Joseph Black Prize Competition.

Essay on

"Condensation"

with

Note of

a Research on the action of

Hydriodic acid on Phenyl-paraconic

acid.

by John Shields

April 16th, 1890
20 Rue du Mont Blanc
Genève
Condensation.

To anyone but the Chemist, the first idea which this word conveys is a physical one. In this sense it is used to denote the passage from the gaseous to the liquid state, which passage consists in the reduction of the mean distances and speed of the atoms which compose the gas, to such an extent that, under the existing circumstances, it becomes a liquid.

The same word however has found its way into chemical literature and it is the purpose of this paper to point out its significance and use.

In the year 1839 Gerhardt laid before the Chemical World his Theory of Reets. He employed himself almost entirely with the development and explanation of Double Decomposition, but in his statement of the Theory he shows that he was aware of another kind of combination. The further study of this however was left to Berthelot, who about the year 1866 discovered that when acetylene is led through a tube heated to bright redness Benzene is formed.

In the same way he discovered that
Diphenyl is produced from Benzene and anthracene from Toluene. In an interesting paper on this subject, he says that the formation of Benzene from Acetylene "is not a decomposition, but is on the other hand a combination of a higher order, brought about by the reciprocal union of several molecules of acetylene." He then goes on to show that the formation of acetylene, naphthalene or from methane, cannot be represented as a polymeric transformation and that, in fact, methane itself cannot give birth to polymers but that when it is led through a porcelain tube heated to