml).

During the work-up diethyl ether (20ml) was added as the ammonia evaporated. Water (40ml) was added as usual. The two phases were separated and the aqueous layer was extracted with diethyl ether. The ether extracts were combined, dried over magnesium sulphate and the solvent was evaporated. Distillation (b.p. 108-116°C, 0.1mm; lit. \(\text{b.p. 154-155°C, 1mm}\) produced an oil (1.43g, 13.9%) which GC/MS indicated was 92.7% pure, and contained benzaldehyde (5.1%),
cis- and trans-cinnamionitriles (2.0%) and a fourth impurity (0.2%).

$^1$H nmr spectrum $^{151}$ (60MHz, CDCl$_3$): δ 2.63 (d, J=6Hz, 2H, CH$_2$), 3.40 (broad, 1H, OH), 4.9 (t, J=6Hz, 1H, CH), 7.30 (s, 5H, C$_6$H$_5$); ir spectrum $^{151}$: $\nu$ _max_ 3430 cm$^{-1}$ (s, broad, OH), 2260 (m, CN).

**Preparation of 3,3-diphenylglutaronitrile**

3-Phenylcinnamionitrile (4.1g, 0.02mol) was added to acetonitrile (0.82g, 0.02mol) and lithium amide (0.22g lithium, 0.03mol) in liquid ammonia (50ml).

Addition of water (15ml) on work-up produced a water-insoluble orange material which was extracted into diethyl ether. The ethereal solution was washed with saturated aqueous sodium chloride solution and dried over magnesium sulphate. Evaporation of solvent left a dark red oil from which a light coloured powder (1.23g, 25%) precipitated on addition of carbon tetrachloride. The powder was recrystallised from methanol and washed with carbon tetrachloride to give white crystals m.p. 119.5-126°C (lit. $^{149}$ m.p. 124-125°C); $^1$H nmr spectrum (60MHz, CDCl$_3$): δ 3.33 (s, 4H, 2CH$_2$CN), 7.0-7.5 (m, 10H, 2C$_6$H$_5$); ir spectrum $^{149}$: $\nu$ _max_ 2250 cm$^{-1}$ (CN), 1600 cm$^{-1}$ (aromatic stretching vibration). HPLC indicated that the crystals were contaminated with benzophenone and 3-phenylcinnamionitrile. Mass spectroscopy indicated a parent ion at m/e 246 with a major fragment at m/e 206.

**Attempted preparation of 3-phenylglutaronitrile**

Cinnamionitrile (3.89g, 0.03mol) was added to acetonitrile (1.25g, 0.03mol) and lithium amide (0.42g lithium, 0.06mmol) in liquid ammonia (60ml).

The work-up produced a thick, dark grey residue insoluble in water or diethyl ether but soluble in acetone. Vacuum distillation
(0.1-0.2mm) of the residue gave three fractions b.p. < 140°C. The
$^1H$ nmr spectrum (60MHz, CDCl$_3$) of each fraction had a doublet at
$\delta$ 2.85 (J=6Hz) which was believed to be characteristic of 3-phenyl-
glutaronitrile. The three fractions were combined (1.13g, 27%).
Trituration (lit. m.p. 26°C) was attempted from methanol, diethyl
ether and carbon tetrachloride but without success. The product was
redistilled (b.p. 120-132°C, 0.1-0.2mm) yielding a yellow oil. The
$^1H$ nmr spectrum of the yellow oil indicated cinnamonic acid was a major
impurity, while gas chromatography showed the presence of five components
including cinnamonic acid.

**Preparation of 3-phenylglutaronitrile**

Benzaldehyde (8.4g, 0.079mol) was refluxed for 4.5h
with cyanoacetic acid (18.7g, 0.22mol) and piperidine (0.75ml) in
pyridine (40ml). The solvent was removed under vacuum (0.1mm) at room
temperature and the remaining liquid was dissolved in benzene. This
solution was washed with aqueous sodium bisulphite until there was no
further colour extraction, with water, then with aqueous sodium carbonate
until there was no further colour extraction, and finally with water.
The solvent was removed on a rotary evaporator; yield 11.9g (88%).
Distillation (150-4°C/0.2-0.4mm) gave a clear liquid; $^1H$ nmr spectrum
(60MHz, CDCl$_3$): $\delta$ 2.85 (d, J=6Hz, 4H, 2CH$_2$CN), 3.2-3.7 (m, 1H, CH) and
7.38 (s, 5H, C$_6$H$_5$). GC/MS indicated the presence of trace amounts (less
than 1%) of cis- and trans-cinnamonic acid.

**Preparation of 3-phenylcinnamonic acid**

3-Hydroxy-3,3-diphenylpropionitrile (26.3g, 0.11mol),
glacial acetic acid (55ml) and sulphuric acid (2.4ml, d 1.16g/ml$^{-1}$) were
refluxed for 1 min. The reaction mixture was cooled, diluted with water (60 ml) and extracted twice with diethyl ether. The combined ether extracts were neutralised with aqueous sodium bicarbonate, washed with a saturated sodium chloride solution and dried over magnesium sulphate. Evaporation of the solvent yielded an orange oil which was vacuum distilled; the main fraction (b.p. 135-42°C/0.1 mm) was recrystallised from methanol m.p. 38-42°C (11.1 g, 46% yield). Further recrystallisation from methanol produced white needle crystals m.p. 45.5°C (lit. 45°C) which were shown to be pure by HPLC; 1H nmr spectrum (60 MHz, CDCl₃): δ 5.70 (s, 1H, CH), 7.38 (d, J = 5 Hz, 10H, 2CH₃); ir spectrum: ν_max 2210 cm⁻¹ (s, CN).

**Preparation of cis-cinnamonic acid**

This required the synthesis of α-cyano-β-phenylacrylic acid from sodium cyanoacetate and benzaldehyde as described by Lapworth and Baker, followed by cuprous oxide catalysed, thermal decarboxylation in vacuo as described by Fairhurst and co-workers.

A mixture of monochloroacetic acid (50 g, 0.53 mol), water (50 ml) and sodium carbonate (75 g, 0.26 mol) was warmed gently, and neutralised with sodium carbonate solution using litmus as indicator. Sodium cyanide (26 g, 0.53 mol) in warm water (50 ml) was added to the mixture. After 10 min the solution started to darken and much heat was evolved. After cooling, the reaction mixture was neutralised to pH 4 with hydrochloric acid.

The sodium cyanoacetate solution was treated with sodium hydroxide (2.5 g, 0.065 mol) in water (200 ml), the mixture was warmed before adding benzaldehyde (50 g, 0.47 mol), and it was then shaken vigorously. The reaction mixture was allowed to stand for 1 h and then
hydrochloric acid (d 1.16g/ml) was added until the solution was acid to litmus. A further 40ml hydrochloric acid (d 1.16g/ml) was added and the mixture was shaken vigorously. After 1h the precipitate was filtered off, washed with cold water and dried in an oven. The powdered material was shaken with benzene, filtered off, washed with benzene, and dried in a vacuum desiccator. The yield of α-cyano-β-phenylacrylic acid was 52.2g (64%).

α-Cyano-β-phenylacrylic acid (25g, 0.145mol) was intimately mixed with cuprous oxide (1.0g) in a round bottom flask, which was clamped in a horizontal position and was connected by a short glass joint to a receiver cooled in liquid nitrogen. The apparatus was evacuated (0.1-0.2mm) and the flask was heated until gas evolution stopped (approximately 20min). The material in the receiver was allowed to warm to room temperature and the liquid was then filtered. The yield was 11.2g (59%); 1H nmr spectroscopy indicated that the ratio of cis- to trans-isomers was 3. Vacuum distillation (110-20°C/3mm) in a Fischer Spaltrohr apparatus produced cis-cinnamonic acid which was pure by GC on 10% ApL; 1H nmr spectrum (60MHz, CDCl₃): δ 5.42 (d, J=12Hz, 1H, CHCN), 7.10 (d, J=12Hz, 1H, PhCH), 7.3-7.9 (m, 5H, C₆H₅).

Hydrogenation of cinnamonic acid

The cinnamic acid (5 or 10mmol) was added to a hydrogenation flask containing 10% palladium on charcoal (12mg), ethyl acetate (75ml), and glacial acetic acid (1ml/mmol cinnamonic acid). The apparatus was filled with hydrogen at atmospheric pressure and the reaction mixture was stirred until the theoretical uptake of hydrogen had been exceeded. The mixture was filtered, the ethyl acetate was evaporated and the crude product was dissolved in diethyl ether. The
ethereal solution was neutralised with sodium bicarbonate solution, dried over magnesium sulphate, and concentrated.

i) 3-Phenylcinnamonic acid.- Hydrogenation of 3-phenylcinnamonic acid (1.039, 0.007mol) for 65h at atmospheric pressure yielded a damp, white solid. This material was washed with carbon tetrachloride, leaving a white solid (0.56g, 54%) which was recrystallised from methanol to give white crystals of 3,3-diphenylpropionitrile (0.40g, 39%), m.p. 88-9°C (lit. 158 m.p. 88.5°C); 1H nmr spectrum (60MHz, CDCl₃): δ 3.03 (t, J=7.5Hz, 2H, CH₂CN), 4.38 (t, J=7.5Hz, 1H, Ph₂CH), 7.27 (s, 10H, C₆H₅).

ii) Cinnamonic acid.- Hydrogenation of cinnamonic acid (1.28g, 0.010mol) for 16h at atmospheric pressure yielded a yellow oil which on distillation (b.p. 120-13°C/30mm) yielded a clear liquid distillate of 3-phenylpropionitrile (0.516g, 39.0%) which was pure by GC. The 1H nmr spectrum (60MHz, CDCl₃) of this compound is shown in Figure 23: δ 2.4-3.1 (m, 4H, -CH₂CH₂-) and 7.27 (s, 5H, C₆H₅).

Preparation of 2-methylglutaronitrile

Potassium cyanide (16g, 0.25mol) was added to 1,3-dibromo-2-butane (25.1g, 0.116mol) dissolved in ethanol-water (19:1, 25ml). The mixture was refluxed for 3h, during which period more aqueous ethanol (15ml) was added. The alcohol was removed on a rotary evaporator, and the remaining aqueous solution was extracted with ether. Concentration of the ether extract yielded a red oil (14.0g). GC indicated that two main components were present. Distillation (b.p. 106-12°C, 10mm) yielded a clear liquid (8.87g); ir spectrum: ν film 2245cm⁻¹ (saturated CN). GC of this distillate showed that it consisted predominantly of the first component and that the ratio of the peak heights of the 1st to the 2nd components was 7.5. Microdistillation (13mm) of the residue
produced two fractions: (i) b.p. < 126 °C (1.02 g) and (ii) b.p. 126-45 °C (lit. 134 °C; 0.84 g). GC indicated that both fractions contained the same two components as in the red oil and in the main distillate; the peak height ratio was 1.2 for fraction (i) and 0.17 for fraction (ii). 13C nmr spectra (CDCl 3 ) with off-resonance H decoupling; fraction (ii): 2416 (singlet, CN), 2356 (singlet, CN), 580 (triplet, CH 2 CN), 484 (doublet, CHCN), 339 (quartet, CH 3 ), 109 (triplet, CH 2 ); main distillate: 2370 (singlet, CN), 960 (doublet, CHBr), 721 (triplet, CH 2 CN), 517 (quartet, CH 2 ), 319 (triplet, CH 2 ). Thus the major component of fraction (ii) was 2-methylglutaronitrile while the major component of the main distillate was 3-bromobutanenitrile. GC/MS confirmed these conclusions; first component: 83(12), 82(100, P-Br), 55(100), 54(74), 41(79), 39(49); second component: (see Table 42, 2-methylglutaronitrile).

Preparation of 1-amino-2-cyanocyclopent-1-ene

i) Attempted by Thorpe's method 16. Adiponitrile (5.0 g, 0.094 mol) was mixed with absolute alcohol (20 ml) in a flask fitted with a reflux condenser and a cube of sodium (of approximately 1 cm side) was added. The reaction mixture was heated for 1 1/2 h and then allowed to cool. No precipitate formed even on cooling in ice, but a yellow liquid separated out below the alcohol layer. Ir analysis of the yellow liquid indicated a very low yield of 1-amino-2-cyanocyclopent-1-ene 16. v film 2190 cm⁻¹ (conjugated nitrile), 1645 cm⁻¹ (NH 2 ), 1605 cm⁻¹ (olefinic linkage characteristic of cyclopentene).

ii) Using sodium t-butoxide 16. Sodium (1.15 g, 0.05 mol) was added to toluene (30 ml) and heated for 1 h at reflux with rapid stirring. The reaction mixture was allowed to cool to 60-70 °C, treated dropwise with t-butyl alcohol (4.35 g, 0.059 mol) which was rinsed in with toluene (a few
mis), and then the mixture was heated at reflux for 15min. Adiponitrile (5.39g, 0.102mol) was added dropwise and washed in with a little toluene. The mixture was heated at reflux for a further 1.25h, then allowed to cool before water (20ml) was added. The toluene and aqueous phases were separated and the organic phase extracted with water. The aqueous phases were combined and extracted with chloroform. The toluene and chloroform extracts were combined and the solvent was removed on a rotary evaporator, yielding a brown solid. This was dissolved in chloroform, washed with water and then recrystallised twice from chloroform to give pale crystals (1.54g, 28.6%) m.p. 143-5.5°C (lit. 162 m.p. 147-9°C) which were pure by GC; \(^1\)H nmr spectrum (60MHz, CDCl\(_3\); δ 1.95 (q, J=6Hz, 2H), 2.5 (m, 4H), 4.5 (broad, 2H, NH\(_2\)); ir spectrum \(^{161}\) : \(\nu_{\text{max}}\) 2180cm\(^{-1}\) (conjugated nitrile), 3420 and 1640cm\(^{-1}\) (olefinic linkage characteristic of cyclopentene).

Preparation of 3-aminocrotononitrile

The method used followed modifications by Bullock and Gregory \(^{163}\) to the method of Adkins and Whitman \(^{164}\).

Sodium metal (15.6g, 0.69mol) was cut into small pieces and added to sodium-dried benzene (160ml) in a 3-necked flask fitted with a mechanical stirrer, condenser and dropping funnel. Purified acetonitrile (49.5g, 1.21mol) was added slowly over a period of 1h. No external cooling was required, and once the reaction was underway, the reaction mixture was heated at reflux for 4h. The cooled reaction mixture was filtered, the solid was suspended in diethyl ether (200ml), and the suspension was cooled to 4°C. Water was added, at such a rate that the temperature never rose above 9°C, until the solid disappeared. The ether layer was separated, dried over magnesium sulphate, and
concentrated, yielding a solid which was recrystallised from benzene (14.7 g, 27%). $^1$H nmr spectroscopy (60MHz, CDCl$_3$) showed the presence of two isomers in the ratio of 4:1; $^6$ 1.97 (s, 3H, CH$_3$ of major isomer), 2.17 (s, 3H, CH$_3$ of minor isomer), 3.93 (s, 1H, CH of major isomer), 4.23 (s, 1H, CH of minor isomer) and 4.8 (broad, 2H, NH$_2$ of both isomers). The major isomer was assigned as having the Z-configuration$^{165}$. GC using 5% Carbowax 20M and 10% ApL showed only one peak with a mass spectrum (GC/MS): m/e 82(P, 100), 67(P-15, 80), 42(P-40, 85), 41(P-41, 55) and 40(P-42, 23). 3-Aminocrotonitrile was found to be unstable in chloroform solution (by GC/MS).

Preparation of N,N-dimethyl-p-nitrosoaniline$^{166}$

N,N-Dimethylaniline (16 g, 0.13 mol) was dissolved in hydrochloric acid (100 ml, d 1.16 g ml$^{-1}$) and treated with ice (50 g). Aqueous sodium nitrite (7 g in 20 ml) was added slowly keeping the temperature below 5°C. A brick red solid separated; this was filtered off and washed with dilute hydrochloric acid (1:1). The solid hydrochloride was transferred to a separating funnel, a little water was added followed by 10% aqueous sodium hydroxide until the mixture was alkaline. The free base (green) was extracted into chloroform and recrystallised from ether.

Thin layer chromatography (alumina developed with ether/hexane (50:50)) indicated that at least three components were present. Column chromatography followed by recrystallisation of the main component from toluene yielded green crystals m.p. 79-84°C (lit. 167-185°C). Variable temperature $^1$H nmr spectroscopy (100 MHz, CDCl$_3$) was in agreement with Sandstrom's$^{168}$ data: at 65°C, $^6$ 3.10 (s, 6H, 2CH$_3$), 6.58 (d, J=9 Hz, 2H, aromatic H meta to nitroso group),
7.61 (d, J=9Hz, 2H, aromatic H ortho to nitroso group). The doublet at 7.61 broadened as the temperature was lowered to room temperature, and by \(-40^\circ\text{C}\), had resolved into two doublets at 6.39 (J=9Hz) and 8.77 (J=9Hz) while the aromatic proton signals showed fine structure. The ir spectrum was in complete agreement with the literature\(^{169}\). Found: C 63.89, H 6.67 and N 18.54 (C\(_6\)H\(_{10}\)N\(_2\)O requires: C 63.98, H 6.71 and N 18.66).

**Preparation of azopyridines**

Kirpal and Reiter\(^{170}\) prepared 2,2'-azopyridine by the oxidation of 2-aminopyridine with hypochlorite. Henderson\(^{171}\) found this method was generally applicable for the synthesis of azopyridines. Calcium hypochlorite (160g, 1.12mol) was added to aqueous potassium hydroxide (80g, 1.43mol in 500ml) to form a slurry. The necessary aminopyridine (10g, 0.106mol) was dissolved in water (50ml) and added slowly to the stirred slurry so that the temperature did not exceed 15\(^{\circ}\text{C}\). After stirring for 2-3h, the mixture was filtered and the solid was washed several times with chloroform. The filtrate was kept chilled until it was extracted with chloroform. The chloroform extracts were combined and concentrated.

i) 2,2'-Azopyridine. - 7.60g (78%) of crude product was obtained. Chromatography on a 6% deactivated alumina "dry" column\(^{172}\) (20in long x 2in diameter) developed with diethyl ether yielded a dark red liquid (6.10g, 63%) which showed only one spot on TLC (alumina, ether). Addition of a little petroleum ether (b.p. 60-80\(^{\circ}\text{C}\)) precipitated orange crystals (3.60g, 37%) which were recrystallised from petroleum ether (b.p. 60-80\(^{\circ}\text{C}\)) to give orange needles (1.31g, 13%) m.p. 85-88\(^{\circ}\text{C}\) (lit.\(^{171}, 170\) m.p. 85\(^{\circ}\text{C}\), 87\(^{\circ}\text{C}\)).
ii) 4,4'-Azopyridine.- During the work-up, the filtrate was not kept chilled and the solution decomposed. Therefore only the chloroform washings of the solid were collected and evaporated to give a red solid (4.46g, 46%). Medium pressure liquid chromatography was performed (in three portions) on a 60μ silica column (100cm long x 2cm diameter), using diethyl ether as eluting solvent; yield (2.7g, 28%). Recrystallisation from petroleum ether (b.p. 60-80°C) gave orange crystals m.p. 106-109°C (lit.171 108-109°C).

Preparation of benzencesulphonylacetonitrile 28

Chloroacetonitrile (20.5g, 0.275mol) was added to a stirred suspension of sodium benzenesulphinate (41g, 0.25mol) in DMF (150ml) at 80°C. The temperature was not allowed to rise above 80°C. The mixture was stirred at 80°C for 3h; it was then cooled, filtered and the filtrate was concentrated in vacuo. The crude product was recrystallised (4 times) from ethanol and finally washed with dry ether to give white crystals (18.59g, 41%). These were dried in vacuo at 100°C in the presence of phosphorus pentoxide; m.p. 114-115°C (lit., 173 112°, 114°C); 1H nmr spectrum (60MHz, CDCl3): δ 4.10 (s, 2H, CH2), 7.6-8.2 (m, 5H, C6H5).
<table>
<thead>
<tr>
<th>compound</th>
<th>controlled-potential</th>
<th>galvanostatic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%yield</td>
<td>%conversion</td>
</tr>
<tr>
<td>Ph$_2$CO</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>Ph$_2$CHCHOH</td>
<td>26</td>
<td>39</td>
</tr>
<tr>
<td>Ph$_2$(OH)CH$_2$CN</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ph$_2$C=CHCN</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Ph$_2$CHCH$_2$CN</td>
<td>34</td>
<td>52</td>
</tr>
<tr>
<td>Ph$_2$C(CH$_2$CN)$_2$</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Mercury (3ml) pool cathode; 0.1M Et$_4$NBF$_4$ in acetonitrile dried by CaH$_2$/P$_2$O$_5$/CaH$_2$ treatment. The yields and conversions represent the maximum values since they were calculated by assuming that these six compounds were the only products.

a) -2.55V vs. Ag/0.1M AgNO$_3$ for 2.5h, electrolyte volume = 100ml.
b) 20mA for 24h, electrolyte volume = 150ml.

$^1$H nmr spectra (60MHz, CDCl$_3$) of electrolyses products:

<table>
<thead>
<tr>
<th>δ</th>
<th>integral</th>
<th>assigned to</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 3.00</td>
<td>54</td>
<td>(d, J = 7.5Hz, 2H, CH$_2$CN)</td>
</tr>
<tr>
<td>4.33</td>
<td>22</td>
<td>(t, J = 7.5Hz, 1H, Ph$_2$CH)</td>
</tr>
<tr>
<td>5.70</td>
<td>1</td>
<td>(s, CHCN) increased in height on add$^n$ of Ph$_2$C=CHCN</td>
</tr>
<tr>
<td>5.77</td>
<td>18</td>
<td>(s, Ph$_2$CH) increased in height on add$^n$ of Ph$_2$CHOH</td>
</tr>
<tr>
<td>b) 2.81</td>
<td>18</td>
<td>(d, J = 7.5Hz, 2H, CH$_2$CN)</td>
</tr>
<tr>
<td>4.23</td>
<td>8</td>
<td>(t, J = 7.5Hz, 1H, Ph$_2$CH)</td>
</tr>
<tr>
<td>3.10</td>
<td>6</td>
<td>(s, CH$_2$CN)</td>
</tr>
<tr>
<td>5.70</td>
<td>2</td>
<td>(s, Ph$_2$CH)</td>
</tr>
</tbody>
</table>
Table 2: Results of galvanostatic electrolyses of trans-cinnaminitrile in purified acetonitrile.

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial</th>
<th>yield</th>
<th>( \text{PhCH(}2\text{CN)} _2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>94</td>
<td>23</td>
<td>( i = 30\text{mA, 150ml electrolyte} )</td>
</tr>
<tr>
<td>B</td>
<td>42</td>
<td>31</td>
<td>( i = 40\text{mA} )</td>
</tr>
<tr>
<td>C</td>
<td>81</td>
<td>20</td>
<td>( i = 40\text{mA} )</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>46</td>
<td>( i = 40\text{mA} )</td>
</tr>
<tr>
<td>E</td>
<td>21</td>
<td>44</td>
<td>( i = 80\text{mA} )</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>20</td>
<td>56</td>
<td>( T = 40-46^\circ\text{C} )</td>
</tr>
<tr>
<td>H</td>
<td>20</td>
<td>49</td>
<td>( \text{[Et}_4\text{NBF}_4 \text{]} = 0.2\text{M} )</td>
</tr>
<tr>
<td>I</td>
<td>23</td>
<td>46</td>
<td>acetonitrile passed down column of freshly activated Woelm alumina</td>
</tr>
<tr>
<td>J</td>
<td>24</td>
<td>44</td>
<td>( + \text{H}_2\text{O (2.5 x 10}^{-2}\text{% of catholyte volume)} )</td>
</tr>
<tr>
<td>K</td>
<td>23</td>
<td>47</td>
<td>( + \text{H}_2\text{O (2.5 x 10}^{-2}\text{% of catholyte volume)} )</td>
</tr>
<tr>
<td>L</td>
<td>23</td>
<td>20</td>
<td>( + \text{H}_2\text{O (0.23% of catholyte volume)} )</td>
</tr>
<tr>
<td>M</td>
<td>23</td>
<td>36</td>
<td>( + \text{H}_2\text{O (0.20% of catholyte volume)} )</td>
</tr>
<tr>
<td>N</td>
<td>23</td>
<td>47</td>
<td>( \text{[Et}_4\text{NBF}_4 \text{]} = 0.02\text{M} )</td>
</tr>
<tr>
<td>O</td>
<td>10</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>20</td>
<td>73</td>
<td>( T = 72-75^\circ\text{C} )</td>
</tr>
<tr>
<td>Q</td>
<td>10</td>
<td>80</td>
<td>( i = 10\text{mA, } T = 79-81^\circ\text{C} )</td>
</tr>
<tr>
<td>R</td>
<td>22</td>
<td>45</td>
<td>( \text{[Bu}_4\text{NBF}_4 \text{]} = 0.1\text{M} )</td>
</tr>
<tr>
<td>S</td>
<td>21</td>
<td>38</td>
<td>saturated solution of ( \text{Me}_4\text{NBF}_4 )</td>
</tr>
<tr>
<td>T</td>
<td>22</td>
<td>41</td>
<td>( \text{[Et}_4\text{NOtS} \text{]} = 0.1\text{M, PhCH(}2\text{CN)} _2 \text{yield } = 3% )</td>
</tr>
<tr>
<td>U</td>
<td>21</td>
<td>0</td>
<td>( \text{[LIClO}_4 \text{]} = 0.1\text{M, PhCH(}2\text{CN)} _2 \text{yield } = 3% )</td>
</tr>
<tr>
<td>V</td>
<td>21</td>
<td>0</td>
<td>( \text{[NaI] = 0.1M} )</td>
</tr>
<tr>
<td>W</td>
<td>21</td>
<td>46</td>
<td>( \text{[Et}_4\text{NI} \text{]} = 0.1\text{M} )</td>
</tr>
</tbody>
</table>

Mercury (Jml) pool cathode, acetonitrile purified by \( \text{NaH/P}_2\text{O}_5/\text{CaH}_2 \) treatment and stored over 42 molecular sieve. Except where otherwise stated; \( i = 20\text{mA, \ [Et}_4\text{NBF}_4 \text{]} = 0.1\text{M, } T = 22-40^\circ\text{C, 50ml electrolyte.} \)

a) for 53% conversion of cinnaminitrile in 17min; selectivity for \( \text{PhCH(}2\text{CN)} \_2 \) = 38%
b) occurs for ca. 80% conversion of cinnaminitrile (see Graph 9)
c) for 18% conversion of cinnaminitrile in 16min; selectivity for \( \text{PhCH(}2\text{CN)} \_2 \) = 28%
d) for 24% conversion of cinnaminitrile in 20min
Table 3: Results of galvanostatic electrolyses of cinnamoylchloride in acetonitrile: the effect of cinnamoylchloride concentration.

<table>
<thead>
<tr>
<th>Run</th>
<th>initial $[\text{PhCHCHCN}]$ [mM]</th>
<th>$[\text{Et}_4\text{NBF}_4]$</th>
<th>yield $\text{PhCH(CH}_2\text{CN)}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>81</td>
<td>0.81</td>
<td>20</td>
</tr>
<tr>
<td>b</td>
<td>42</td>
<td>0.42</td>
<td>31</td>
</tr>
<tr>
<td>b</td>
<td>20</td>
<td>0.20</td>
<td>46</td>
</tr>
<tr>
<td>a</td>
<td>10</td>
<td>0.10</td>
<td>61</td>
</tr>
</tbody>
</table>

Mercury pool cathode, 50ml 0.1M Et$_4$NBF$_4$ in acetonitrile purified by NaH/P$_2$O$_5$/CaH$_2$/4Å molecular sieve treatment, $T = 22-40^\circ\text{C}$.  

$i = a)$ 40mA, $b)$ 20mA
Table 4: Results of galvanostatic electrolyses of cinnamonic acid (ca. 20mM) in acetonitrile at different currents.

<table>
<thead>
<tr>
<th>Run</th>
<th>( i ) mA</th>
<th>( \text{yield} ) PhCH(CH(_2)CN)(_2) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>20</td>
<td>46</td>
</tr>
<tr>
<td>D</td>
<td>40</td>
<td>46</td>
</tr>
<tr>
<td>E</td>
<td>80</td>
<td>44</td>
</tr>
</tbody>
</table>

Mercury pool cathode, 50ml 0.1M Et\(_4\)NBF\(_4\) in acetonitrile purified by NaH/P\(_2\)O\(_5\)/CaH\(_2\)/4Å molecular sieve treatment, T = 22-4°C.
Table 5: Results of galvanostatic electrolyses of cinnamonnitrile in acetonitrile: the effect of supporting electrolyte concentration.

<table>
<thead>
<tr>
<th>Run</th>
<th>PhCHCHCN (mM)</th>
<th>Et₄NBF₄ (mM)</th>
<th>PhCHCHCN/Et₄NBF₄</th>
<th>Yields PhCH(CH₂CN)₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>20</td>
<td>200</td>
<td>0.1</td>
<td>49</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>100</td>
<td>0.2</td>
<td>46</td>
</tr>
<tr>
<td>N</td>
<td>23</td>
<td>23</td>
<td>1.0</td>
<td>47</td>
</tr>
</tbody>
</table>

Mercury pool cathode, 50ml acetonitrile purified by NaH/P₂O₅/CaH₂/4Å molecular sieve treatment, T = 22-4°C, i = 20mA.
Table 6: Results of galvanostatic electrolyses of cinnamonomitride in acetonitrile: the effect of temperature.

<table>
<thead>
<tr>
<th>Run</th>
<th>[PhCHCHCN] mM</th>
<th>temperature °C</th>
<th>yield PhCH(CH₂CN)₂ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>20</td>
<td>22-4</td>
<td>46</td>
</tr>
<tr>
<td>G</td>
<td>20</td>
<td>40-6</td>
<td>56</td>
</tr>
<tr>
<td>P</td>
<td>20</td>
<td>72-6</td>
<td>73</td>
</tr>
<tr>
<td>O</td>
<td>10</td>
<td>22-4</td>
<td>61</td>
</tr>
<tr>
<td>Q^a</td>
<td>10</td>
<td>79-81</td>
<td>80</td>
</tr>
</tbody>
</table>

Mercury pool cathode, 50ml 0.1M Et₄NBF₄ in acetonitrile purified by NaH/P₂O₅/CaH₂/4Å molecular sieve treatment, i = 20mA [except a) 10mA]
Table 7: Results of galvanostatic electrolyses of cinnamonomitrile (ca. 20 mM) in acetonitrile: the effect of water.

<table>
<thead>
<tr>
<th>Run</th>
<th>added water</th>
<th>yield PhCH(CH₂CN)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vol%</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>(a)</td>
<td>46</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>46</td>
</tr>
<tr>
<td>J</td>
<td>0.25×10⁻³</td>
<td>44</td>
</tr>
<tr>
<td>K</td>
<td>0.25×10⁻¹</td>
<td>47</td>
</tr>
<tr>
<td>M</td>
<td>0.20</td>
<td>36</td>
</tr>
<tr>
<td>L</td>
<td>0.25</td>
<td>20 b</td>
</tr>
</tbody>
</table>

Mercury pool cathode, 50 ml 0.1 M Et₄NBF₄ in acetonitrile purified by NaH/P₂O₅/CaH₂/4Å molecular sieve treatment, T = 22-40°C, i = 20 mA.

a) acetonitrile passed down a column of activated alumina

b) for 53% conversion of cinnamonomitrile in 17 min; selectivity for PhCH₂CH₂CN = 38%
Table 8: Results of galvanostatic electrolyses of cinnamono-nitrile (ca. 20mM) in acetonitrile using various supporting electrolytes.

<table>
<thead>
<tr>
<th>Run</th>
<th>supporting electrolyte</th>
<th>yield PhCH(CH_2-CN)₂</th>
<th>yield PhCH₂-C≡N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cation</td>
<td>anion</td>
<td>%</td>
</tr>
<tr>
<td>F</td>
<td>Et₄N⁺</td>
<td>BF₄⁻</td>
<td>46</td>
</tr>
<tr>
<td>W</td>
<td>Et₄N⁺</td>
<td>I⁻</td>
<td>46</td>
</tr>
<tr>
<td>T</td>
<td>Et₄N⁺</td>
<td>OTs⁻</td>
<td>41</td>
</tr>
<tr>
<td>R</td>
<td>Bu₄N⁺</td>
<td>BF₄⁻</td>
<td>45</td>
</tr>
<tr>
<td>S</td>
<td>Me₄N⁺</td>
<td>BF₄⁻</td>
<td>36ᵃ</td>
</tr>
<tr>
<td>V</td>
<td>Na⁺</td>
<td>I⁻</td>
<td>0ᵇ</td>
</tr>
<tr>
<td>U</td>
<td>Li⁺</td>
<td>ClO₄⁻</td>
<td>0ᶜ</td>
</tr>
</tbody>
</table>

Mercury pool cathode, 50ml 0.1M supporting electrolyte in acetonitrile purified by NaH/P₂O₅/CaH₂/4Å molecular sieve treatment, T = 22-24°C, i = 20mA.

a) occurs for ca. 80% conversion of cinnamoniitrile (see Graph 9)

b) for 24% conversion of cinnamoniitrile in 20min

c) for 18% conversion of cinnamoniitrile in 16min; selectivity for PhCH₂-C≡N = 27%.
Table 9: Galvanostatic electrolyses of cinnamonic acid: the relationships of charge to reacted cinnamic acid.

<table>
<thead>
<tr>
<th>Run conditions</th>
<th>initial</th>
<th>i</th>
<th>( t_c )</th>
<th>( 10^4 ) charge</th>
<th>loss of PhCH(\text{CN} )</th>
<th>formation of PhCH(\text{CN} )) (2 )</th>
<th>remaining PhCH(\text{CN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[PhCH(\text{CN} )]</td>
<td>mN</td>
<td>mA</td>
<td>min</td>
<td>mF</td>
<td>mol</td>
<td>mol(^{-1} )</td>
</tr>
<tr>
<td>i</td>
<td></td>
<td>20</td>
<td>20</td>
<td>12.8±1.2</td>
<td>1.59</td>
<td>0.795</td>
<td>5.0±2%</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>21</td>
<td>80</td>
<td>3.3±0.2</td>
<td>1.64</td>
<td>0.804</td>
<td>4.90±5%</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>81</td>
<td>40</td>
<td>41</td>
<td>10.2</td>
<td>3.40</td>
<td>3.33</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>42</td>
<td>40</td>
<td>15</td>
<td>3.73</td>
<td>1.70</td>
<td>4.56</td>
</tr>
<tr>
<td>average for (i)</td>
<td></td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>T = 40-60°C</td>
<td>20</td>
<td>20</td>
<td>11</td>
<td>1.37</td>
<td>0.802</td>
<td>3.85</td>
</tr>
<tr>
<td>Q</td>
<td>T = 79-81°C</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0.622</td>
<td>0.409</td>
<td>6.58</td>
</tr>
<tr>
<td>M</td>
<td>0.20% ( \text{H}_{2}\text{O} ) added</td>
<td>23</td>
<td>20</td>
<td>29</td>
<td>3.61</td>
<td>0.943</td>
<td>2.61</td>
</tr>
<tr>
<td>T</td>
<td>( \text{Et}_4\text{N} )</td>
<td>22</td>
<td>20</td>
<td>20</td>
<td>2.49</td>
<td>0.823</td>
<td>3.31</td>
</tr>
<tr>
<td>G</td>
<td>LiClO(_4)</td>
<td>21</td>
<td>20</td>
<td>16(^g)</td>
<td>1.99</td>
<td>0.150</td>
<td>0.75</td>
</tr>
<tr>
<td>V</td>
<td>NaI</td>
<td>21</td>
<td>20</td>
<td>20(^g)</td>
<td>2.49</td>
<td>0.197</td>
<td>0.79</td>
</tr>
</tbody>
</table>

a) except where otherwise stated; supporting electrolyte = \( \text{Et}_4\text{N} \) \( \text{BF}_4\) and \( T = 22-40°C \).

b) \( t_c \) = time required for reaction to reach completion, (i.e. for the yield of PhCH\(\text{NH}_2 \)) \( \text{CN} \) to reach a maximum, and for the concentration of PhCH\(\text{CN} \) to decrease to a minimum of ca. 0%.

c) unaccounted for by cyanomethylation or by reduction to PhCH\(\text{NH} \)) \( \text{CN} \).

d) yield of PhCH\(\text{NH}_2 \)) \( \text{CN} \) = 3%

e) time for 18% conversion

f) selectivity for PhCH\(\text{NH}_2 \)) \( \text{CN} \) = 27%

g) time for 24% conversion
Table 10: Results of a galvanostatic (20mA) electrolysis of benzaldehyde (13.6mM) in purified acetonitrile.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>i</th>
<th>ii</th>
<th>% iii</th>
<th>iv</th>
<th>v</th>
<th>vi</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>70.5</td>
<td>12</td>
<td>trace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>59</td>
<td>24</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>52</td>
<td>28</td>
<td>0.4</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>41</td>
<td>40</td>
<td>0.8</td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>30</td>
<td>56</td>
<td>1.2</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>18</td>
<td>86</td>
<td>1.0</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>13</td>
<td>58</td>
<td>1.8</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>4</td>
<td>68</td>
<td>2.3</td>
<td>0.4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>11.5</td>
<td>2</td>
<td>68</td>
<td>2.3</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>13.2</td>
<td>3</td>
<td>46</td>
<td>9.9</td>
<td>1.8</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>14.8</td>
<td>3</td>
<td>48</td>
<td>7.4</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>16.3</td>
<td>3</td>
<td>43</td>
<td>11.2</td>
<td>1.0</td>
<td>5.6</td>
<td>0.8</td>
</tr>
<tr>
<td>18.7</td>
<td>0</td>
<td>38</td>
<td>8.8</td>
<td>0.6</td>
<td>7.0</td>
<td>5.6</td>
</tr>
<tr>
<td>21.2</td>
<td>26</td>
<td>2.2</td>
<td>trace</td>
<td>9.4</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>25.1</td>
<td>-</td>
<td>0.7</td>
<td>trace</td>
<td>11.4</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>

i: PhCHO  
ii: PhCH(OH)CH₂CN  
iii: trans-PhCHCHCN  
iv: cis-PhCHCHCN  
v: PhCH₂CH₂CN  
vi: PhCH (CH₂CN)₂

Mercury (3ml) pool cathode, acetonitrile (50ml) purified by NaH/P₂O₅/CaH₂ treatment and stored over 4Å molecular sieve, supporting electrolyte = 0.1M Et₄NBF₄, catholyte volume = 35ml, T = 23-4°C.
Table 1: Results of galvanostatic (10 mA) electrolyses of acrylonitrile in purified acetonitrile.

<table>
<thead>
<tr>
<th>Run</th>
<th>% conversion of acrylonitrile</th>
<th>% yield</th>
<th>% selectivity</th>
<th>molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>G</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>0.74</td>
<td>2.4</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>1.70</td>
<td>3.5</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>2.74</td>
<td>5.0</td>
<td>0.84</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>0.02</td>
<td>0</td>
<td>0.44</td>
</tr>
<tr>
<td>6</td>
<td>21</td>
<td>0.02</td>
<td>0</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>31</td>
<td>0.92</td>
<td>1.6</td>
<td>0.36</td>
</tr>
</tbody>
</table>

D: an olefinic C₆-dinitrile
G: glutaronitrile
A: adiponitrile

Mercury (3ml) pool cathode; acetonitrile (150ml) purified by NaH/P₂O₅/CaH₂ treatment and stored over 4Å molecular sieve; supporting electrolyte = 6.1M Et₄NBF₄; acrylonitrile (10mmol) dissolved in the catholyte.

Except where otherwise stated, the duration of the electrolysis was 10min and the reaction was terminated immediately afterwards by the addition of an aqueous solution of NH₄Cl.

a) termination by addition of solid NH₄Cl
b) 20min electrolysis
c) bis-cyanoethyl ether detected

Compounds added to the catholyte before electrolysis commenced:
d) 0.145mmol glacial acetic acid
e) 1.0ml water
f) 0.045 mmol hydroquinone
Table 12: Results of galvanostatic (10mA) electrolyses of acrylonitrile in purified acetonitrile.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>[Et₄NBF₄] M</th>
<th>% conversion of acrylonitrile</th>
<th>% yield D</th>
<th>% yield G</th>
<th>% yield A</th>
<th>% selectivity D</th>
<th>% selectivity G</th>
<th>% selectivity A</th>
<th>molar ratio G/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>20</td>
<td>0.3</td>
<td>21</td>
<td>0.82</td>
<td>5.27</td>
<td>0.65</td>
<td>3.9</td>
<td>25.2</td>
<td>3.1</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>0.1</td>
<td>25</td>
<td>2.03</td>
<td>2.06</td>
<td>0.52</td>
<td>8.3</td>
<td>8.4</td>
<td>2.1</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>0.3</td>
<td>23</td>
<td>0.96</td>
<td>2.07</td>
<td>0.61</td>
<td>4.2</td>
<td>8.9</td>
<td>2.6</td>
<td>7</td>
</tr>
<tr>
<td>11</td>
<td>19</td>
<td>0.1</td>
<td>26</td>
<td>1.31</td>
<td>4.30</td>
<td>0.58</td>
<td>5.1</td>
<td>16.7</td>
<td>2.3</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>26</td>
<td>0.1</td>
<td>26</td>
<td>1.42</td>
<td>5.67</td>
<td>0.87</td>
<td>5.6</td>
<td>22.2</td>
<td>3.4</td>
<td>13</td>
</tr>
</tbody>
</table>

D: an olefinic C₆-dinitrile
G: glutaronitrile
A: adiponitrile

Mercury (3ml) pool cathode; acetonitrile (100ml) purified by NaH/P₂O₅/CaH₂ treatment and stored over 4Å molecular sieve; supporting electrolyte = Et₄NBF₄; acrylonitrile (6.9mmol) dissolved in the catholyte. These 10min electrolyses were followed immediately by the addition of an aqueous solution of NH₄Cl.
Table 13: Results of galvanostatic (10mA) electrolyses of acrylonitrile in purified acetonitrile.

<table>
<thead>
<tr>
<th>Run</th>
<th>initial [acrylonitrile] mM</th>
<th>% yielda</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>90</td>
<td>18 6</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>26 5</td>
</tr>
<tr>
<td>16</td>
<td>24</td>
<td>46 3</td>
</tr>
<tr>
<td>17</td>
<td>12</td>
<td>45 4</td>
</tr>
<tr>
<td>18b</td>
<td>12</td>
<td>47 3</td>
</tr>
<tr>
<td>20c</td>
<td>12</td>
<td>51 3</td>
</tr>
<tr>
<td>21d</td>
<td>46</td>
<td>32 6</td>
</tr>
<tr>
<td>22e</td>
<td>46</td>
<td>17 10</td>
</tr>
<tr>
<td>23f</td>
<td>45</td>
<td>32 6</td>
</tr>
<tr>
<td>24</td>
<td>46</td>
<td>23 3</td>
</tr>
</tbody>
</table>

G: glutaronitrile  
A: adiponitrile

Mercury (3ml) pool cathode; acetonitrile (50ml) purified by NaH/P2O5/CaH2 treatment and stored over 4Å molecular sieve. Except where otherwise stated: supporting electrolyte = 0.1M Et4NBF4; T = 21-4°C.  
a) calculated assuming the catholyte volume = 38ml  
b) the acrylonitrile contained 0.035mol% of N,N-dimethyl-p-nitrosoaniline  
c) the acrylonitrile contained 0.45mol% of N,N-dimethyl-p-nitrosoaniline  
d) supporting electrolyte = 0.3M Et4NBF4  
e) supporting electrolyte = 0.3M Et4N0Ts  
f) T = 34-7°C
<table>
<thead>
<tr>
<th>Electroactive Substrate</th>
<th>% Decrease in $i_{p(c)}(1)$</th>
<th>$E_{p(c)}(1)$</th>
<th>$E_{p(c)}(2)$</th>
<th>% Decrease in $i_{p(c)}(1)$ corrected for dilution</th>
<th>$\Delta G^\circ$</th>
<th>$k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-phenylcinnamonic acid</td>
<td>2 ± 1.5</td>
<td>-2.13</td>
<td>-2.42</td>
<td>-3</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>trans-cinnamonic acid</td>
<td>0 ± 1.5</td>
<td>-2.19</td>
<td>-2.68</td>
<td>-5</td>
<td>0.48</td>
<td>≠ 100</td>
</tr>
<tr>
<td>cis-cinnamonic acid</td>
<td>5 ± 1</td>
<td>-2.19</td>
<td>-2.68</td>
<td>0</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>benzophenone</td>
<td>19 ± 1</td>
<td>-2.15</td>
<td>-2.54</td>
<td>15</td>
<td>0.43</td>
<td>580 ± 20</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>56 ± 9</td>
<td>-2.22</td>
<td>-2.9</td>
<td>54</td>
<td>0.52</td>
<td>?</td>
</tr>
<tr>
<td>acrylonitrile</td>
<td>35 ± 9</td>
<td>-2.52</td>
<td>-</td>
<td>32</td>
<td>0.88</td>
<td>580 ± 20</td>
</tr>
</tbody>
</table>

Electroactive species (2mM) + 4,4'-asopryidine (2mM) in 0.1M Et$_3$NF in purified acetonitrile; v = 0.25Vs$^{-1}$; HDEE: Ag/0.1M AgNO$_3$ reference

a) 4,4'-asopryidine: $E_{p(c)}(1) = -1.20V$, $E_{p(c)}(2) = -1.72V$

b) Corrected value = $100 - (100 - \%$ decrease $) / 0.95$

c) Assuming that for 4,4'-asopryidine: $E^0(2) - E_{p(c)}(2) = 28mV$

d) Assuming $k_2 = 0.48s^{-1}$

? denotes that computer simulation indicates that the decrease is too large to be accounted for by the mechanism in Scheme 3 (Chapter 2) for those particular $\Delta G^\circ$ and $k_2$. 

Table 14: Results for the addition of 4,4'-asopryidine$^a$ to solutions of electroactive substrates in acetonitrile.
Table 15: Results for the addition of 4,4'-azopyridine to benzophenone in acetonitrile.

<table>
<thead>
<tr>
<th>$\frac{V}{V_s}$</th>
<th>$%$ decrease</th>
<th>$%$ decrease corrected for dilution$^a$</th>
<th>$k_c^b$</th>
<th>l mol$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>22</td>
<td>18</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>22</td>
<td>18</td>
<td>630</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>18</td>
<td>14</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>48</td>
<td>45</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

$E_{pc}(1)$ for 4,4'-azopyridine = -1.31V

$E_{pc}(2)$ for 4,4'-azopyridine = -1.78V

$E_{pc}(1)$ for benzophenone = -2.26V

Benzophenone (1.9mM) + 4,4'-azopyridine (1.9mM) in 0.1M Et$_4$NBF$_4$ in purified acetonitrile; HMDE; Ag/0.1M AgNO$_3$ reference.

$^a$ corrected value = $\left\{\frac{100 - (100 - \% \text{ decrease})}{0.95}\right\}$

$^b$ assuming $\Delta E^0' = 0.48V$ and $k_1 = 0.487s^{-1}$
Table 16: $L_{sv} (v = 0.20Vs^{-1})$ results for the addition of azo compounds to benzophenone in acetonitrile.

<table>
<thead>
<tr>
<th>azo compound</th>
<th>$E_{pc}(1)/V$</th>
<th>$E_{pc}(2)/V$</th>
<th>$\Delta E_{pc}(1)/V$</th>
<th>$\Delta E^{0'}a$</th>
<th>%decrease in $E_{pc}(1)$ of $\text{Ph}_2\text{CO}$</th>
<th>%decrease corrected for dilution</th>
<th>$k_2/1 \text{ mol}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-phenylazopyridine</td>
<td>-1.56</td>
<td>-2.00</td>
<td>0.70</td>
<td>0.26</td>
<td>41</td>
<td>38</td>
<td>?*</td>
</tr>
<tr>
<td>2,2'-azopyridine</td>
<td>-1.49</td>
<td>-1.89</td>
<td>0.77</td>
<td>0.37</td>
<td>36</td>
<td>33</td>
<td>1780</td>
</tr>
<tr>
<td>4,4'-azopyridine</td>
<td>-1.31</td>
<td>-1.78</td>
<td>0.95</td>
<td>0.48</td>
<td>18</td>
<td>14</td>
<td>60</td>
</tr>
</tbody>
</table>

Benzophenone (1.9mM) + azo compound (1.9mM) in 0.1M $\text{Et}_4\text{NBF}_4$ in purified acetonitrile; HMDE; $\text{Ag}/0.1M \text{AgNO}_3$ reference

a) assuming $\Delta E^{0'} = \Delta E_{pc}'$, where $\Delta E_{pc}' = E_{pc}(2)\{\text{azo}\} - E_{pc}(1)\{\text{Ph}_2\text{CO}\}$

and $E_{pc}(1)\{\text{Ph}_2\text{CO}\} = -2.26V$

b) corrected value = $100 - \frac{(100 - \%\text{decrease})}{0.95}$

c) ? denotes that computer simulation indicates that the decrease is too large to be accounted for by the mechanism in Scheme 3 (Chapter 2) for those particular $\Delta E^{0'}$ and $k_2$. 

$k_1 = 0.487s^{-1}$, $4.87s^{-1}$
Table 17: Estimation of the 1st order rate constants, $k_1$, for the azopyridine dianions.

<table>
<thead>
<tr>
<th>Azo compound</th>
<th>$\nu$</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$i_{pa}(2)/i_{pc}(2)$</th>
<th>$E_{pa}(2)-E_{pc}(2)$</th>
<th>$E_A - E_{pc}(2)$</th>
<th>$\gamma$</th>
<th>$k_1 \tau$</th>
<th>$k_1 = (k_1 \tau) / \gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-azopyridine</td>
<td>0.25</td>
<td>0.50-2.0</td>
<td>0.05-0.2</td>
<td>0.025</td>
<td>0.075</td>
<td>0.40</td>
<td>0.835</td>
<td>0.19</td>
</tr>
<tr>
<td>2,2'-azopyridine</td>
<td>0.20</td>
<td>3.9</td>
<td>0.5</td>
<td>0.020</td>
<td>0.100</td>
<td>0.60</td>
<td>0.70</td>
<td>0.40</td>
</tr>
<tr>
<td>4-phenylazopyridine</td>
<td>0.20</td>
<td>3.9</td>
<td>0.5</td>
<td>0.020</td>
<td>0.100</td>
<td>0.60</td>
<td>0.65</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Table 18: Estimates of the rate constant for the cyano-methylation of benzophenone in acetonitrile using azo compounds as probes.

<table>
<thead>
<tr>
<th>azo compound</th>
<th>$\Delta E^o'/V$</th>
<th>$\nu$ vs$^{-1}$</th>
<th>% decrease (corrected for dilution)</th>
<th>$k_2/1$ mol$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-azopyridine</td>
<td>0.43</td>
<td>0.25</td>
<td>15</td>
<td>580±20</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>0.25</td>
<td>18</td>
<td>630</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>0.20</td>
<td>14</td>
<td>60</td>
</tr>
<tr>
<td>2,2'-azopyridine</td>
<td>0.37</td>
<td>0.25</td>
<td>26</td>
<td>6300</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.25</td>
<td>31</td>
<td>?</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>0.20</td>
<td>33</td>
<td>1800</td>
</tr>
<tr>
<td>4-phenylazopyridine</td>
<td>0.26</td>
<td>0.20</td>
<td>38</td>
<td>?</td>
</tr>
</tbody>
</table>

? denotes that computer simulation indicates that the decrease is too large to be accounted for by the mechanism in Scheme 3 (Chapter 2) for those particular $\Delta E^o'$ and $k_1$. 
Table 19: Cv of 2,2'-asopyridines (1mM) in super-dry DMF containing ethyl phenylacetate (0.25vol%).

<table>
<thead>
<tr>
<th>( v )/Vs(^{-1})</th>
<th>( \text{1(A)}/\text{i}_{\text{pc}(1)} )</th>
<th>( \text{1(B)}/\text{i}_{\text{pc}(1)} )</th>
<th>( \text{i(A)}/\text{i}_{\text{pc}(1)} )</th>
<th>( \text{i(B)}/\text{i(A)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.36</td>
<td>0.24</td>
<td>0.59</td>
<td>0.67</td>
</tr>
<tr>
<td>0.227</td>
<td>0.33</td>
<td>0.13</td>
<td>0.46</td>
<td>0.39</td>
</tr>
<tr>
<td>0.094</td>
<td>0.24</td>
<td>0.06</td>
<td>0.29</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Conditions: activated alumina suspension; 0.1M Bu₄NBF₄; PDE; Ag wire reference; \( T = -50°C \)
Table 20: Decrease in $i_{pc} (%)$ for various electroactive substrates (2mM) in DMF on the addition of benzenesulphonylacetonitrile (4mM)\(^a\)

<table>
<thead>
<tr>
<th>Electroactive Substrate</th>
<th>$v/Vs^{-1}$:</th>
<th>0.03</th>
<th>0.10</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td></td>
<td>77.8(76.6)</td>
<td>73.8(72.4)</td>
<td></td>
<td></td>
<td>70.2(68.6)</td>
<td></td>
</tr>
<tr>
<td>Propiophenone</td>
<td>69.2(67.6)</td>
<td>68.8(67.2)</td>
<td>67.3(65.6)</td>
<td>66.7(64.9)</td>
<td>64.6(62.7)</td>
<td>67.8(66.1)</td>
<td></td>
</tr>
<tr>
<td>Propiophenone (+1% H(_2)O)</td>
<td>81.3(80.3)</td>
<td>80.4(79.4)</td>
<td>78.9(77.8)</td>
<td>79.9(78.8)</td>
<td>78.9(77.8)</td>
<td>72.7(71.3)</td>
<td></td>
</tr>
<tr>
<td>Isopropyl phenyl ketone</td>
<td>62.5(60.5)</td>
<td>60.0(57.9)</td>
<td>57.2(54.9)</td>
<td>57.8(55.6)</td>
<td>55.4(53.1)</td>
<td>55.3(52.9)</td>
<td></td>
</tr>
<tr>
<td>T-butyl phenyl ketone</td>
<td>61.1(59.1)</td>
<td>51.4(48.8)</td>
<td>48.8(46.1)</td>
<td>46.5(43.7)</td>
<td>43.3(40.3)</td>
<td>43.6(40.6)</td>
<td></td>
</tr>
<tr>
<td>Acetylnaphthalene</td>
<td>23.0(18.9)</td>
<td>16.8(12.4)</td>
<td>13.6( 9.1)</td>
<td>11.7( 7.1)</td>
<td>9.7( 4.9)</td>
<td>9.5( 4.7)</td>
<td></td>
</tr>
<tr>
<td>Trans-stilbene</td>
<td>10.4( 5.7)</td>
<td>4.6(-0.4)</td>
<td>1.2(-4.0)</td>
<td></td>
<td></td>
<td>-3.0(-8.4)</td>
<td>0(-5.3)</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td></td>
<td>38.6(^b)(32.7)</td>
<td>39.2(^b)(33.4)</td>
<td></td>
<td></td>
<td></td>
<td>39.7(^b)(34.0)</td>
</tr>
</tbody>
</table>

HMDE; 0.1M Et\(_4\)NBF\(_4\) in DMF (20ml) + electroactive substrate in DMF (1.0ml)

+ benzenesulphonylacetonitrile in DMF (a:1.0ml, b:2.0ml).

Values in brackets are corrected for dilution.
### Table 21: Peak potential separation, $\Delta E'_{pc}$, and standard potential separation, $\Delta E^0'$, data for benzenesulphonylacetonitrile with various electroactive substrates in DMF

<table>
<thead>
<tr>
<th>Electroactive Substrate</th>
<th>$\Delta E'_{pc}$</th>
<th>$\Delta E^0'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td>Propiophenone</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>Isopropyl phenyl ketone</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>$t$-Butyl phenyl ketone</td>
<td>0.28</td>
<td>0.19</td>
</tr>
<tr>
<td>Acetylmesitylene</td>
<td>0.62</td>
<td>0.53</td>
</tr>
<tr>
<td>Trans-stilbene</td>
<td>0.37</td>
<td>0.28</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.28</td>
<td>0.28</td>
</tr>
</tbody>
</table>

HMDE; 0.1M Et$_4$NBF$_4$ in DMF; electroactive substrate (2mM); benzenesulphonylacetonitrile (4mM); $v = 0.25$Vs$^{-1}$

a) $\Delta E'_{pc}$ is based on $E'_{pc}$ (substrate) before addition and $E'_{pc}$ (PhSO$_2$CH$_2$CN) after addition.

b) Assuming $E^0$(PhSO$_2$CH$_2$CN) = $E'_{pc}$ (PhSO$_2$CH$_2$CN) - 0.07

and $E^0$(substrate) = $E'_{pc}$ (substrate) + 0.02

then $\Delta E^0' = \Delta E'_{pc} - 0.09$

where $\Delta E' = E$(PhSO$_2$CH$_2$CN) - $E$(substrate)

c) Assuming $\Delta E^0' = \Delta E'_{pc}$
Table 22: Results for the addition of benzenesulphonylacetonitrile to acrylonitrile in DMF

<table>
<thead>
<tr>
<th>$\frac{V}{Vs^{-1}}$</th>
<th>% decrease in $i_{pc}(l)$ of $\text{CH}_2\text{CHCN}$</th>
<th>% decrease corrected for dilution$^a$</th>
<th>$\Gamma^b$</th>
<th>$\frac{k_2}{\text{mol}^{-1}\text{s}^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>30</td>
<td>26</td>
<td>2.80</td>
<td>100-200</td>
</tr>
<tr>
<td>0.25</td>
<td>29</td>
<td>25</td>
<td>1.12</td>
<td>300</td>
</tr>
<tr>
<td>0.50</td>
<td>29</td>
<td>25</td>
<td>0.56</td>
<td>600</td>
</tr>
<tr>
<td>0.75</td>
<td>31</td>
<td>28</td>
<td>0.37</td>
<td>800</td>
</tr>
<tr>
<td>1.00</td>
<td>34</td>
<td>31</td>
<td>0.28</td>
<td>1200</td>
</tr>
</tbody>
</table>

Acrylonitrile (1.9mM) + benzenesulphonylacetonitrile (1.9mM) in 0.1M Et$_4$NBF$_4$ in DMF; HMDE; Ag/0.1M AgNO$_3$ reference.

a) corrected value = 100 - (100 - % decrease) / 0.95

b) assuming $\Delta E^0' = 0.28V$
Table 23: Anodic peak potential, $E_{pa}$, as a function of switching potential, $E^\lambda$, for a reversible charge transfer: comparison of simulation results with those of Nicholson and Sham 127

<table>
<thead>
<tr>
<th>$(E^0 - E^\lambda)$ mV</th>
<th>$(E_{pa} - E^0)$ mV</th>
<th>$i_{pa}/i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicholson and Sham</td>
<td>simulation</td>
<td>simulation</td>
</tr>
<tr>
<td>75</td>
<td>33.3</td>
<td>33.1</td>
</tr>
<tr>
<td>100</td>
<td>32.0</td>
<td>31.6</td>
</tr>
<tr>
<td>150</td>
<td>30.7</td>
<td>30.2</td>
</tr>
<tr>
<td>200</td>
<td>29.8</td>
<td>29.6</td>
</tr>
<tr>
<td>300</td>
<td>29.3</td>
<td>29.0</td>
</tr>
<tr>
<td>550</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$c = 0.002M$

$v = 0.25Vs^{-1}$

$D = 2 \times 10^{-5}cm^2s^{-1}$

$\delta = 0.039cm$

$\Delta x = 4.24 \times 10^{-4}cm$

$\Delta t = 3.34 \times 10^{-3}s$
Table 24: Computer simulation of a reversible electron transfer: effect of the concentration of the electroactive species

<table>
<thead>
<tr>
<th>c_b (mM)</th>
<th>i_{pc} (A/cm²)</th>
<th>(E_{pc} - E^0) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.2018</td>
<td>-28.4</td>
</tr>
<tr>
<td>4</td>
<td>2.4036</td>
<td>-28.4</td>
</tr>
<tr>
<td>6</td>
<td>3.6054</td>
<td>-28.4</td>
</tr>
</tbody>
</table>

v = 0.25Vs⁻¹
D = 2 x 10⁻⁵cm²s⁻¹
δ = 0.039cm
Δx = 4.24 x 10⁻⁴cm
Δt = 3.34 x 10⁻³s
Table 25: Comparison of simulation results with those of Nicholson and Shia\textsuperscript{127} for an EC process

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( \frac{(E_{pc} - E^0)}{mV} )</th>
<th>( \frac{i_{pc}}{Acm^{-2}} )</th>
<th>current function ( \sqrt{\pi} X(at) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{simulation} )</td>
<td>( \text{Nicholson and Sha} )</td>
<td>( \text{simulation} )</td>
<td>( \text{Nicholson and Sha} )</td>
</tr>
<tr>
<td>0.05</td>
<td>-27.5</td>
<td>-27.7</td>
<td>1.208</td>
</tr>
<tr>
<td>0.2</td>
<td>-25.0</td>
<td>-25.2</td>
<td>1.223</td>
</tr>
<tr>
<td>0.5</td>
<td>-21.0</td>
<td>-21.1</td>
<td>1.246</td>
</tr>
<tr>
<td>1.0</td>
<td>-16.1</td>
<td>-16.4</td>
<td>1.269</td>
</tr>
<tr>
<td>1.6</td>
<td>-11.8</td>
<td>-11.8</td>
<td>1.286</td>
</tr>
<tr>
<td>4.0</td>
<td>-1.9</td>
<td>-1.5</td>
<td>1.311</td>
</tr>
<tr>
<td>10.0</td>
<td>+8.5</td>
<td>+9.8</td>
<td>1.326</td>
</tr>
</tbody>
</table>

\[ a \] = \( \frac{nFy}{RT} \) s\textsuperscript{-1}

\[ i_{pc} = nFAc^b \sqrt{\pi D} \sqrt{\pi} X(at) \] A

\[ = 2.692 \sqrt{\pi} X(at) \] Acm\textsuperscript{-2}

\text{\textsuperscript{*} reversible charge transfer followed by an irreversible chemical reaction}

\[ v = 0.25Vs^{-1} \]
\[ c^b = 0.002M \]
\[ D = 2 \times 10^{-5}cm^2s^{-1} \]

\[ \delta = 0.039cm \]
\[ \Delta x = 4.24 \times 10^{-4}cm \]
\[ \Delta t = 3.34 \times 10^{-3}s \]
**Table 26:** Computer simulation results for a reversible charge transfer followed by an irreversible, 1st-order chemical reaction

<table>
<thead>
<tr>
<th>$k_1 \tau$</th>
<th>$k_1$</th>
<th>$\tau$</th>
<th>$\log_{10}(k_1 \tau)$</th>
<th>$i_{pa}/i_{pc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03894</td>
<td>0.1947</td>
<td>0.2</td>
<td>-1.4096</td>
<td>0.980</td>
</tr>
<tr>
<td>0.05841</td>
<td>0.1947</td>
<td>0.3</td>
<td>-1.2335</td>
<td>0.946</td>
</tr>
<tr>
<td>0.07788</td>
<td>0.1947</td>
<td>0.4</td>
<td>-1.1086</td>
<td>0.925</td>
</tr>
<tr>
<td>0.09736</td>
<td>0.4868</td>
<td>0.2</td>
<td>-1.0016</td>
<td>0.920</td>
</tr>
<tr>
<td>0.1948</td>
<td>0.4868</td>
<td>0.4</td>
<td>-0.7104</td>
<td>0.828</td>
</tr>
<tr>
<td>0.3894</td>
<td>1.947</td>
<td>0.2</td>
<td>-0.4096</td>
<td>0.703</td>
</tr>
<tr>
<td>0.4868</td>
<td>0.4868</td>
<td>1.0</td>
<td>-0.3127</td>
<td>0.654</td>
</tr>
<tr>
<td>0.5841</td>
<td>1.947</td>
<td>0.3</td>
<td>-0.2335</td>
<td>0.615</td>
</tr>
<tr>
<td>0.7788</td>
<td>1.947</td>
<td>0.4</td>
<td>-0.1086</td>
<td>0.549</td>
</tr>
<tr>
<td>0.9736</td>
<td>1.947</td>
<td>0.5</td>
<td>-0.0116</td>
<td>0.497</td>
</tr>
<tr>
<td>0.9736</td>
<td>4.868</td>
<td>0.2</td>
<td>-0.0116</td>
<td>0.491</td>
</tr>
<tr>
<td>1.168</td>
<td>1.947</td>
<td>0.6</td>
<td>+0.0675</td>
<td>0.455</td>
</tr>
<tr>
<td>1.460</td>
<td>4.868</td>
<td>0.3</td>
<td>+0.1644</td>
<td>0.425</td>
</tr>
<tr>
<td>1.947</td>
<td>1.947</td>
<td>1.0</td>
<td>+0.2893</td>
<td>0.349</td>
</tr>
</tbody>
</table>

$c = 0.002\text{M}$

$\nu = 0.25\text{Vs}^{-1}$

$D = 2 \times 10^{-5}\text{cm}^2\text{s}^{-1}$

$\delta = 0.039\text{cm}$

$\Delta x = 4.24 \times 10^{-4}\text{cm}$

$\Delta t = 3.34 \times 10^{-3}\text{s}$
Table 27: Values of the error function of \( Z \) (erfZ)

<table>
<thead>
<tr>
<th>( Z )</th>
<th>erfZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \infty )</td>
<td>1.0000</td>
</tr>
<tr>
<td>3.0</td>
<td>0.9999</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9996</td>
</tr>
<tr>
<td>2.0</td>
<td>0.9953</td>
</tr>
<tr>
<td>1.6</td>
<td>0.9764</td>
</tr>
<tr>
<td>1.2</td>
<td>0.9103</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8427</td>
</tr>
</tbody>
</table>

\[
\text{erf} Z = 2 \pi \int_0^\infty e^{-y^2} dy
\]

Table 28: Calculated diffusion layer thicknesses, $\delta$, for a variety of sweep times at several values of $z$.

<table>
<thead>
<tr>
<th>$t$</th>
<th>$v$</th>
<th>Z:</th>
<th>1.0</th>
<th>1.2</th>
<th>1.6</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0.500</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0253</td>
<td>0.0316</td>
<td>0.0379</td>
</tr>
<tr>
<td>2.50</td>
<td>0.400</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0283</td>
<td>0.0354</td>
<td>0.0424</td>
</tr>
<tr>
<td>3.33</td>
<td>0.300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0326</td>
<td>0.0408</td>
<td>0.0490</td>
</tr>
<tr>
<td>4.00</td>
<td>0.250</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0358</td>
<td>0.0447</td>
<td>0.0537</td>
</tr>
<tr>
<td>5.00</td>
<td>0.200</td>
<td>0.0200</td>
<td>0.0240</td>
<td>0.0320</td>
<td>0.0400</td>
<td>0.0500</td>
<td>0.0600</td>
<td></td>
</tr>
<tr>
<td>6.67</td>
<td>0.150</td>
<td>0.0231</td>
<td>0.0277</td>
<td>0.0370</td>
<td>0.0462</td>
<td>0.0578</td>
<td>0.0693</td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>0.100</td>
<td>0.0283</td>
<td>0.0339</td>
<td>0.0452</td>
<td>0.0566</td>
<td>0.0707</td>
<td>0.0848</td>
<td></td>
</tr>
<tr>
<td>13.33</td>
<td>0.075</td>
<td>0.0326</td>
<td>0.0392</td>
<td>0.0552</td>
<td>0.0653</td>
<td>0.0816</td>
<td>0.0979</td>
<td></td>
</tr>
<tr>
<td>20.00</td>
<td>0.050</td>
<td>0.0400</td>
<td>0.0480</td>
<td>0.0640</td>
<td>0.0800</td>
<td>0.1000</td>
<td>0.1200</td>
<td></td>
</tr>
</tbody>
</table>

$D = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$

* assuming a single sweep of 1.0V or a triangular sweep of 0.5V
Table 29: Effect of using different diffusion layer thicknesses in the computer simulation

<table>
<thead>
<tr>
<th>$\frac{V}{Vs^{-1}}$</th>
<th>$k_2$ 1mol$^{-1}$s$^{-1}$</th>
<th>NR</th>
<th>$\delta_{\text{max}}$</th>
<th>$\delta$</th>
<th>$i_{\text{pc(B)}}$ Acm$^{-2}$</th>
<th>$E_{\text{pc(B)}} - E^0_{\text{B}}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>400</td>
<td>93</td>
<td>0.039$^1$</td>
<td>0.039</td>
<td>0.7691</td>
<td>-28.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93</td>
<td>0.039$^4$</td>
<td>0.031</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>143</td>
<td>0.060$^4$</td>
<td>0.048</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.150</td>
<td>400</td>
<td>93</td>
<td>0.039$^1$</td>
<td>0.039</td>
<td>0.5058</td>
<td>-29.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119</td>
<td>0.050$^1$</td>
<td>0.050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>400</td>
<td>93</td>
<td>0.039$^1$</td>
<td>0.039</td>
<td>0.2825</td>
<td>-30.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>166</td>
<td>0.070$^4$</td>
<td>0.056</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>51,200</td>
<td>93</td>
<td>0.039$^1$</td>
<td>0.039</td>
<td>0.0773</td>
<td>-51.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>166</td>
<td>0.070$^4$</td>
<td>0.056</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$c_A^b = c_B^b = 0.002$M

$D_A = D_B = 2 \times 10^{-5}$cm$^2$s$^{-1}$

$k_1 = 97.357$ s$^{-1}$

$\Delta E^{0'} = 0.400$V

$\Delta t = 3.34 \times 10^{-3}$s

$E^0(B) - E_I = 0.600$V

1: Program EGB1 used

4: Program EGB4 used

* X: For a maximum sweep of 1.0V, i.e. 4s.

** X: Diffusion layer thickness operative at $E_{\text{pc(B)}}$. 

\[ V = \frac{k_2}{1\text{mol}^{-1}\text{s}^{-1}} \]
Table 30: The maximum time and distance increments as defined by Joslin and Fletcher's criteria* for various values of the 1st-order constant.

<table>
<thead>
<tr>
<th>$k_1$ $\text{s}^{-1}$</th>
<th>$t_{\text{max}} (=k_1^{-1})$ $\text{s}$</th>
<th>$\Delta x_{\text{max}} (=\sqrt{D/k_1})$ $\text{cm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$1 \times 10^{-2}$</td>
<td>$4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>500</td>
<td>$2 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>1,000</td>
<td>$1 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>5,000</td>
<td>$2 \times 10^{-4}$</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>10,000</td>
<td>$1 \times 10^{-4}$</td>
<td>$4.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>50,000</td>
<td>$2 \times 10^{-5}$</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

* Joslin and Fletcher's criteria:

\[(27) \ldots \quad \Delta x < \sqrt{D/k_1}\]
\[(28) \ldots \quad \Delta t < k_1^{-1}\]
Table 31: Correlation between the choice of the constants \( l \) and \( m \), the grid parameters \( \Delta y \) and \( \Delta t \), and the optimum number simulation points \( N_Y \).

<table>
<thead>
<tr>
<th>( l = m )</th>
<th>( y_{max} )</th>
<th>( \Delta t )</th>
<th>( 10^3 \times \Delta y ) (NY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.980</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.03</td>
<td>0.971</td>
<td>368 (3)</td>
<td>212 (5)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.952</td>
<td>220 (5)</td>
<td>127 (8)</td>
</tr>
<tr>
<td>0.10</td>
<td>0.909</td>
<td>110 (9)</td>
<td>63.7 (15)</td>
</tr>
<tr>
<td>0.20</td>
<td>0.833</td>
<td>55.0 (16)</td>
<td>31.8 (27)</td>
</tr>
<tr>
<td>0.50</td>
<td>0.667</td>
<td>22.0 (31)</td>
<td>12.7 (53)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.500</td>
<td>11.0 (46)</td>
<td>6.37 (79)</td>
</tr>
<tr>
<td>3.00</td>
<td>0.250</td>
<td>3.68 (68)</td>
<td>2.12 (118)</td>
</tr>
</tbody>
</table>

\[ D_1 = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \]
\[ \delta = 0.039 \text{cm} \]

Calculations used:
\[ \star (32) \ldots \quad y_{max} = \frac{l}{m} - \frac{1}{m+1} \]
\[ \star \star (33) \ldots \quad \Delta y = \frac{(D_1 \Delta t)^{\frac{1}{2}}}{0.6 \delta} \times \frac{l}{m^2} \]
Table 32: Computer simulation of the ISV experiment: effect of grid parameters

<table>
<thead>
<tr>
<th>$k_2$</th>
<th>$\Delta t$</th>
<th>Program (EGB)</th>
<th>$\Delta x$</th>
<th>$l=(m$, $\Delta y(NY)$</th>
<th>$i_{pc}(A)$</th>
<th>$E_{pc}(A)-E^0(A)$</th>
<th>$i_{pc}(B)$</th>
<th>$E_{pc}(B)-E^0(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1mol$^{-1}$s$^{-1}$</td>
<td>s</td>
<td>cm</td>
<td>mol$^{-1}$</td>
<td>cm</td>
<td></td>
<td>Ac$^{-2}$</td>
<td>mV</td>
<td>Ac$^{-2}$</td>
</tr>
<tr>
<td>1,600</td>
<td>3.339x10$^{-3}$</td>
<td>1</td>
<td>4.24x10$^{-4}$</td>
<td>-</td>
<td>1.326</td>
<td>+8.5</td>
<td>0.5722</td>
<td>-30.4</td>
</tr>
<tr>
<td>1.112x10$^{-3}$</td>
<td>4</td>
<td>2.53x10$^{-4}$</td>
<td>-</td>
<td>1.325</td>
<td>+9.4</td>
<td>0.5718</td>
<td>-30.2</td>
<td></td>
</tr>
<tr>
<td>1.112x10$^{-3}$</td>
<td>6</td>
<td>-</td>
<td>0.20, 3.09x10$^{-2}$</td>
<td>(28)</td>
<td>1.325</td>
<td>+9.6</td>
<td>0.5718</td>
<td>-30.2</td>
</tr>
<tr>
<td>2.985x10$^{-5}$</td>
<td>7</td>
<td>-</td>
<td>0.03, 3.47x10$^{-3}$</td>
<td>(29)</td>
<td>1.324</td>
<td>+9.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>51,200</td>
<td>3.336x10$^{-3}$</td>
<td>1</td>
<td>4.24x10$^{-4}$</td>
<td>-</td>
<td>1.326</td>
<td>+8.5</td>
<td>0.2252</td>
<td>-</td>
</tr>
<tr>
<td>2.985x10$^{-5}$</td>
<td>7</td>
<td>-</td>
<td>0.03, 3.47x10$^{-3}$</td>
<td>(29)</td>
<td>1.324</td>
<td>+9.8</td>
<td>0.2251</td>
<td>-44.35</td>
</tr>
</tbody>
</table>

$c_A^b = c_B^b = 0.002M$

$k_1 = 97.3578^{-1}$

$D_A = D_B = 2 \times 10^{-5}$cm$^2$s$^{-1}$

$\delta = 0.039$cm

$\nu = 0.25$Vs$^{-1}$

$\Delta E^0' = 0.250V$

(except $\times$ where $\Delta E^0' = 0.252V$)
Table 33: Computer simulation of the LSV experiment: effect of $k_1$

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$k_1/a$</th>
<th>% decrease in $i_{pc}(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.487</td>
<td>0.05</td>
<td>13.6</td>
</tr>
<tr>
<td>1.947</td>
<td>0.20</td>
<td>32.8</td>
</tr>
<tr>
<td>4.868</td>
<td>0.50</td>
<td>43.3</td>
</tr>
<tr>
<td>9.736</td>
<td>1.00</td>
<td>47.6</td>
</tr>
<tr>
<td>15.577</td>
<td>1.60</td>
<td>49.3</td>
</tr>
<tr>
<td>38.943</td>
<td>4.00</td>
<td>51.3</td>
</tr>
<tr>
<td>97.357</td>
<td>10.00</td>
<td>52.4</td>
</tr>
<tr>
<td>500.0</td>
<td>51.36</td>
<td>53.7</td>
</tr>
<tr>
<td>800.0</td>
<td>82.17</td>
<td>53.9</td>
</tr>
</tbody>
</table>

$c_A^b = c_B^b = 0.002M$

$D_A = D_B = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

$\nu = 0.25 \text{Vs}^{-1}$

$k_2 = 1.600 \text{ mol}^{-1} \text{s}^{-1}$

$\Delta E^0' = 0.250V$

(except * where $\Delta E^0' = 0.252V$)
Table 34: Computer simulation of the LSV experiment:

**effect of relative concentration**

<table>
<thead>
<tr>
<th>$c_A^b$ mM</th>
<th>$c_B^b$ mM</th>
<th>$c_A^b / c_B^b$</th>
<th>$\Delta E^0 / V$</th>
<th>% decrease in $i_{pc}(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>0.252</td>
<td>37.1</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.5</td>
<td>0.252</td>
<td>39.7</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.0</td>
<td>0.250</td>
<td>60.8</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1.0</td>
<td>0.250</td>
<td>67.8</td>
</tr>
</tbody>
</table>

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$

$V = 0.25 \text{Vs}^{-1}$

$k_1 = 97.36 \text{s}^{-1}$

$k_2 = 6000 \text{lmol}^{-1} \text{s}^{-1}$
Table 35: Computer simulation of the LSV experiment: effect of concentration

<table>
<thead>
<tr>
<th>$\Delta E^{0'}$ (mV)</th>
<th>$c_B^b$ (mM)</th>
<th>% decrease in $i_{pc}(B)$</th>
<th>$E_{pc}(B) - E^{0}(B)$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>2</td>
<td>52.4</td>
<td>-30.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>34.0</td>
<td>-30.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>24.6</td>
<td>-29.6</td>
</tr>
<tr>
<td>500</td>
<td>2</td>
<td>61.8</td>
<td>-31.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>37.9</td>
<td>-30.6</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>26.7</td>
<td>-29.8</td>
</tr>
<tr>
<td>750</td>
<td>2</td>
<td>66.7</td>
<td>-32.1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>39.8</td>
<td>-30.4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>27.8</td>
<td>-29.5</td>
</tr>
</tbody>
</table>

$c_A^b = 2$ mM

$D_A = D_B = 0.2 \times 10^{-5}$ cm$^2$ s$^{-1}$

$v = 0.25$ Vs$^{-1}$

$k_1 = 97.36$ s$^{-1}$

$k_2 = 1600$ 1mol$^{-1}$s$^{-1}$
Table 36: Computer simulation of the LSV experiment: effect of $v$ and $\Delta E^0$'  

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$\frac{v}{Vs^{-1}}$</th>
<th>$\frac{\Delta E^0}{V}$</th>
<th>$\frac{k_2}{l mol^{-1}s^{-1}}$</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>800</th>
<th>1,200</th>
<th>4,000</th>
<th>51,200</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.800</td>
<td>0.50</td>
<td>0.400</td>
<td>7.66</td>
<td>13.86</td>
<td>23.33</td>
<td>35.43</td>
<td>42.86</td>
<td>61.18</td>
<td>80.16</td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>0.240</td>
<td></td>
<td>8.22</td>
<td></td>
<td>24.51</td>
<td>-</td>
<td>43.88</td>
<td>61.36</td>
<td>80.04</td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>0.50</td>
<td>0.500</td>
<td>9.22</td>
<td>16.40</td>
<td>26.85</td>
<td>39.44</td>
<td>46.77</td>
<td>63.97</td>
<td>81.54</td>
<td></td>
</tr>
<tr>
<td>1.008</td>
<td>0.25</td>
<td>0.252</td>
<td>10.09</td>
<td>17.71</td>
<td>28.46</td>
<td>40.91</td>
<td>47.95</td>
<td>64.02</td>
<td>81.30</td>
<td></td>
</tr>
<tr>
<td>2.000</td>
<td>0.40</td>
<td>0.800</td>
<td>16.25</td>
<td></td>
<td>39.43</td>
<td>-</td>
<td>58.09</td>
<td>71.36</td>
<td>85.17</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.500</td>
<td></td>
<td>17.14</td>
<td>27.27</td>
<td>39.92</td>
<td>52.08</td>
<td>58.11</td>
<td>70.91</td>
<td>84.73</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>0.400</td>
<td></td>
<td>17.03</td>
<td>27.68</td>
<td>40.28</td>
<td>52.27</td>
<td>58.18</td>
<td>70.73</td>
<td>84.61</td>
<td></td>
</tr>
<tr>
<td>4.000</td>
<td>0.20</td>
<td>0.800</td>
<td>26.96</td>
<td></td>
<td>52.14</td>
<td>-</td>
<td>66.81</td>
<td>76.65</td>
<td>87.66</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.400</td>
<td></td>
<td>28.08</td>
<td>40.73</td>
<td>52.68</td>
<td>62.15</td>
<td>66.50</td>
<td>75.89</td>
<td>87.28</td>
<td></td>
</tr>
</tbody>
</table>

$e_A^b = e_B^b = 0.002M$

$D_A = D_B = 2 \times 10^{-5}cm^2s^{-1}$

$k_1 = 97.357s^{-1}$
Table 37: Computer simulation of the LSV experiment: regeneration of species Z

<table>
<thead>
<tr>
<th>$[^b]b$</th>
<th>$[^b]k_3$</th>
<th>% decrease in $[^i]p_c(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mM</td>
<td>s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>67.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>~99.0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>99.0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>98.9</td>
</tr>
</tbody>
</table>

$c_A = 2$ mM

$D_A = D_B = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$

$v = 0.25$ V s$^{-1}$

$\Delta E^{0'} = 0.252$ V

$k_1 = 97.35$ s$^{-1}$

$k_2 = 6,000$ mol$^{-1}$ s$^{-1}$
Table 38: Computer simulation of the LSV experiment: 1st-order reaction of B^-

<table>
<thead>
<tr>
<th>( k_i ) ( \text{s}^{-1} )</th>
<th>% decrease in ( i_{pc}(B) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81.3</td>
</tr>
<tr>
<td>0.487</td>
<td>81.3</td>
</tr>
<tr>
<td>1.547</td>
<td>81.2</td>
</tr>
<tr>
<td>4.868</td>
<td>81.2</td>
</tr>
<tr>
<td>9.736</td>
<td>81.1</td>
</tr>
<tr>
<td>15.577</td>
<td>81.1</td>
</tr>
<tr>
<td>38.943</td>
<td>81.0</td>
</tr>
<tr>
<td>97.357</td>
<td>80.8</td>
</tr>
</tbody>
</table>

\( c_A = c_B = 0.002 \text{M} \)
\( D_A = D_B = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \)
\( v = 0.25 \text{V s}^{-1} \)
\( k_1 = 97.357 \text{s}^{-1} \)
\( k_2 = 51,200 \text{ mol}^{-1} \text{s}^{-1} \)
\( \Delta E^{\circ'} = 0.250 \text{V} \)

(except * where \( \Delta E^{\circ'} = 0.252 \text{V} \))
Table 39: Computer simulation of the LSV experiment: 1st order reaction of B$^-$

<table>
<thead>
<tr>
<th>$k_1$ $s^{-1}$</th>
<th>$k_4$ $s^{-1}$</th>
<th>% decrease in $i_{pc}(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.487</td>
<td>0</td>
<td>23.1</td>
</tr>
<tr>
<td>1.947</td>
<td>0</td>
<td>54.6</td>
</tr>
<tr>
<td>4.868</td>
<td>0</td>
<td>70.2</td>
</tr>
<tr>
<td>9.736</td>
<td>0</td>
<td>75.8</td>
</tr>
<tr>
<td>15.577</td>
<td>0</td>
<td>78.0</td>
</tr>
<tr>
<td>38.943</td>
<td>0</td>
<td>80.3</td>
</tr>
<tr>
<td>97.357</td>
<td>0</td>
<td>81.3</td>
</tr>
</tbody>
</table>

$[b]_{A} = [b]_{B} = 0.002 M$

$D_{A} = D_{B} = 2 \times 10^{-5} \text{cm}^2\text{s}^{-1}$

$v = 0.25 \text{Vs}^{-1}$

$k_2 = 51,200 \text{mol}^{-1}\text{s}^{-1}$

for $k_4 = 0$ : $\Delta E^0 = 0.252 V$

for $k_4 = 97.357 \text{s}^{-1}$ : $\Delta E^0 = 0.250 V$
Table 40: Computer simulation of the LSV experiment. 

1st-order reaction of $B^-$

<table>
<thead>
<tr>
<th>$k_2$ ($\text{mol}^{-1} \text{s}^{-1}$)</th>
<th>$k_4$ (s$^{-1}$)</th>
<th>% decrease in $i_{pc}(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>97.357</td>
</tr>
<tr>
<td>400</td>
<td>-28.5</td>
<td>26.1</td>
</tr>
<tr>
<td>5,200</td>
<td>81.3</td>
<td>80.8</td>
</tr>
</tbody>
</table>

$c_A^b = c_B^b = 0.002 \text{M}$

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$

$V = 0.25 \text{Vs}^{-1}$

$k_1 = 97.357 \text{s}^{-1}$

For $k_4 = 0$:

$\Delta E^{0'} = 0.252 \text{V}$

For $k_4 = 97.357 \text{s}^{-1}$:

$\Delta E^{0'} = 0.250 \text{V}$
Table 41: Computer simulation of the LSV experiment: dimerisation of $B^{-}$

<table>
<thead>
<tr>
<th>$k_5$ (1mol$^{-1}$s$^{-1}$)</th>
<th>$k_5c_B^b/a$</th>
<th>$k_2$ (1mol$^{-1}$s$^{-1}$)</th>
<th>% decrease in $i_{pc}(B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
<td>10.1  28.5  81.3</td>
</tr>
<tr>
<td>7.302 x $10^2$</td>
<td>0.150</td>
<td>400</td>
<td>10.1  28.5  81.4</td>
</tr>
<tr>
<td>3.286 x $10^3$</td>
<td>0.675</td>
<td>51,200</td>
<td>10.2  28.8  81.8</td>
</tr>
<tr>
<td>1.704 x $10^4$</td>
<td>3.50</td>
<td></td>
<td>10.1  28.6  82.3</td>
</tr>
<tr>
<td>1.704 x $10^5$</td>
<td>35.0</td>
<td></td>
<td>9.4   27.3  81.9</td>
</tr>
</tbody>
</table>

$c_A^b = c_B^b = 0.002$M

$D_A = D_B = 2 \times 10^{-5}$ cm$^2$s$^{-1}$

$v = 0.25$ Vs$^{-1}$

$k_1 = 97.357$s$^{-1}$

$\Delta E^0' = 0.250$V

(except $\times$ where $\Delta E^0' = 0.252$V)
Table 42: Mass spectra

<table>
<thead>
<tr>
<th>compound</th>
<th>m/e ratio</th>
<th>relative intensity</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>glutaronitrile (mw 94)</td>
<td>54</td>
<td>100</td>
<td>P - 40</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>94</td>
<td>CH₃CN</td>
</tr>
<tr>
<td>adiponitrile (mw 108)</td>
<td>68</td>
<td>68</td>
<td>P - 40</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>52</td>
<td>P + 2</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>100</td>
<td>CH₃CN</td>
</tr>
<tr>
<td>2-methylglutaronitrile (mw 108)</td>
<td>68</td>
<td>100</td>
<td>P - 40</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>95</td>
<td>P + 2</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>100</td>
<td>CH₃CN</td>
</tr>
<tr>
<td>unknown compound A</td>
<td>106</td>
<td>36</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>100</td>
<td>P - 40</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>15</td>
<td>or</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>49</td>
<td>CH₃CN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>or CH₃CN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>or CH₂CH₂CN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(mw 106)</td>
</tr>
<tr>
<td>unknown compound B</td>
<td>84</td>
<td>38</td>
<td>P - 40</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>100</td>
<td>CH₂CH₂CN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>or CH₂CH₂CN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>or CH₂CH₂CN</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(mw 124)</td>
</tr>
</tbody>
</table>
Graph 1: Galvanostatic electrolysis of trans-cinnammitrile in acetonitrile; Run F.

% of initial cinnammitrile
% yield of 3-phenylglutaronitrile

Mercury pool cathode, 50ml 0.1M Et₄NF₄ in acetonitrile purified by NaH/P₂O₅/CaH₂ treatment, initial [PhCH=CHCN] = 20mM, i = 20mA, T = 22.4°C.
Graph 2: Galvanostatic electrolyses of cinnamonic acid (ca. 20mM) in acetonitrile at different currents (descending curves represent loss of PhCH₂CN, ascending curves represent formation of PhCH(C₂CN)₂).

- Run E, i = 80mA
- Run D, i = 40mA
- Run F, i = 20mA
Graph 3: Galvanostatic (40mA) of cinnamonic acid in acetonitrile: effect of cinnamonic acid concentration.
(descending curves represent loss of PhCHCHCN, ascending curves represent formation of PhCH(CH₂CN)₂)

- Run D, [PhCHCHCN] = 20mM
- Run B, [PhCHCHCN] = 42mM
- Run C, [PhCHCHCN] = 81mM
Graph 4: Galvanostatic (20mA) electrolyses of cinnamonic acid in acetonitrile: effect of cinnamonic acid concentration. (descending curves represent loss of PhCHCHCN, ascending curves represent formation of PhOH(CH₂CN)₂)

- ○○ Run 0, [PhCHCHCN] = 10mM
- ×× Run F, [PhCHCHCN] = 20mM
Graph 5: Galvanostatic (20mA) electrolyses of cinnaminitrile (20mM) in acetonitrile:
effect of temperature.

descending curves represent loss of PhCHCHCN, ascending curves represent formation of
PhCH(CH₂CN)₂

- - - - Run F, T = 22-4°C
○○○○ Run G, T = 40-6°C
△△△△ Run P, T = 72-6°C.
Graph 6: Galvanostatic (10mA) electrolysis of cinnamonic acid (10mM) in acetonitrile at 80°C (Run Q).

(descending curve ○○ represents loss of PhCHCHCN,

ascending curve ×× represents formation of PhCH(CH₂CN)₂)
Graph 7: Galvanostatic (20mA) electrolyses of cinnamonic acid (ca. 20mM) in acetonitrile: the effect of water.

(descending curves represent loss of PhCHCHCN, ascending curves represent formation of PhCH(CH₂CN)₂)

- Run F, H₂O ≤ 0.01%
- Run M, H₂O = 0.2%
- Run L, H₂O = 0.25%
Graph 8: Galvanostatic (20mA) electrolyses of cinnamonic acid (ca. 20mM) in acetonitrile using different tetraethylammonium salts.

(descending curves represent loss of PhCHCHCN, ascending curves represent formation of PhCH(CH₂CN)₂)

- Run T, anion = toluene-p-sulphonate
- Run W, anion = iodide
Graph 2: Galvanostatic (20mA) electrolyses of cinnamonic acid (ca. 20mM) in acetonitrile using different tetraalkylammonium fluoroborates.

(descending curves represent loss of PhCHCHCN, ascending curves represent formation of PhCH(CH₂CN)₂)
Graph 10: Product profiles during the galvanostatic (20mA) electrolysis of benzaldehyde (13.6mM) in acetonitrile.

Mercury pool cathode, 50ml 0.1M Et₄NBF₄ in acetonitrile purified by NaH/P₂O₅/CaH₂ treatment, T = 23-4°C.
Graph II: Galvanostatic (10mA) electrolysis of acrylonitrile (ca. 80mM) in acetonitrile (Run 1).

Mercury pool cathode; electrolyte = 30ml 0.1M Et₄NBF₄ in acetonitrile purified by NaH/P₂O₅/CaH₂ treatment.
Graph 12: Galvanostatic (10mA) electrolysis of acrylonitrile (90mM) in acetonitrile at 22-40°C (Run 13).
Graph 13: Galvanostatic (10mA) electrolyses of acrylonitrile (45mM) in acetonitrile at 21-4°C (Run 24) and 34-7°C (Run 23).
Graph 14: Galvanostatic (10mA) electrolyses of acrylonitrile in acetonitrile: Effect of the initial concentration of acrylonitrile on the yield of glutaronitrile.
Graph 15: Galvanostatic electrolyses of \(\alpha,\beta\)-unsaturated nitriles in acetonitrile: Effect of initial concentration of the \(\alpha,\beta\)-unsaturated nitrile on the yield of the corresponding glutaronitrile.

Mercury pool cathode, acetonitrile purified by NaH/P\(_2\)O\(_{5}\)/CaH\(_2\) treatment, \([\text{Et}_4\text{NBF}_4]=0.1\text{M}, T=21-40\text{C},\) electrolyte volume = 50ml.
Graph 16: Galvanostatic (10mA) electrolysis of acrylonitrile (46mM) in acetonitrile using Et$_4$NBF$_4$ (Run 21) and Et$_4$NOTs (Run 22) as supporting electrolytes.
Graph 17: Galvanostatic (10mA) electroyles of acrylonitrile (45mM) in acetonitrile in divided (Run 24) and undivided (Run 19) cells.
Graph 18: The effect of sweep rate on $i_{pc}(1)$ for benzophenone (2mM) in purified acetonitrile on the addition of 2,2'-azopyridine (2mM); HMDE; 0.1M Et$_4$NBF$_4$. 

---

% decrease in $i_{pc}(1)$ (corrected for dilution)
Graph 19: The effect of sweep rate, $v$, on the peak potential, $E_{pc}$, of the 1st reduction peak of trans-cinnamonic alcohol (2mM) in purified acetonitrile: HMDE; 0.1M $\text{Et}_4\text{NBF}_4$

($E_{pc}$ was corrected by subtracting the measured shift in $E_{pc}(1) \{ \text{Ph}_2\text{CO}\}$ for each value of $v$)
Graph 20: Controlled-potential electrolysis of benzenesulphonyl-acetonitrile and acetophenone in DMF.

Material consumed mmol

- PhCOCH$_3$ consumed $\times - \times$, slope = 0.33 mol F$^{-1}$
- PhSO$_2$CH$_2$CN consumed $\circ - \circ$, slope = 0.68 mol F$^{-1}$
- (PhCOCH$_3$ + PhSO$_2$CH$_2$CN) consumed $\triangle - \triangle$, slope = 1.01 mol F$^{-1}$

Initial quantities: 1.92 mmol PhCOCH$_3$
3.82 mmol PhSO$_2$CH$_2$CN

Conditions: 50 ml 0.1M Et$_4$NBF$_4$ in dry DMF, 3m1 mercury pool cathode; Ag/0.1M AgNO$_3$ reference
Graph 21: Galvanostatic (50mA) electrolysis of benzenesulphonyl-acetonitrile and acetophenone in DMF

Initial quantities: 0.810 mmol PhCOCH₃
0.808 mmol PhSO₂CH₂CN

Conditions: 50ml 0.1M Et₄NBF₄ in dry DMF; 3ml mercury pool cathode; Ag/0.1M AgNO₃ reference
Graph 22: Controlled potential (-2.1V) electrolysis of benzene-sulphonylacetonitrile and acrylonitrile in DMF.

Graph of mm vs. m Faraday

- PhSO₂CH₂CN (Δ--Δ)
- Glutaronitrile (---)
- Acrylonitrile (×--×)
- Adiponitrile (+-+)

Initial quantities:
- 3.82 mmol PhSO₂CH₂CN
- 1.94 mmol CH₂=CHCN

Conditions:
- 50 ml 0.1M Et₄NBF₄ in dry DMF
- 3 ml mercury pool cathode
- Ag/o.1M AgNO₃ reference
Graph 23: Controlled potential (-1.8V) electrolysis of benzene-sulphonylacetonitrile and acrylonitrile in DMF.

- PhSO₂CH₂CN
- Glutaronitrile
- Acrylonitrile
- Adiponitrile
- Acetonitrile
- Propionitrile

Initial quantities: 3.82mmol PhSO₂CH₂CN
1.92mmol CH₂=CHCN

Conditions: 50ml 0.1M Et₄NBF₄ in dry DMF
3ml mercury pool cathode
Ag/0.1M AgNO₃ reference
Graph 24: Addition of benzene sulphonylacetoneitrile (4mM) to various electroactive species (2mM) in DMF

% decrease in ipc (corrected for dilution)

acetophenone □
propio phenone •
iso propyl phenyl ketone △
t-butyl phenyl ketone +
acrylonitrile ★
acetyl mesitylene ◆
trans-stilbene ×

HMDE; 0.1M Et_4NBF_4 in DMF
(+1% H_2O  ●)
Graph 25: Comparison of the LSV results for the addition of benzenesulphonylacetonitrile to acrylonitrile in DMF with working curves derived from the simulation study

\[
\frac{k_2}{1 \text{ mol}^{-1}\text{s}^{-1}}
\]

% decrease in \(i_{oc}\)
(coefficient for dilution)

\[\Gamma/s\]

Acrylonitrile(1.9mM) + benzenesulphonylacetonitrile(1.9mM) in 0.1M Et\(_4\)NBF\(_4\) in DMF; HMDE
Graph 26: Effect of sweep rate on the 1st reduction peak height, \( i_{pc}(1) \), of propiophenone (\( \times \times \)) or acetylmesitylene (\( \circ \circ \)) (each 2mM in DMF) on the addition of benzenesulphonylacetonitrile (4mM): HMDE; 0.1M Et_4NBF_4
Graph 27: Comparison of simulation data (x) to Nicholson and Shain's results\textsuperscript{127} (o) for an EC process (reversible electron transfer, irreversible chemical reaction)
Graph 28: The relationship between $\overline{x}$ and $\overline{y}$ for two values of the constants $L$ and $m$

\[
l = m = 0.20 \quad (---)
\]
\[
l = m = 0.03 \quad (-----)
\]

\[
y = \overline{f}(
\overline{x}) = \frac{1}{m} - \frac{1}{m + \overline{x}}
\]

\[
\overline{y} = \frac{y}{y_{\text{max}}}
\]
Graph 29: Simulation results: effect of $k_1$ on % decrease in $i_{pcB}$

% decrease in $i_{pcB}$

$k_2 = 51,200 \text{ mol}^{-1}\text{s}^{-1}$

$k_2 = 1,600 \text{ mol}^{-1}\text{s}^{-1}$

$c_A^b = c_B^b = 0.002\text{M}$

$D_A = D_B = 2 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$

$\Delta E^{\circ} = 0.25\text{V}$

$V = 0.25\text{Vs}^{-1}$
Graph 30: Simulation results: effect of $k_2$ on % decrease in $i_{pc}(B)$; $c_A^b = c_B^b = 0.002M$;

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$; $\Delta E^o = 0.252V$; $v = 0.25 \text{Vs}^{-1}$

% decrease in $i_{pc}(B)$

$10^{-4} \times k_2/\text{1 mol}^{-1} \text{s}^{-1}$

$k_1$ $s^{-1}$

97.357

0.487
Graph 31: Simulation results: effect of $k_2$ on % decrease in $i_{pc}(B)$

$c_A = c_B = 0.002$ M
$D_A = D_B = 2 \times 10^{-5}$ cm$^2$s$^{-1}$
$E^{\circ'} = 0.252$ V
$\Delta v = 0.25$ V$s^{-1}$
$k_1 = 97.357$s$^{-1}$
Graph 32: Simulation results: effect of $\Delta E^o'$ on the decrease in $i_{pc}(B)$

- $k_2 = \frac{1}{1 \text{ mol}\cdot\text{l}^{-1}\cdot\text{s}^{-1}}$
- $51200$
- $10000$
- $1600$
- $400$
- $100$

% decrease in $i_{pc}(B)$ vs $\Delta E^o'/V$

- $c_A^b = c_B^b = 0.002$ M
- $D_A = D_B = 2 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$
- $v = 0.25 \text{ vs}^{-1}$
- $k_1 = 0.487 \text{ s}^{-1}$
Graph 33: Simulation results: effect of $\Delta E^0$ on the decrease in $i_{pc}(B)$.

\[ \frac{k_2}{1 \text{ mol}^{-1}\text{s}^{-1}} \]

\[
\begin{array}{c}
\begin{align*}
51200 & \\
10000 & \\
1600 & \\
400 & \\
100 &
\end{align*}
\end{array}
\]

% decrease in $i_{pc}(B)$

$\frac{\Delta E^0}{V}$

$c_A = c_B = 0.002 \text{M}$

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2\text{s}^{-1}$

$V = 0.25 \text{Vs}^{-1}$

$k_- = 4.867 \text{s}^{-1}$
Graph 3: Simulation results: effect of $\Delta E^0'$ on the decrease in $i_{pc}(B)$. 

$k_2 = \frac{1}{1 \text{ mol}^{-1}\text{s}^{-1}}$ 

$k_1 = 0.487 \text{s}^{-1}$ 

$c_A^0 = c_B^0 = 0.002 \text{V}$ 

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2\text{s}^{-1}$ 

$\nu = 0.20 \text{Vs}^{-1}$ 

$\Delta E^0' / \nu$ 

% decrease in $i_{pc}(B)$
Graph 35: Simulation results: effect of $\Delta E^0'$ on the decrease in $i_{pc}(B)$.

- $k_2 = \frac{51200}{l \text{ mol}^{-1} \text{s}^{-1}}$
- $10000$
- $1600$
- $400$
- $100$

% decrease in $i_{pc}(B)$

$\frac{\Delta E^0'}{V}$

$c_A^0 = c_B^0 = 0.002 M$

$D_A = D_B = 2 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$

$V = 0.20 \text{Vs}^{-1}$

$k_1 = 4.667 \text{s}^{-1}$
Graph 36: Simulation results: working curves for $v = 0.25 \text{Vs}^{-1}$

$\left( c_{A}^{b} = c_{B}^{b} = 0.002 \text{M}, D_{A} = D_{B} = 2 \times 10^{-5} \text{cm}^{2} \text{s}^{-1} \right)$

% decrease in \( \frac{1}{p_{c}^{b}}(B) \)

$\log_{10}(k_{2}/ \text{mol}^{-1} \text{s}^{-1})$

\( \Delta_{E_{o}}^{\prime} \)

- $k_{1} = 4.868 \text{s}^{-1}$
- $k_{1} = 0.487 \text{s}^{-1}$
Graph 37: Simulation results: working curves for $v = 0.20 \text{Vs}^{-1}$

$c_A^b = c_B^b = 0.002 \text{M}$, $D_A = D_B = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$

$\frac{\Delta E^{0'}}{v}$

$k_1 = 4.868 \text{s}^{-1}$

$k_1 = 0.487 \text{s}^{-1}$

$\log_{10}(k_2/1 \text{ mol}^{-1} \text{s}^{-1})
\[
\begin{align*}
\tau &= 97.35 \pm 1 \\
\Delta &= 0.04 \\
D &= 2 \times 10^{-5} \\
N &= 0.02 M
\end{align*}
\]

Graph 38: Simulation results: effect of \( \Delta \) on \( \% \) decrease in \( \bar{p}_c(B) \)
Graph 39: Working curves for the estimation of $k_2$.

\[ \frac{k_2}{1 \text{ mol}^{-1}\text{s}^{-1}} \]

\[ \begin{align*}
51200 \\
25600 \\
10000 \\
4000 \\
2000 \\
1200 \\
800 \\
400 \\
200 \\
100
\end{align*} \]

% decrease in $i_0$ (A)

\[ \Gamma / s \]

$c_A = c_B = 0.002 \text{M}$.

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2\text{s}^{-1}$

$k_1 = 97.357\text{s}^{-1}$
Graph 40: Simulation results: effect of $k_2$ on $E_{pc}(B)$

$\left[ E^0(B) - E_{pc}(B) \right] / \text{mV}$

$\log_{10}(k_2/1 \text{ mol}^{-1} \text{s}^{-1})$

$c_A^b = c_B^b = 0.002\text{M}$

$D_A = D_B = 2 \times 10^{-5} \text{cm}^2\text{s}^{-1}$

$v = 0.25\text{vs}^{-1}$

$\Delta E^0' = 0.50\text{V}$

$k_1 = 97.357\text{s}^{-1}$
Graph 41: Simulation results: effect of \( v \) on \( E_{pc}(B) \)

\[
[\Delta E^o(B) - E_{pc}(B)] / \text{mV}
\]

\[
\frac{k_2}{1 \text{ mol}^{-1}\text{s}^{-1}}
\]

- 51200
- 25600
- 10000
- 800
- 400
- 400
- 200

\[
\frac{v}{v_s^{-1}}
\]

- \( c_A^b = c_B^b = 0.002M \)
- \( D_A = D_B = 2 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \)
- \( \Delta E^{o'} = 0.40 \text{V} \)
- \( k_1 = 97.357 \text{s}^{-1} \)
Figure 1: Cyclic voltammetry (cv) of

a) benzophenone and b) trans-cinnaminitrile

conditions: 0.1M Et$_4$NBF$_4$ in acetonitrile dried by CaH$_2$/P$_2$O$_5$/CaH$_2$

substrate concentration = 2mM; v = 0.23Vs$^{-1}$; HMDE; Ag/0.1M AgNO$_3$ reference.

a)
Figure 2: CV of 4,4'-azopyridine (2mM) in purified acetonitrile

Conditions: 0.1M Et$_4$NBF$_4$ in acetonitrile purified by NaH/P$_2$O$_5$/CaH$_2$ treatment; $v = 0.25$V$s^{-1}$; HDME; Ag/0.1M AgNO$_3$ reference.
Figure 3: CV of 4-phenylazopyridine (2mM) in purified acetonitrile.

Conditions: 0.1M Et$_4$NBF$_4$ in acetonitrile purified by NaH/P$_2$O$_5$/CaH$_2$ treatment; v = 0.20V s$^{-1}$; HMDE; Ag/0.1M AgNO$_3$ reference.
conditions: 0.1M Et₄NBF₄ in acetonitrile purified by NaH/P₂O₅/CaH₂ treatment; v = 0.20Vs⁻¹; HMDE; Ag/0.1M AgNO₃ reference.
Figure 5: CV of benzaldehyde (2mM) in purified acetonitrile

conditions: \( v = 0.25 \text{Vs}^{-1} \)

HMDE

Ag/0.1M AgNO\(_3\) reference

0.1M Et\(_4\)NB\(_4\) in acetonitrile

purified by NaH/P\(_2\)O\(_5\)/CaH\(_2\) treatment
Figure 6: Cyclic voltammetry (CV) of azobenzene (1 mM) in super-dry DMF; addition of ethyl phenylacetate.

Conditions: active neutral alumina suspension; 0.1 M Et$_4$NBF$_4$; T = -6 to -10 °C; v = 0.227 V s$^{-1}$; PDE; Ag wire reference.

[ethyl phenylacetate] = 0 mM (-----), 1.3 mM (------), 2.6 mM (-----).
Figure 7: Cyclic voltammetry (1 mM) in super-dry DMF; addition of ethyl acetate.

Conditions: active neutral alumina suspension; 0.1M Et₄NBF₄; room temperature; \( v = 0.227 \text{Vs}^{-1} \); PDE; Ag wire reference;

\( [\text{EtOAc}] = 0 \text{vol\%} \) (---)

2.5 vol\% (-----)
Figure 8: Cyclic voltammetry of azobenzene (1mM) in super-dry DMF: addition of distilled water.

Conditions: activated alumina suspension; T = -5 to -15°C; PDE; Ag wire reference;

- Potential 
(lcm = 0.1V)

0.1M Et₄NBF₄; ν = 0.227Vs⁻¹;

absence of water (-----); + a few drops of distilled water (----).
Figure 9: Cyclic voltammetry of azobenzene (2 mM) in super-dry DMF: addition of purified acetonitrile.

Conditions: activated alumina suspension; 0.1 M Et₄NBF₄; T = 5°C; FDE; Ag wire reference; v = 0.227 V s⁻¹;

[acetonitrile] = 0 mM (---), 2.5 mM (----), 168 mM (=1.0 vol%) (-----).
Figure 10: Cyclic voltammetry of azobenzene (1mM) in DMF.

Conditions: 0.1M Et$_4$NBF$_4$; room temperature; HMDE; Ag wire reference;

\[ \nu = 1.0 \text{Vs}^{-1} (---), 0.111 \text{Vs}^{-1} (~-~). \]

[Different Y-scales are used for each cyclic voltammogram]
Figure 11: Cv of azobenzene (1mM) in DMF

conditions: 0.1M Et₄NBF₄ in DMF which had been dried over 5Å molecular sieve; room temperature; PDE; Ag wire reference; \( v = 0.30 \text{Vs}^{-1} \);
before addition of activated alumina (---)
after addition of activated alumina (-----)
Figure 12: Cyclic voltammetry (1 mM) in purified acetonitrile.

Conditions: 0.1M Et$_4$NBF$_4$; HMDE; Ag wire reference; room temperature.

Potential range: 1 cm = 0.1 V

Current density: $y = 1.0 \text{Vs}^{-1}$

Current density: $y = 0.227 \text{Vs}^{-1}$

Current density: $y = 0.054 \text{Vs}^{-1}$ (different Y-scale)
Figure 13: Cyclic voltammetry of 2,2'-azopyridine (1mM) in super-dry DMF.

Conditions: activated alumina suspension; 0.1M Et₄NBF₄; HMDE; Ag wire reference; v = 0.227Vs⁻¹

a) T = 22°C; [acetonitrile] = 0mM

- Potential
(1cm = 0.1V)

T = 2-5°C; b) [acetonitrile] = 0mM (- - - -)
c) [acetonitrile] = 0.9mM (- - - -)
Figure 14: CV of 2,2'-azopyridine (1mM) in super-dry DMF containing ethyl phenylacetate (0.25vol%).

- Potential

(1cm = 0.1V)

conditions: activated alumina suspension; PFE;
Ag wire reference; v = 0.227Vs⁻¹;
T = 0°C (---), -50°C (-----)
conditions: 0.1M Et₄NBF₄; HMDE; Ag/0.1M AgNO₃ reference;

v = a) 1.0Vs⁻¹  b) 0.3Vs⁻¹  c) 0.1Vs⁻¹

the sensitivity of the current axis in

a) is 0.25 times that in (b) and (c)
Figure 16: Simulated cyclic voltammograms for an EC process involving a reversible 1-electron transfer and an irreversible chemical reaction

\[
\begin{align*}
\text{C} &= 0.002 \text{M} \\
D &= 2 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \\
\Delta E^0 &= -2.75 \text{ V} \\

v &= 0.25 \text{ V s}^{-1}
\end{align*}
\]

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<th></th>
<th>(k_1)</th>
<th>(k_1/a)</th>
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<tr>
<td>a</td>
<td>0.487</td>
<td>0.05</td>
</tr>
<tr>
<td>b</td>
<td>1.947</td>
<td>0.20</td>
</tr>
<tr>
<td>c</td>
<td>4.868</td>
<td>0.50</td>
</tr>
<tr>
<td>d</td>
<td>9.736</td>
<td>1.00</td>
</tr>
<tr>
<td>e</td>
<td>97.357</td>
<td>10.00</td>
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Figure 17: Simulated cyclic voltammograms for an EEC process involving reversible 1-electron transfers and an irreversible chemical reaction

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<th>$k_1/a$</th>
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<tr>
<td>b)</td>
<td>1.947</td>
<td>0.20</td>
</tr>
<tr>
<td>c)</td>
<td>4.868</td>
<td>0.50</td>
</tr>
<tr>
<td>d)</td>
<td>97.357</td>
<td>10.00</td>
</tr>
</tbody>
</table>

$c^b = 0.002M$

$D = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

$E^{o}(1) = -1.20V$

$E^{o}(2) = -1.65V$

$v = 0.25 \text{Vs}^{-1}$
Figure 18: Preparative electrolysis cell

a: port for addition of material and removal of samples
b: reference electrode (R.E.)
c: platinum wire contact
d: anodic compartment
e: carbon rod secondary electrode (S.E.)
f: glass frit divider
g: water jacket
h: magnetic stirrer bar
i: mercury pool working electrode (W.E.)
Figure 19: Electroanalytical cell

a: port for sample addition
b: reference electrode (R.E.)
c: platinum foil secondary electrode (S.E.)
d: magnetic stirrer bar
e: working microelectrode (W.E.)
Figure 20: Current vs. potential (a) and current vs. time (b) curves for benzophenone in purified acetonitrile; HMDE; 0.1M Et₄NBF₄; v = 0.25Vs⁻¹
Benzophenone (2mM) and 4,4'-azopyridine (2mM) in purified acetonitrile containing 0.1M Et$_4$NB$_4$; HMDE; $v = 0.25 V s^{-1}$; Ag/0.1M AgNO$_3$ reference
Degassing and stirring of the electrolyte solution was carried out by blowing $N_2$ down tube c. The cell solution could be transferred to the drying tower through tube c by forcing $N_2$ into the top of the electrolysis cell.
Figure 23: $^1$H nmr spectrum (CDCl$_3$, 600 MHz) of 3-phenylpropionitrile
Appendix 1: Mathematical description of the model system in Chapter 3.

Scheme 1.

(1) \[ \frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} \]

(2) \[ \frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - k_1 c_A \]

(3) \[ \frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - k_2 c_B c_Z \]

(4) \[ \frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} \]

(5) \[ \frac{\partial c_Z}{\partial t} = D_Z \frac{\partial^2 c_Z}{\partial x^2} - k_2 c_B c_Z + k_1 c_A \]

Boundary conditions:

a) \[ t = 0; \quad c_A(x,0) = c^0_A, \quad c_B(x,0) = c^0_B \]

\[ c_A(x,0) = c_B(x,0) = 0 \]

b) \[ t > 0, \quad x \to \infty, \quad c_A(x,t) = c^b_A, \quad c_B(x,t) = c^b_B \]

\[ c_A(x,t) = c_B(x,t) = c(x,t) = 0 \]

c) \[ t > 0, \quad x = 0; \]

(6) \[ \frac{c_A(0,t)}{c_A(0,t)} = \exp \left\{ \frac{nF}{RT} \left[ E_t - E^0(A) \right] \right\} \]
(7) \[ \frac{c_B(0,t)}{c_B^0(0,t)} = \exp\left\{ \frac{nF}{RT} [E_t - E^0(B)] \right\} \]

(8) \[ D_A \frac{\partial c_A}{\partial x} \bigg|_{x=0} = - D_A \frac{\partial c_A}{\partial x} \bigg|_{x=0} \]

(9) \[ D_B \frac{\partial c_B}{\partial x} \bigg|_{x=0} = - D_B \frac{\partial c_B}{\partial x} \bigg|_{x=0} \]

(10) \[ D_Z \frac{\partial c_Z}{\partial x} \bigg|_{x=0} = 0 \]
### Appendix 2: Definition of symbols used in Chapter 3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>( a )</td>
<td>( a = \frac{nFv}{RT} )</td>
<td>( \text{s}^{-1} )</td>
</tr>
<tr>
<td>( c_i(x,t) )</td>
<td>concentration of species ( i ) at distance ( x ) from electrode surface at time ( t )</td>
<td>( \text{mol} \ \text{l}^{-1} )</td>
</tr>
<tr>
<td>( c_i^b )</td>
<td>bulk concentration of species ( i )</td>
<td>( \text{mol} \ \text{l}^{-1} )</td>
</tr>
<tr>
<td>( D_i )</td>
<td>diffusion coefficient of species ( i )</td>
<td>( \text{cm}^2 \ \text{s}^{-1} )</td>
</tr>
<tr>
<td>( \delta )</td>
<td>diffusion layer thickness</td>
<td>( \text{cm} )</td>
</tr>
<tr>
<td>( E^0(i) )</td>
<td>standard potential of species ( i )</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>( E_i )</td>
<td>electrode potential at time ( t=0 )</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>( E_t )</td>
<td>electrode potential at time ( t )</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>( E^\lambda )</td>
<td>electrode potential at which the direction of the potential sweep is reversed</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>( \Delta E^0' )</td>
<td>( E^0(A) - E^0(B) )</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>( E_p(i) )</td>
<td>electrode potential at which a current maximum for species ( i ) occurs: additional subscripts 'a' or 'c'</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>symbol</td>
<td>definition</td>
<td>units</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>-------</td>
</tr>
<tr>
<td>F</td>
<td>Faraday's constant</td>
<td>C mol(^{-1})</td>
</tr>
<tr>
<td>(i_i)</td>
<td>current due to species i; subscript 'p' denotes current maximum; subscripts 'a' or 'c' denote oxidation or reduction currents respectively</td>
<td>A cm(^{-2})</td>
</tr>
<tr>
<td>(k_1)</td>
<td>1st-order rate constant for (A^- \rightarrow Z)</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>(k_2)</td>
<td>2nd-order rate constant for (B + Z \rightarrow Y)</td>
<td>1 mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td>(k_3)</td>
<td>1st-order rate constant for (Y \rightarrow Z)</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>(k_4)</td>
<td>1st-order rate constant for (B^- \rightarrow YY)</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>(k_5)</td>
<td>2nd-order rate constant for dimerisation of (B^-): (2B^- \rightarrow B_2)</td>
<td>1 mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td>(l, m)</td>
<td>constants used in the function (f(\lambda))</td>
<td></td>
</tr>
<tr>
<td>symbol</td>
<td>definition</td>
<td>unit</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>time at which the direction of the potential sweep is reversed</td>
<td>s</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>elapsed time between $E^0(A)$ and $E^0(B)$: $\Gamma = \Delta E^0/v$</td>
<td>s</td>
</tr>
<tr>
<td>$t$</td>
<td>time from the initiation of the experiment</td>
<td>s</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>incremental time interval</td>
<td>s</td>
</tr>
<tr>
<td>$\tau$</td>
<td>time taken between $E^0$ and $E_{\lambda}$</td>
<td>s</td>
</tr>
<tr>
<td>$v$</td>
<td>potential sweep rate</td>
<td>$Vs^{-1}$</td>
</tr>
<tr>
<td>$x$</td>
<td>distance from the electrode surface</td>
<td>cm</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>incremental distance interval</td>
<td>cm</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>normalised distance from the electrode surface, $\bar{x} = x/\delta$</td>
<td></td>
</tr>
<tr>
<td>$y$</td>
<td>transformed distance from the electrode surface, $y = f(\bar{x})$</td>
<td></td>
</tr>
<tr>
<td>$\bar{y}$</td>
<td>normalised, transformed distance from the electrode surface, $\bar{y} = y/y_{\text{max}}$</td>
<td></td>
</tr>
</tbody>
</table>
Appendix 3: Program EGB1

IMPLICIT REAL*8(A-H.O-Z)
REAL*8 K1,K2
DIMENSION Z(120),A(120),B(120),AM(120),BM(120)
AREA=1.00
F=9.6487D4
R=6.314300
T=298.00

C....INPUT DATA.
READ(5,10) EI,EF,ERATE
READ(5,10) EA,EGB
READ(5,10) CA,CB,DTHICK,DA,DB
READ(5,11) K1,K2
READ(5,11) NT,NR
10 FORMAT(3F10.1,2D8.1)
11 FORMAT(2I4)
C.....CALCULATE THE GRID PARAMETERS.
17 SCAN TIME.
TIME=(EI-EF)/ERATE
C....TIME INCREMENT.
DT=TIME/DFLOAT(NT-1)
C.....RADIAL INCREMENT.
DR=DTHICK/DFLOAT(NR-1)
C....PARAMETERS EMPLOYED IN THE INTEGRATION.
P1=DT*OA/DR**2
P2=DT*DB/DR**2
G1=K1*DT
G2=K2*DT

C.....OUTPUT THE DATA FOR REFERENCE.
WRITE(6,12) EI,EF,ERATE
12 FORMAT(' POTENTIAL RANGE',2F7.3,' RATE',F7.3,'V/S LAG=6')
WRITE(6,13) CA,EA,DA,CB,EGB,DB
13 FORMAT(' CA=',F8.4,' EA=',F7.3,' DA=',D10.3,/
' CB=',F8.4,' EGB=',F7.3,' DB=',D10.3)
WRITE(6,20) DTHICK
20 FORMAT(' DIFFUSION THICKNESS',F8.4)
WRITE(6,14) K1,K2
14 FORMAT(' RATE CONSTANT AM->Z',F8.3,' AS',/
' SEC ORDER B+Z->Y',F12.3,' L/MOLE/S')
WRITE(6,15) NT,NR,P1,P2,G1,G2
15 FORMAT(' PARAMETER VALUES', NT, NR, P1, P2, G1 AND G2',/
'1215',4F8.4)

C.....initialise the RUN.
DO 1 I=1,NT
A(I)=CA
B(I)=CB
AM(I)=0.00
BM(I)=0.00
Z(I)=0.00
1
C.....compute the POTENTIAL INCREMENT IN TIME DT.
DELE=DT*ERATE
C.....START SCANING THROUGH THE POTENTIAL RANGE.
EPOT=EI
NTH=NT-1
CONST=F/R/T
C1=0.00
FACT=1.00
WRITE(6,16) EPOT,C1,C1,C1
16 FORMAT(' E APPLIED',4X,'A CURRENT',5X,/
'1\' CURRENT',6X,'TOTAL',/F12.8,3D14.6)
WRITE(6,17) EPOT+DELE
17 FORMAT(F12.8,3D14.6)
DO 2 I=1,NTH
2 EPOT=EPOT+DELE

C......IMPOSE THE BOUNDARY CONDITIONS IN THE REGION FAR FROM C......THE ELECTRODE SURFACE.

A(NR)=CA
B(NR)=CB
AM(NR)=0.DO
BM(NR)=0.DO
Z(NR)=0.DO
M=NR
N=NR+1
A2=A(N)
A1=A(N)
B2=B(N)
B1=B(N)
AM2=AM(N)
AM1=AM(N)
BM2=BM(N)
BM1=BM(N)
Z2=Z(N)
Z1=Z(N)
C......NOW SWEEP DOWN TO ELECTRODE SURFACE.

DO 3 J=2,N
M=M-1
MM=M-1
A0=A(MM)
B0=B(MM)
AM=AM(MM)
BM=BM(MM)
Z0=Z(MM)
GA=DELB1(A2,A1,A0,P1)
GB=DELB1(B2,B1,B0,P2)
GAM=DELB1(AM2,AM1,AM0,P1)
GBM=DELB1(BM2,BM1,BM0,P2)
GZ=DELB1(Z2,Z1,Z0,P1)
A(M)=A2+GA
B(M)=B2+GB-GBK
Z(M)=Z2+GZ-BZK+Q1*AM2
AM(M)=AM2+GA-M-Q1*AM2
BM(M)=BM2+GBM
3 CONTINUE

C......NOW IMPOSE THE BOUNDARY CONDITIONS APPROPRIATE TO C......THE ELECTRODE SURFACE. FOR THIS PROGRAM, WE HAVE C......ASSUMED REVERSIBLE REDUCTION. IT SHOULD BE TRIVIAL C......TO GENERALISE TO OTHER CASES.

RAT1=DEXP(CONST*(EPOT-EOA))
RAT2=DEXP(CONST*(EPOT-EOB))
BB=A(2)+AM(2)
CC=A(3)+AM(3)
DD=A(4)+AM(4)
EE=A(5)+AM(5)
FF=A(6)+AM(6)
AM1=600.DO*(BB-CC)+400.DO*DD-150.DO*EE+24.DO*FF
AM(1)=AM1/274.DO/(1.DO+RAT1)
A(1)=RAT1*AM(1)
BB=B(2)+BM(2)
CC=B(3)+BM(3)
DD=B(4)+BM(4)
EE=B(5)+BM(5)
FF=B(6)+BM(6)
BM1=600.DO*(BB-CC)+400.DO*DD-150.DO*EE+24.DO*FF
BM(1)=BM1/274.DO/(1.DO+RAT2)
B(1)=RAT2*BM(1)
C......FOR THE SPECIES Z, PUT DZ/DX=0 AT ELECTRODE.

Z(1)=600.DO*(Z(2)-Z(3))+400.DO*Z(4)-150.DO*Z(5)+24.DO*Z
I
(6)

129  Z(1)=Z(1)/274.DO

130  C.....NOW CALCULATE THE CURRENT.

131  BB=274.DO*A(1)+600.DO*(A(2)-A(3))+400.DO*A(4)-

132  1 150.DO*A(5)+24.DO*A(6)

133  BB=BB/(120.DO*DR)

134  CURRI=F*AREA*BB

135  CC=DB*(-274.DO*B(1)+600.DO*(B(2)-B(3))+400.DO*B(4)

136  1-150.DO*B(5)+24.DO*B(6))/(120.DO*DR)

137  CURR2=F*AREA*CC

138  CURR=CURR1+CURR2

139  WRITE(6,17) EPOT,CURR1,CURR2,CURR

140  C.....CHECK THAT THE SOLUTION IS NOT OSCILLATING.

141  IF(FACT*CURR.LT.0.DO) GOTO 18

142  FACT=CURR

143  2 CONTINUE

144  STOP

145  18 WRITE(6,19)

146  19 FORMAT(‘ CURRENT IS OSCILLATING, CHECK PARAMETERS’) 

147  STOP

148  END

149  C

G

150  REAL FUNCTION DELB1*8(A2,A1,A0,P1)

151  IMPLICIT REAL*8(A-H,O-Z)

152  C.....THIS FUNCTION SUPPLIES PART OF THE SECOND

153  C.....DERIVATIVE. IT ALSO SETS UP THE A'S FOR THE NEXT RUN.

154  DELB1=P1*(A2-2.DO*A1+A0)

155  A2=A1

156  A1=A0

157  RETURN

158  END
Appendix 4: Modifications to program EGB1

a) to simulate cyclic voltammograms:
After line 53, insert " NTP=2xNTM ".
Instead of line 61, insert " DO 2 I=1,NTP IF(I-NT)200,100,200 100 DELE=-DELE 200 CONTINUE ".
Instead of lines 141 and 142, insert
" IF(DABS(CURR).GT.20.D0) GOTO 18 ".

b) to obtain program EGB4:
After line 2, insert " REALx4 Y ".
After line 27, insert " Y=FLOAT(NR-1)/SQRT(FLOAT(NT-1)) ".
After line 64, insert
" NX=INT(SQRT(FLOAT(I))xY)+1 IF(NX-10) 58,58,60 58 NX=10 60 CONTINUE ".
Replace "NR" by "NX" in lines 65-71.

c) to obtain regeneration of species Z:
Replace lines 2 and 3 with
" REALx8 K1,K2,K3 DIMENSION Z(120),A(120),B(120),AM(120),BM(120),Y(120) ".
Replace line 12 with " READ(5,10) K1,K2,K3 ".
After line 27, insert " Q3=K3xDT ".
Instead of line 38, insert
" 1' SECOND ORDER B+Z- Y',FL2.3,' L/MOLE/S',/ 2'REGENERATION CONST Y Z',FL2.3,'/S') ".
After line 47, insert "Y(I)=0.DO ".
After line 68, insert "Y(NR)=0.DO ".
After line 79, insert "Y2=Y(M)
Y1=Y(N) ".
After line 89, insert "Y0=Y(MM) ".
After line 94, insert "GY=DELB1(Y2,Y1,Y0,P1) ".
Instead of line 99, insert
"Y(M)=Y2+GY+BZK-Q3XY2
Z(M)=Z2+GZ-BZK+Q1xAM2-Q3XY2

After line 126, insert
"C.....FOR THE SPECIES Y, PUT DY/DX=0 AT ELECTRODE.
Y(1)=600.DOx(Y(2)-Y(3))+400.DOxY(4)-150.DOxY(5)+24.DOxY(6)
Y(1)=Y(1)/274.DO"

d) to include a 1st-order reaction of species B:
Replace line 2 with "REALx8 K1,K2,K4 ".
Replace line 12 with "READ(5,10) K1,K2,K4 ".
After line 27, insert "Q4=K4xDT ".
Modify lines 36-41 appropriately.
Replace line 101 with "BM(M)=BM2+GBM-Q4xBM2 ".
e) to include dimerisation of species B:
Carry out all but the last of the modifications described in (d) except that "K5" and "Q5" should be used instead of "K4" and "Q4".
Replace line 101 with "BM(N)=BM2+GBM-Q5xBM2xx2 ". 

### Appendix 5: Definition of important computer program variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>definition</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(I), B(I), Z(I)</td>
<td>concentration of species A, or B, or Z at distance point I</td>
<td>mol l(^{-1})</td>
</tr>
<tr>
<td>AM(I), BM(I)</td>
<td>concentration of species A(^{-}), or B(^{-}), at distance point I</td>
<td>mol l(^{-1})</td>
</tr>
<tr>
<td>AREA</td>
<td>electrode area</td>
<td>cm(^2)</td>
</tr>
<tr>
<td>CA, CB</td>
<td>bulk concentration of species A or B</td>
<td>mol l(^{-1})</td>
</tr>
<tr>
<td>CURR1</td>
<td>current due to species A/A(^{-})</td>
<td>A cm(^{-2})</td>
</tr>
<tr>
<td>CURR2</td>
<td>current due to species B/B(^{-})</td>
<td>A cm(^{-2})</td>
</tr>
<tr>
<td>CURR</td>
<td>total current due to species A/A(^{-}) and B/B(^{-})</td>
<td>A cm(^{-2})</td>
</tr>
<tr>
<td>DA, DB</td>
<td>diffusion coefficient of species A, or B</td>
<td>cm(^2) s(^{-1})</td>
</tr>
<tr>
<td>DELB1</td>
<td>real function which performs the function:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( c_i(x,t + \Delta t) - c_i(x,t) = )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{D_i \Delta t}{(\Delta x)^2} \left[ c_i(x + \Delta x,t) - 2c_i(x,t) + c_i(x - \Delta x,t) \right] )</td>
<td></td>
</tr>
<tr>
<td>DELB3</td>
<td>real function which performs the calculation in Equation 30</td>
<td></td>
</tr>
<tr>
<td>DEIE</td>
<td>potential increment in time DT</td>
<td>V</td>
</tr>
<tr>
<td>DR</td>
<td>incremental distance interval</td>
<td>cm</td>
</tr>
<tr>
<td>DRY</td>
<td>incremental transformed-distance interval</td>
<td></td>
</tr>
<tr>
<td>variable</td>
<td>definition</td>
<td>units</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>DT</td>
<td>incremental time interval</td>
<td>s</td>
</tr>
<tr>
<td>DTHICK</td>
<td>diffusion layer thickness</td>
<td>cm</td>
</tr>
<tr>
<td>EF</td>
<td>final potential</td>
<td>V</td>
</tr>
<tr>
<td>EI</td>
<td>initial potential</td>
<td>V</td>
</tr>
<tr>
<td>EOA, EOB</td>
<td>standard potential of species A, or B</td>
<td>V</td>
</tr>
<tr>
<td>EPOT</td>
<td>applied potential</td>
<td>V</td>
</tr>
<tr>
<td>ERATE</td>
<td>potential sweep rate</td>
<td>Vs⁻¹</td>
</tr>
<tr>
<td>F</td>
<td>Faraday's constant</td>
<td>C mol⁻¹</td>
</tr>
<tr>
<td>FF(J)</td>
<td>the value of the function dy/dx at the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>transformed-distance point J</td>
<td></td>
</tr>
<tr>
<td>HA, HB</td>
<td>constants used in the function f(x)</td>
<td></td>
</tr>
<tr>
<td>K1, K3, K4</td>
<td>1st-order rate constants k₁, k₂, k₄</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>K2, K5</td>
<td>2nd-order rate constants k₂, k₅</td>
<td>l mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>NR</td>
<td>in EGB1: number of distance points</td>
<td></td>
</tr>
<tr>
<td></td>
<td>in EGB4: maximum number of distance points</td>
<td></td>
</tr>
<tr>
<td>NT</td>
<td>number of time points</td>
<td></td>
</tr>
<tr>
<td>NX</td>
<td>variable number of distance points</td>
<td></td>
</tr>
<tr>
<td>NYMAX</td>
<td>the number of transformed-distance points</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>gas constant</td>
<td>J⁰ K⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>variable</td>
<td>definition</td>
<td>units</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>RAT1, RAT2</td>
<td>Nernst equations for species A, or B</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>°K</td>
</tr>
<tr>
<td>XBAR(J)</td>
<td>normalised distance from the electrode surface for point J</td>
<td></td>
</tr>
<tr>
<td>YMAX</td>
<td>the maximum value of the function</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$y = f(x)$</td>
<td></td>
</tr>
</tbody>
</table>
Appendix 6: Program EGB6

C.....THIS PROGRAM USES VARIABLE DX.
IMPLICIT REAL*8(A-H,0-Z)
REAL*8 K1,K2
DIMENSION Z(120),A(120),B(120),AM(120),BM(120),XBAR(240)
FF(240)

AREA=1.D0
F=9.648704
R=0.31430
T=298.0.D0

C.....INPUT DATA.
READ(5,10) EI,EY,ERATE
READ(5,10) CA,CB,DTHICK,DA,DB
READ(5,10) K1,K2
READ(5,10) HA,HB
READ(5,11) NT
10 FORMAT(3F10.1,208.1)
11 FORMAT(15)

C.....CALCULATE THE GRID PARAMETERS.
C...TIME SCAN.
TIME=(EI-EF)/ERATE
C...TIME INCREMENT.
TIME (DT)=TIME/DFLOAT (NT-1)
C...RADIAL INCREMENT.
CONST1=.66D0*HA**2*DTHICK
DRY=DSQRT (DA*DT)*HA/CONST1
CONST2=HB*(HB+1.D0)
YMAX=HA/CONST2
NYMAX=IDINT(YMAX/DRY)+1
NR=NYMAX+1

YMAX=HA/CONST2
NYMAX=IDINT(YMAX/DRY)+1
NR=NYMAX+1
DRYYMAX=V
V

P5=DA*DT/DTHICK**2/DRY**2
P5=DA*DT/DTHICK**2/DRY**2
AB2=HA/HB**2

PARAM=P5*AB2**2
PARAM=P5*AB2**2
D2=2D0/2
D2=2D0/2

DO 21 NT=N2MAX+1
21 CONTINUE
XXBAR(J)=0.D0
XBAR(NY2MAX)=XBAR(J)

C...PARAMETERS EMPLOYED IN THE INTEGRATION.
Q1=K1*DT
Q2=K2*DT

C.....OUTPUT THE DATA FOR REFERENCE.
WRITE(6,12) EI,EY,ERATE
WRITE(6,12) EI,EY,ERATE
12 FORMAT(' POTENTIAL RANGE',2F7.3,' RATE',F7.3,'V/9 ')
WRITE(6,13) CA,EA,DA,CB,EB,EB,EB,EB,EB
WRITE(6,13) CA,EA,DA,CB,EB,EB,EB,EB,EB
13 FORMAT(' CA=',F8.4,' EA=',F7.3,' DA=',D10.3,/
13 FORMAT(' CA=',F8.4,' EA=',F7.3,' DA=',D10.3,/
1' CB=',F8.4,' EB=',F7.3,' DB=',D10.3)
WRITE(6,20) DTHICK
WRITE(6,20) DTHICK
20 FORMAT(' DIFFUSION THICKNESS',F8.4)
WRITE(6,14) K1,K2
WRITE(6,14) K1,K2
14 FORMAT(' RATE CONSTANT AM->Z',F8.3,/
14 FORMAT(' RATE CONSTANT AM->Z',F8.3,/
' Bd->Y**,F12.3,' L/MOLE/S')
WRITE(6,15) NR,PA,PARAM,01,02,03,DRY
WRITE(6,15) NR,PA,PARAM,01,02,03,DRY
15 FORMAT(' PARAMETER VALUES, NT, NR, PS, PARAM, Q1, Q2, DT ')

AND DRY',/AND DRY',/
1215*4.F8.4*2012.4)

C.....INITIALISE THE RUN.
DO 1 I=1,NT
AC(I)=CA
BC(I)=CB
AM(I)=D0.00
BM(I)=D0.00
1 Z(I)=0.D0

C...COMPUTE THE POTENTIAL INCREMENT IN TIME DT.
DELX=DTERMATE
DELX=DTERMATE
C.....START SCANNING THROUGH THE POTENTIAL RANGE.

    EPOT=EI
    NTM=NT-1
    CONST=F/R/T
    C1=0.DO
    FACT=1.DO

16   WRITE(6,16) EPOT,C1,C1,C1
16 FORMAT(' E APPLIED','4X','A CURRENT','5X,'B CURRENT','6X','TOTAL','/F12.8,3D14.6)
17   DO 2 I=1,NTM
17   EPOT=EPOT-DELE

C.....IMPOSE THE BOUNDARY CONDITIONS IN THE REGION FAR FROM THE ELECTRODE SURFACE.

   A(NR)=CA
   BN=CB
   BM(NR)=0.DO
   Z(NR)=0.DO
   M=NR
   N=NR-1
   NX=2*N
   A2=A(N)
   A1=A(N)
   B2=B(N)
   B1=B(N)
   AM2=AM(N)
   AM1=AM(N)
   BM2=BM(N)
   BM1=BM(N)
   Z2=Z(N)
   Z1=Z(N)
   FF2=FF(NX)

C.....NOW SWEEP DOWN TO ELECTRODE SURFACE.

   DO 3 J=2,N
   MM=M-1
   NX=NX-2
   NNX=NX+1
   FF1=FF(NNX)
   FF0=FF(NX)
   A0=A(MM)
   B0=B(MM)
   AM0=AM(MM)
   BM0=BM(MM)
   Z0=Z(MM)
   GA=DELB3(A2+A1,A0,P5,FF2,FF1,FF0)
   GB=DELB3(B2,B1,B0,P5,FF2,FF1,FF0)
   GAM=DELB3(AM2,AM1,AM0,P5,FF2,FF1,FF0)
   GBM=DELB3(BM2,BM1,BM0,P5,FF2,FF1,FF0)
   GZ=DELB3(Z2,Z1,Z0,P5,FF2,FF1,FF0)
   FF2=FF0
   A(M)=A2+GA
   BZK=02*B2*Z2
   B(M)=B2+GB-BZK
   Z(M)=Z2+GZ-BZK+G1*AM2
   AM(M)=AM2+GAM-G1*AM2
   BM(M)=BM2+GBM

3   CONTINUE

C.....NOW IMPOSE THE BOUNDARY CONDITIONS APPROPRIATE TO THE ELECTRODE SURFACE. FOR THIS PROGRAM, WE HAVE ASSUMED REVERSIBLE REDUCTION. IT SHOULD BE TRIVIAL TO GENERALISE TO OTHER CASES.

    RAT1=DEXP(CONST*(EPOT-EOA))
RAT2=DEXP(CONST*(EPOT-E0))
BB=A(2)+AM(2)
CC=A(3)+AM(3)
DD=A(4)+AM(4)
EE=A(5)+AM(5)
GG=A(6)+AM(6)
AM1=400.DO*(BB-CC)+400.DO*DD-150.DO*EE+24.DO*GG
AM(1)=AM1/274.DO/(1.DO+RAT1)
A(1)=RAT1*AM(1)
BB=B(2)+BM(2)
CC=B(3)+BM(3)
DD=B(4)+BM(4)
EE=B(5)+BM(5)
GG=B(6)+BM(6)
BM1=400.DO*(BB-CC)+400.DO*DD-150.DO*EE+24.DO*GG
BH(1)=BM1/274.DO/(1.DO+RAT2)
B(1)=RAT2*BM(1)
Z1=600.DO*(Z(2)-Z(3))+400.DO*Z(4)-150.DO*Z(5)+24.DO*Z
BB=274.DO*A(1)+600.DO*(A(2)-A(3))+400.DO*A(4)-150.DO*A(5)+24.DO*A(6)
BBnDA*BB/(120.DO*DRY) - CURR1F*AREA*BB*AB2/DTHICK
CC=-274.DO*B(1)+600.DO*(B(2)-B(3))+400.DO*B(4)-150.DO*B(5)+24.DO*B(6)
CCDB*CC/(120.DO*DRY)
CURR2=AREA*CC*AB2/DTHICK
CURR=CURR1 + CURR2
WRITE(6,17) EPOT,CURR1.CURR2,CURR
CHECK THAT THE SOLUTION IS NOT OSCILLATING.
IF(FACT*CURR.LT,0.DO) GOTO 18
FACT=CURR
2 CONTINUE
STOP
WRITE(6,19)
FORMAT(' CURRENT IS OSCILLATING, CHECK PARAMETERS')
END

REAL FUNCTION DELB3*8(A2,A1,A0,P5,FF2,FF1,FO)
IMPLICIT REAL*(A-H,O-Z)
THIS FUNCTION SUPPLIES PART OF THE SECOND
DERIVATIVE. IT ALSO SETS UP THE A'S FOR THE NEXT RUN.
DELB3=P5*FF1*(FF2*(A2-A1)-FO*(A1-A0))
A2=AI
A1=AO
RETURN
END
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is likely subject to steric influence because of the crowded transition state. It appears to have little temperature
dependence.

EXPERIMENTAL

Determination of the amount of ethyl azidoformate (I) decomposed, and qualitative analysis of the products, trans- and cis-4-ethoxy carbonyl-3-isopropyl-3-methylaziridines (IIa and b), ethyl N-cyclohexylcarbamate (III), and ethyl 1,4-dioxan-2-carboxylate (IV), were carried out as described previously.1 Cyclohexane and 1,4-dioxan were purified by standard methods before use. Both trans- and cis-4-methylpent-2-ene were purified by distillation, b.p. 59—59.5 and 55—58.5°, respectively, of commercial materials (Wako, reagent grade). Azide (I), b.p. 45—46° at 20
mm Hg, and trans- and cis-aziridines (IIa and b), b.p. 56—60° and 54—55° at 3 mm Hg, respectively, were obtained by literature methods.

Photochemical Reactions and Analyzes.—Azide (I) and trans-4-methylpent-2-ene in the molar ratio ca. 1:10 were placed in a quartz vessel (25 cm x 1.8 cm). Cyclohexane or 1,4-dioxan was added, resulting in a 10.0 ml solution with an olefin concentration of 10 or 7 mole %.

In order to provide further support for our proposed reaction mechanism, we embarked upon a study of the two addition steps in the Scheme, using electroanalytical experiments in which the nucleophile, \(-\text{CH}_2\text{CN} \) was used to study the addition of electrogenerated \(-\text{CH}_2\text{CN} \) to aromatic carbonyl compounds. The cyanomethyl anion has been generated in two ways. (1) by reduction of azobenzene in acetonitrile, which involves protonation of the diazonium by the solvent, and (2) by reduction of cyanomethyltriphenylphosphonium and triphenylcarbinol in dimethylformamide, which involves reductive cleavage. A computer simulation of the electroanalytical experiments is described and representative results are given, including estimates of the rate constants for the addition of \(-\text{CH}_2\text{CN} \) to a series of alkyl phenyl ketones.

In 1974, we reported \(^1\) that the electroreduction of aromatic carbonyl compounds (I) in dry acetonitrile gave significant amounts of 3-substituted propiononitriles (IV) and glutaronitriles (V). By analogy with the known reaction of the conjugate base of azomethine with carbonyl compounds \(^2\) we suggested that the first step in the formation of these products involves the addition of \(-\text{CH}_2\text{CN} \) to the carbonyl group to form a hydroxynitrile (II). The nitrilephile might be formed initially via reduction of the carbonyl compound, but sub-

\(^1\) No reprints available.


\(\text{J.C.S. Perkin II} \)

The Use of Linear Sweep Voltammetry to study the Addition of Electro

By Anthony J. Bellamy,1 George Howat, and Iain S. MacKirdy, Chemistry Department, University of Edin-

burgh, West Mains Road, Edinburgh EH9 3JU

A general electroanalytical method for studying the rate of reaction between an electrogenerated species, e.g., nucleophile, base, electrophile, acid, or radical and an electroactive substrate is described. The method has been used to study the addition of electrogenerated \(-\text{CH}_2\text{CN} \) to aromatic carbonyl compounds. The cyanomethylenel anion has been generated in two ways. (1) by reduction of azobenzene in acetonitrile, which involves protonation of the diazonium by the solvent, and (2) by reduction of cyanomethyltriphenylphosphonium and triphenylcarbinol in dimethylformamide, which involves reductive cleavage. A computer simulation of the electroanalytical experi-

ments is described and representative results are given, including estimates of the rate constants for the addition of \(-\text{CH}_2\text{CN} \) to a series of alkyl phenyl ketones.

In 1974, we reported \(^1\) that the electroreduction of aromatic carbonyl compounds (I) in dry acetonitrile gave significant amounts of 3-substituted propiononitriles (IV) and glutaronitriles (V). By analogy with the known reaction of the conjugate base of azomethine with carbonyl compounds \(^2\) we suggested that the first step in the formation of these products involves the addition of \(-\text{CH}_2\text{CN} \) to the carbonyl group to form a hydroxynitrile (II). The nitrilephile might be formed initially via reduction of the carbonyl compound, but sub-

\(^1\) No reprints available.

generated electrochemically in the presence of either an aromatic carbonyl compound or corresponding unsaturated nitrile. The present paper describes results relating to the carbonyl addition.  

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**Scheme**  

The basis of the electroanalytical method involves recording the linear sweep voltammogram of the carbonyl compound alone (Figure, curve A) and then in the presence of an easily reduced compound (Figure, curve B), the reduction of which generates, either directly or indirectly, \( \text{CH}_2\text{CN} \). Thus \( \text{CH}_2\text{CN} \) is formed at, or close to, the electrode and reacts with the carbonyl compound. By the time the linear sweep reaches the potential necessary for reduction of the carbonyl compound, some of the latter will have been converted into the non-reducible adduct and thus the peak current for the first electron transfer of the carbonyl compound will be less than in the original sweep. The magnitude of the decrease in \( i_p \) can then be used to determine the rate constant for the addition step \( k_2 \). Apart from the rate constant for the carbonyl addition, the decrease in \( i_p \) is dependent upon several other factors, the most important being the absolute and relative concentrations of the carbonyl compound and the \( \text{CH}_2\text{CN} \) precursor, the rate at which the reduced precursor liberates \( \text{CH}_2\text{CN} \), \( k_1 \), the difference in \( E^\circ \) between the two compounds \( (\Delta E^\circ) \), and the rate at which the voltage is increased \( (\nu) \). The latter two factors determine the time scale of the experiment, increasing \( \Delta E^\circ \) and/or decreasing \( \nu \) producing a larger decrease in \( i_p \), while decreasing \( \Delta E^\circ \) and/or increasing \( \nu \) producing a smaller decrease in \( i_p \), for given values of \( k_1 \) and \( k_2 \). Obviously the electroanalytical method is a general one and may be used to study the rate of reaction between any electrogenerated species, e.g. nucleophile, base, or even electrophile, acid, or radical, and an electroactive substrate.

Perhaps the simplest way of generating \( \text{CH}_2\text{CN} \) electrochemically is via protonation of a reduced species by acetonitrile, the latter being used as the solvent. It has been shown \( ^4 \) that the reduction of azobenzene in acetonitrile involves two reversible one-electron transfer steps, the radical-anion being stable but the dianion being rapidly protonated by the solvent to give the conjugate base of hydrazobenzene and the cyanomethyl anion \( (\text{CH}_2\text{CN}) \). Since the second electron transfer to azobenzene occurs at a less negative potential than the first electron transfer for many of the carbonyl compounds we wished to study, the reduction of azobenzene in acetonitrile appeared suitable for the generation of \( \text{CH}_2\text{CN} \) in the type of electroanalytical experiment outlined above. The reduced form(s) of azobenzene has been previously used as an electrogenerated base for Michael additions, \(^5\) and for Wittig reactions, \(^6\) and the basicity versus nucleophilicity of azobenzene dianion has also been studied.\(^7\)

When an equimolar amount of azobenzene \( [E]_0 \) \( (2) \) \(-2.18 V) \) was added to a nm solution of acetoophenone \( [E]_0 \) \( (1) \) \(-2.45 V) \) in acetonitrile, the peak current for acetoophenone was only 25\% of the corresponding peak current measured before the addition of azobenzene, i.e. reaction with the generated \( \text{CH}_2\text{CN} \) gave a 75\% reduction in \( i_p \) \( (\text{acetoophenone}) \). The conditions used to obtain the present result are considered to be more carefully controlled than those used previously. Increasing the sweep rate from 214 mV s \(^{-1}\) to 25 V s \(^{-1}\) considerably increased \( i_p \) for acetoophenone relative to that for acetoophenone.\(^8\)

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\(^3\) M. M. Baizer, J. L. Chittem, and D. A. White, Tetrahedron Letters, 1975, 4039.


mode of reaction is impossible for benzophenone. However, when the experiment was repeated using a 2mM solution of benzophenone (E<sub>on</sub> (1) = -2.19 V) in acetonitrile, the t<sub>r</sub> of the latter was decreased by 70% (Table I). In this latter case, the second and first reduction peaks of azobenzene and benzophenone respectively coincide and the portion of the composite peak due to benzophenone can only be calculated by assuming that E<sub>r</sub>. (1) for azobenzene remains unchanged in the presence of benzophenone; this ratio was found to be unchanged in the presence of acetonitrile.

If the interpretation of the decrease in t<sub>r</sub> for acetonitrile and benzophenone on addition of azobenzene is correct, then changing the solvent from acetonitrile to dimethylformamide could reasonably be expected to produce no decrease in t<sub>r</sub>. For the control experiments in dimethylformamide, azobenzene could not be used because its E<sub>r</sub> (1) is too cathodic in this solvent, i.e., more cathodic than E<sub>r</sub> (1) of benzophenone. Therefore 2,2'-azonaphthalene was substituted for azobenzene in the dimethylformamide experiments since it is reduced at less negative potentials but exhibits similar electrochemical behaviour to azobenzene in both dimethylformamide and acetonitrile. Unfortunately, 2,2'-azonaphthalene has a low solvability in acetonitrile, and thus the same azo-compound could not be used in both solvents.

As anticipated the addition of an equimolar amount of 2,2'-azonaphthalene (E<sub>on</sub> (2) = -2.28 V) to a 2mM solution of benzophenone (E<sub>on</sub> (1) = -2.28 V) in dimethylformamide produced no decrease in the t<sub>r</sub> of benzophenone, but a similar experiment with acetonitrile (E<sub>on</sub> (1) = -2.54 V) produced a decrease of 40%. A possible explanation for this latter result is that benzophenone could react via deprotonation by the 2,2'-azonaphthalene dianion or some intermediate base; this mode of reaction is impossible for benzophenone.

For the control experiments in acetonitrile was added to acetophenone in acetonitrile was that the cyclic voltammogram of acetonitrile changed from being partially irreversible (t<sub>r</sub>/t<sub>r</sub> = 0.56: 0.55 s<sup>1</sup>) to being almost completely reversible, similar behaviour was observed with propiophenone. This behaviour can be attributed to a lowering of the water content of the solvent close to the electrode as follows. The partial irreversibility of the cyclic voltammogram of acetonitrile is due to dimers of the radical-anion, and the rate constant for the dimerisation step has been shown to vary with the water content of the solvent, being 1.3 x 10<sup>9</sup> for 0.33% water, 4 x 10<sup>9</sup> for 1.3% water, and 3 x 10<sup>4</sup> for 0.3% water in acetonitrile. This has been attributed to solvation of the radical-anion by water reducing the coulombic repulsion between radical-anions. In our own experiments, the water content of the acetonitrile was 0.01% with an estimated dimerisation rate constant of 3 x 10<sup>4</sup> mol<sup>-1</sup> s<sup>-1</sup>. Extrapolation of these data to lower water levels indicates that reversible cyclic voltammetry behaviour would be observed (t<sub>r</sub>/t<sub>r</sub> = 0.52 s<sup>1</sup>) for a water content of ca. 0.003%, and it seems reasonable that this condition would be achieved in the vicinity of the electrode due to scavenging of residual water by the strong bases formed on reduction of azobenzene.

The results for other carbonyl compounds using azobenzene in acetonitrile are given in Table I. As the carbonyl group of a series of alkyl phenyl ketones becomes more crowded the percentage decrease falls off, as would be expected for a carbonyl addition reaction. The result for indan-1-one is particularly significant; the reduction peak almost entirely disappeared for a 2mM solution of benzophenone (E<sub>on</sub> (1) = -2.28 V) in dimethylformamide produced no decrease in the t<sub>r</sub> of benzophenone, but a similar experiment with acetonitrile (E<sub>on</sub> (1) = -2.54 V) produced a decrease of 40%. The maximum decrease expected for these two cases would be 80 and 35% respectively. The results for indan-1-one were expected using a primary kinetic isotope effect for the deprotonation step of only 2 would reduce the percentage decrease to ca. 25%. Thus the cause of the decrease with acetonitrile in dimethylformamide is uncertain. The absence of any decrease for benzophenone indicates that nucleophilic addition of the dianion of the azo-compound to the carbonyl group is not responsible for the decreases observed for both ketons in acetonitrile. For benzophenone, the decrease in t<sub>r</sub> in acetonitrile can be attributed entirely to the addition of CH<sub>2</sub>CN to the carbonyl group, whereas for acetonitrile the addition of CH<sub>2</sub>CN to the carbonyl group may be only partly responsible for the decrease.

A further change which was observed when azobenzene was added to acetonitrile in acetonitrile was that the cyclic voltammogram of acetonitrile changed from being partially irreversible to being almost completely reversible; similar behaviour was observed with propiophenone. This behaviour can be attributed to a lowering of the water content of the solvent close to the electrode as follows. The partial irreversibility of the cyclic voltammogram of acetonitrile is due to dimers of the radical-anion, and the rate constant for the dimerisation step has been shown to vary with the water content of the solvent, being 1.3 x 10<sup>9</sup> for 0.33% water, 4 x 10<sup>9</sup> for 1.3% water, and 3 x 10<sup>4</sup> for 0.3% water in acetonitrile. This has been attributed to solvation of the radical-anion by water reducing the coulombic repulsion between radical-anions. In our own experiments, the water content of the acetonitrile was 0.01% with an estimated dimerisation rate constant of 3 x 10<sup>4</sup> mol<sup>-1</sup> s<sup>-1</sup>. Extrapolation of these data to lower water levels indicates that reversible cyclic voltammetry behaviour would be observed (t<sub>r</sub>/t<sub>r</sub> = 0.52 s<sup>1</sup>) for a water content of ca. 0.003%, and it seems reasonable that this condition would be achieved in the vicinity of the electrode due to scavenging of residual water by the strong bases formed on reduction of azobenzene.

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Therefore indicate that on average more than one equivalent of the ketone is being converted to a non-reducible form for each \( \text{CH}_2\text{CN} \) initially generated. This could arise as follows: the initial adduct, an oxonium, could abstract a proton from the acetonitrile thus \( \text{CH}_2\text{CN} \), which could then either add to or abstract a proton from another indan-1-one molecule. In view of the result with \( \text{PhH}_2\text{CCH}_2\text{CN} \) in dimethylformamide, deprotonation appears the least likely route. Obviously, the regeneration of \( \text{CH}_2\text{CN} \) may also operate with the other carbonyl compounds, and thus contribute to the decrease observed.

Since the second electron transfer to azobenzene occurs at a potential \( E_{\text{p}} = -2.18 \) V which limits the study of the more readily reducible carbonyl compounds [cf. benzophenone \( E_{\text{p}} = -2.19 \) V] and unsaturated nitriles we have investigated the use of other, more easily reduced azo-compounds as sources of \( \text{CH}_2\text{CN} \), particularly azopyridines. The electroanalytical behaviour of 4,4'-azopyridine in dimethylformamide had already been studied and the reported \( E_{\text{p}} \) values indicated that a study of the isomeric azopyridines, as well as the isomeric benzenecyanopyridines, might be rewarding. However, when reduction to the dianion occurs at a less negative potential, it usually follows that the dianion is more stable and does not protonate as rapidly as the dianion of azobenzene. This is certainly the case for 4,4'-azopyridine \( E_{\text{p}} = -1.195 \) V versus s.c.e., which exhibits a reversible second electron transfer in acetonitrile. The lower rate of protonation of the dianion of 4,4'-azopyridine in dimethylformamide is reflected in a lower percentage decrease in the \( N \) of benzophenone compared with the decrease observed with azobenzene. The electroanalytical behaviour of the isomeric azopyridines and benzenecyanopyridines, and their use as precursors for \( \text{CH}_2\text{CN} \) will be reported later.

In order to avoid the complication of a \( \text{CH}_2\text{CN} \) regeneration process, we have looked at the possibility of using the cation \( \text{CH}_2\text{CN} \) by a reductive cleavage reaction since this could be used in other solvents, particularly dimethylformamide. By working in dimethylformamide, proton abstraction from the medium by an intermediate base would not regenerate \( \text{CH}_2\text{CN} \), and the study of the initial addition step would be simplified. Three potential precursors have been studied, cyanomethyltriphenyl arsonium bromide, cyanomethyltriphenylphosphonium bromide, and cyanoethyltriphenylarsonium bromide. The ammonium salt is unsatisfactory because \( E_{\text{p}} \) for one electron reduction is too high \( -2.47 \) V. The phosphonium salt \( \text{Et}_{\text{N}}\text{CHCN} \) has been shown by Wagenknecht and Baizer to involve the transfer of two electrons at the first reduction peak, generating \( \text{PhP} \) and \( \text{CH}_2\text{CN} \). The ammonium salt has not previously been studied.

The reduction of the cyanomethyltriphenylphosphonium cation has been shown to involve the transfer of two electrons at the first reduction peak, generating \( \text{PhP} \) and \( \text{CH}_2\text{CN} \). The ammonium salt has not previously been studied.

\[
E_{\text{p}} = \text{CH}_2\text{CN} 1^1 \text{ PhH}_2\text{CHCN Br}^- \text{ PhP}\text{CH}_2\text{CN Br}^-  
\]  
\( \text{(VI) (VII)} \)

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The electrochemical behaviour of the arsonium salt has not previously been studied.

\[
E_{\text{p}} = -2.19 \text{ V} \]

The electrochemical behaviour of the cyanomethyltriphenylphosphonium cation is similar to that of the phosphacltriphenylphosphonium cation in acetonitrile. The electrochemical behaviour of the cyanomethyltriphenylphosphonium cation in acetonitrile has been shown to involve the transfer of two electrons at the first reduction peak, generating \( \text{PhP} \) and \( \text{CH}_2\text{CN} \). The ammonium salt has not previously been studied.

The electrochemical behaviour of the cyanomethyltriphenylphosphonium cation in acetonitrile has been shown to involve the transfer of two electrons at the first reduction peak, generating \( \text{PhP} \) and \( \text{CH}_2\text{CN} \). The ammonium salt has not previously been studied.

\[
E_{\text{p}} = -1.55 \text{ V} \]

The electrochemical behaviour of the cyanomethyltriphenylphosphonium cation in acetonitrile has been shown to involve the transfer of two electrons at the first reduction peak, generating \( \text{PhP} \) and \( \text{CH}_2\text{CN} \). The ammonium salt has not previously been studied.

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amounts of cyanomethyltriphenylarsonium bromide added to the same ketone solution gave decreases of 18 and 31% respectively. The addition of an equimolar amount of cyanomethyltriphenylphosphonium bromide to a 2mM solution of indan-1-one (E° = 2.54 V) in dimethylformamide gave a decrease of 23%. The decreases observed in these experiments are significantly less than those found using azobenzene in acetonitrile, and this is presumably due in part to the elimination of the *CH₂CN regeneration process. The smaller decreases observed with benzophenone in the presence of the azonium precursor compared with those with the phosphonium precursor may be due to a larger kinetic acidity of the former cation, even though the thermodynamic acidities are expected to be in the reverse order, making it a more effective competitor for the available \( \text{CH}_2\text{CN} \). Since some of the \( \text{CH}_2\text{CN} \) is being removed from the kinetic system by reaction with the carbonyl compound, it might have been anticipated that the \( \text{t}_{\text{ho}} \) for the \( \text{CH}_2\text{CN} \) precursor would increase in the presence of the carbonyl compound, since less ylide formation might occur and therefore more cation would be available for reduction. However this is not observed to a significant extent, presumably because the adduct formed between \( \text{CH}_2\text{CN} \) and the carbonyl compound, an oxyanion, would still be capable of deprotonating the cation and generating ylides.

**Computer Simulation of the Electroanalytical Experiments and Estimation of \( k_2 \) Values.—**The model system may be written as (a)–(d) in which species A is the precursor for the generation of \( \text{CH}_2\text{CN} \), e.g. azobenzene radical-anion or cyanomethyl 'onium cation, B is the reactive substrate e.g. carbonyl compound, Z is the reactive intermediate e.g. \( \text{CH}_2\text{CN} \), and Y is the electroinactive product from the reaction of B with Z: \( A \) is the rate constant for the formation of Z from \( \text{CH}_2\text{CN} \), and \( k_2 \) is the rate constant for the reaction of B with Z (second order). We have assumed that both electron transfer steps are reversible, and that both chemical steps are irreversible.

The relevant equations for diffusion and chemical reaction are (1a–e) with the concentrations of each species being a function of both distance from the electrode surface, \( x \), and time, \( t \), e.g. \( C_A = C_A(x, t) \).

The boundary conditions to be satisfied by each concentration variable are given by (2)–(4) where \( C_A^b \) and \( C_A^e \) are the bulk concentrations of A and B respectively. Since the electron transfer steps are assumed to be reversible, the Nernst equation may be applied to the concentrations of species A, \( A^+ \), B, and \( B^- \) at the electrode surface (equation (6)) where \( E_i \) is the applied potential at time \( t \), which for a linear sweep equals

\[
\frac{dC_A}{dt} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_A C_A
\]

\[
\frac{dC_A^+}{dt} = D_A \frac{\partial^2 C_A^+}{\partial x^2} - k_A C_A
\]

\[
\frac{dC_A^-}{dt} = D_A \frac{\partial^2 C_A^-}{\partial x^2} - k_A C_A
\]

\[
E_i - \varphi = k_A C_A
\]

\[
E_i = k_A C_A
\]

\[
E_i = k_A C_A
\]

\[
E_i = k_A C_A
\]

\[
E_i = k_A C_A
\]

After solving the equations, the total current at any time may be calculated from equation (6) where \( s \) is the electrode area. The contribution to the current by reduction of B only may be calculated from (7).

\[
i_n = \varphi D_B \frac{\partial C_B}{\partial x} \bigg|_{x=0}
\]

These equations were solved numerically using the so-called explicit, finite difference method. The total time for the potential sweep is divided into small segments, \( \Delta t \), and the derivative \( \frac{\partial C_A}{\partial x} \) for each concentration is replaced by expression (8). Similarly, the variable \( x \) is partitioned into segments, \( \Delta x \), ensuring that the maximum distance from the electrode is greater than the

maximum diffusion layer thickness. The second-order partial derivative $\partial^2 C_A/\partial x^2$, for example, is then replaced by expression (9). Combining equations (8) and (9), the

$$
\frac{\partial C_A}{\partial x} (x, t + \Delta t) = \frac{1}{\Delta x^2} \left( \frac{C_A (x + \Delta x, t) - 2 C_A (x, t) + C_A (x - \Delta x, t)}{\Delta x^2} \right) + \left( \frac{D_A}{\Delta x^2} \right) \frac{\partial C_A}{\partial t} (x, t)
$$

(9)

difference scheme to be employed in solving equation (1b) is obtained from the known concentrations at time $t$ using equation (10). The numerical solution is initiated at $t_0$ using boundary condition 2. Since we have ensured that the computation commences outside the diffusion layer, boundary condition 3 is imposed and the computation proceeds inward towards the electrode. This procedure is continued up to the first point out from $x = 0$. At this stage it is necessary to apply boundary conditions 4 and 5. From pilot calculations it was found necessary to calculate the derivative at $x = 0$ by a six-point Langrangian formula. Thus, assuming the diffusion coefficients of $A$ and $A^-$ to be identical, equation (4a) yields (11) where $[L]$ are the

$$
L = \frac{1}{2} \left( \frac{L_{CA} (n \Delta x, t + \Delta t) \frac{\partial C_A}{\partial t} (n \Delta x, t + \Delta t)}{L_{CA} (n \Delta x, t + \Delta t)} \right)
$$

(11)

Langrangian coefficients. Using equation (8a) one can compute $C_A (0, t + \Delta t)$ and $C_A^+ (0, t + \Delta t)$ and proceed to obtain the current due to the $A/A^-$ redox system. The current due to the $B/B^-$ redox system is computed in a similar manner. Having reached $x = 0$, the time and applied potential are now incremented and the whole computation repeated until the entire voltamogram has been constructed.

The method employed here, based on equation (8), the so-called ‘explicit solution’, is easy to employ but suffers from the limitation that equation (10) is stable only when $D_A \Delta t < \Delta x^2$ for $\Delta x = 0$; it is obvious that a choice of $\Delta x$ dictates the upper limit of $\Delta t$. In order to represent adequately the second-order partial derivative by equation (9), a small $\Delta x$ is desirable, thus forcing a choice of $\Delta t$ which may be smaller than necessary to represent adequately the derivative in equation (8); this results in more computing time.

The problem of choosing a suitable mesh $\Delta x$ is facilitated if one makes use of the results obtained previously by Nicholson and Shaw. For example, setting $k_2 = 0$ effectively decouples the $A$ and $B$ systems, the first being reduced followed by chemical reaction (c.c.) and the second being a reversible reduction. The choice of grid is then one which reproduces previous calculations to a satisfactory accuracy.

In order to test the simulation procedure, the following values were selected: $v = 0.25$ V s$^{-1}$, $C_A^0 = C_B^0 = 2$mM, $E_a^0 = 2.000$ V, $E_b^0 = -2.190$ V, $E_A^0 = 2.442$ V, all diffusion coefficients $2 \times 10^{-6}$ cm$^2$ s$^{-1}$, diffusion layer thickness 0.039 cm, sweep time 4 s, 93 and 1.200 points in $x$ and $t$ respectively. The following cases were investigated: (i) $k_1$ and $k_2$ set to zero, producing two independent, reversible, redox systems. (ii) $k_1$ set to 97.357 s$^{-1}$ and $k_2$ to 0, producing an e.c. system for $A$. The value for $k_1$ (97.357 s$^{-1}$) corresponds, for a sweep rate of 0.25 V s$^{-1}$, to a $k_1/a$ value of 10 in the Nicholson and Shaw treatment of an e.c. system; the latter gave a cyclic voltammogram which closely resembled that of the second electron transfer of azobenzene in acetonitrile. The results obtained from these calculations were in good agreement with those of Nicholson and Shaw for both the reversible, redox system and the e.c. system, and indicated that coupling the $A$ and $B$ systems by introducing non-zero values for $k_2$ should give reliable results.

Some representative results which demonstrate the dependence of the peak current for reduction of $B$ on $k_a$ (B) upon (i) the sweep rate $v$, (ii) the difference in $E^*$ for the $A/A^-$ and $B/B^-$ redox systems, $\Delta E^*$, (iii) the concentrations of $A$ and $B$, $C_A$ and $C_B$, (iv) $k_2$, and (v) $k_1$, and $k_2$ expressed as a percentage decrease from the peak current for reduction of $B$ when $k_1 = 0$, are given in Table 2. From these data we observe that (a) as the time interval for the reaction of $Z$ with $B$ is decreased, either by increasing $v$ or by decreasing $\Delta E^*$, there is a drop in the percentage decrease in $i_{pa} (B)$; (b) as the rate of generation of $Z$ from $A$ is increased, the percentage decrease in $i_{pa} (B)$ also increases initially, but above $k_1 10^3$ any further change is small; (c) above $k_1 10^3$ any further increase in $k_1$ have a progressively smaller effect. As $k_1$ increases from 0 to 5000 1 mol$^{-1}$ s$^{-1}$, there is a small cathodic shift in $E_{pa} (B)$ (16 mV)). The simulation is unstable at $k_1 200$ s$^{-1}$ and at $k_1 10^3$ 1 mol$^{-1}$ s$^{-1}$, and should it become necessary to use higher values of $k_1$, we shall need to use a finer mesh, and hence more computing time.

From the calculations with variation of $k_1$ we have observed that the experimental result for the indan-1-one-azo-benzene-acetonitrile system (see Fig. 2) could never be achieved using this reaction scheme and realistic values of $k_1$. However, if the simulation is extended to include a catalytic process (c) which would correspond to proton abstraction from the solvent by the initial adduct, an oxyanion, and $K_a$ is set equal to $K_1$ (97.357 s$^{-1}$) with $k_2 = 0.000$ 1 mol$^{-1}$ s$^{-1}$, the percentage decrease in $i_{pa} (B)$ is increased from 67.9 to 99.9%.

When the catalytic process is incorporated, the calculated percentage decrease in $i_{pa} (B)$ is probably fairly insensitive to the value of $k_1$. Thus, the regeneration of CH$_2$CN in the indan-1-one-azo-benzene-acetonitrile system is indicated by both the experimental result at concentrations of indan-1-one $>2$mM and by the computer simulation.
Approximate rate constants for the reaction of 
$\text{-CH}_2\text{CN}$ with alky1 phenyl ketones ($k_A$) in the azobenzene-acetonitrile system are included in Table 1. These were calculated by the above simulation programme with the following assumptions: (i) no regeneration of $\text{-CH}_2\text{CN}$ (no catalytic process included), (ii) the rate constant for protonation of azobenzene-dimethylformamide in order of magnitude either way would have only a small effect on the calculated result; see Table 2), (iii) $\Delta\nu/2$ 2 V (e.g., 2 of acenaphthene $2.65 \text{V}$; since we estimate $A_{1,2}^0, A_{1,2}^0$, $A_{1,2}^0$ [for benzene will be at $-2.19 \text{V}$ ] the $\Delta\nu/2$ 2 V is a reasonable average value for all the alkyl phenyl ketones except acetylmesitylene), (iv) $\nu$ 0.25 V s$^{-1}$ (This is slightly greater than the sweep rate actually used, but the error will be small. We hope to improve the accuracy of these calculations by obtaining better estimates of $A_{1,2}$ and $A_{1,2}$ by incorporating the catalytic process where appropriate.

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We shall not attempt to calculate $A_1$ for the cyano- methy1 onium cation-dimethylformamide system in the present paper since at present we have no information on $k_A$ for this system or the rate constants for deprotonation of the cation by $\text{-CH}_2\text{CN}$ and the oxonium.

**EXPERIMENTAL**

Acenaphthilne (Fisons SLR grade) was purified and dried by the method of Forcier and Olver using the sequence (i) sodium hydride, (ii) phosphorus pentaoxide, (iii) calcium hydride and was stored over molecular sieve. The final water content was 0.01%. Acenaphthilne as supplied by Aldrich could not be easily purified using the above procedure. Dimethylformamide was purified and dried by the method of Ritchie and Negele, and was stored over molecular sieve.

2.2'-Azophenolone. - This was prepared from 2-azinophenolone using the method of Corbett. Extensive chromatography and repeated recrystallisation from toluene was required to obtain a pure product, m.p. 208.5-210 °C (lit. 208 °C). 2-2'-Tridentiorthoacetophenone. - A mixture of acetophenone (6.0 g), deuterium oxide (20 ml), and anhydrous potassium carbonate (1 g) was refluxed for 24 h, the aqueous phase was removed and further amounts of deuterium oxide (30 ml) and anhydrous potassium carbonate (1.5 g) were added. After refluxing for a further 20 h, dry ether (50 ml) was added, the aqueous layer was removed, and the organic phase was stirred with deuterium oxide (3 ml) and a small amount of sodium chloride. The organic phase was separated, dried over calcium chloride, concentrated, and distilled, b.p. 89 °C at 10 mm Hg, to give pure 2,2'-tridentiorthoacetophenone.

The deuterium content of the ketone was found (g.l.c.) to be unchanged after treatment with 0.1 m solutions of tetraethylammonium fluoroborate in both acetophenone and dimethylformamide for 2 h, indicating that no exchange would occur during the period required for cyclic voltammetry experiments.

Acetylmesitylene. - This was prepared by acetylation of mesitylene, and was shown to be pure by g.l.c. analysis.

Cyanomethyltriaethylammonium iodide. - A solution of iodooacetone (1.07 g) and triethylamine (1.21 g) in propen-l-ol (20 ml) was left to stand for 24 h before collecting the white crystalline salt, m.p. 187 °C (from propen-l-ol) (lit. 187 °C) and dms.), to be unchanged after treatment with 0.1m solutions of tetraethylammonium fluoride in both acetonitrile and dimethylformamide for 2 h. The final product was shown to be pure by g.l.c. analysis.

Cyanomethyltrihalogenomethanes. - The phosphonium salt was prepared by the method of Wagenknecht and Baisier, and had m.p. 256-258 °C (from ethanol) (lit. 256-258 °C). The yield was prepared by treatment with aqueous sodium hydride, m.p. 101-106 °C (from ethyl acetate) (lit. 105-106 °C). 2-Chloro-2 chloroetyltrimethyl ammonium Bromide. - A solution of bromoacetophenone (1.31 g) and triphenylarsine (0.35 g) in nitromethane (10 ml) was heated in an oil-bath at 110 °C for 9 h. After cooling, the yellow solution was poured into molecular sieves.

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other (100 ml) and the solid was filtered off, crushed and washed with ether. The crude product (3.12 g) was re-crystallised in nitromethane and reprecipitated by adding ether to give a white crystalline solid (2.52 g), m.p. 194—
200°C. It was recrystallised twice from nitromethane only to give constant m.p. 193—210°C [lit. 210°C (decomp.)] (Found: C 56.40; H 4.09; N 3.2. Calc. for
C₉₆H₂₉₅AsBrN: C 56.35; H 4.0; N 3.3%). Although the m.p. had a wide range, the product appeared to be pure as shown by elemental analysis and by comparison of its spectroscopic properties with those of cyanoethyltriphenylphosphonium bromide. It had δCH₃ (Nujol, 290 cm⁻¹; 8CH₂(Nujol, 857 (2 H, s); 7.9 (H, m); δC (DMSO; H decoupled) 134.74 (s. C=), 132.89 and 130.87 (both s, C-2 and -3), 120.23 (s, C-1), 113.78 (s, CN), and 13.82 p.p.m. (6, CH₃) with similar relative intensities to those observed for cyanoethyltriphenylphosphonium bromide; m/z 306 [(—BrCH₂CN), 229 (P₃As), 227, 153, and 122 (no parent ion)].

General Procedure for Electroanalytical Experiments.— The working electrode was a hanging mercury drop, the secondary electrode was platinum, and the reference electrode was Ag-0.1st.AgNO₃. The reference electrode solution was connected to the test solution via a cracked-glass seal. The working electrode was a hanging mercury drop, the acid, the cell and solution were flushed with dry nitrogen. cell, the cell and solution were flushed with dry nitrogen. The averaged value from several runs. The precursor for the generation of CHCN, e.g. azobenzene in acetonitrile or cyanomethyltriphenylphosphonium bromide in dimethylformamide, was then added to the cell as a solution (1.00 ml) in the appropriate solvent (0.2 mmol in 5.0 ml) to give a final concentration of 5 mM. After flushing with nitrogen, the linear sweep or cyclic voltammogram was recorded (Figure, curve A); the peak current for the first electron transfer was the averaged value from several runs. The precursor for the generation of CHCN, e.g. azobenzene in acetonitrile or cyanomethyltriphenylphosphonium bromide in dimethylformamide, was then added to the cell as a solution (1.00 ml) in the appropriate solvent (0.2 mmol in 5.0 ml) to give a final concentration of 5 mM. After further flushing with nitrogen, the linear sweep or cyclic voltammogram was recorded (Figure, curve B). In order to measure the peak current of the first electron transfer of the test substrate, the linear sweep voltammogram was recorded using the time-base of the X-Y-t recorder, first for the full voltage range and then for a limited range stopping just before the reduction peak of the test substrate. Thus an extension of the cathodic peak of the precursor was used as the base line from which to measure the peak current of the test substrate (Figure, curve C). The averaged value from several runs was obtained.

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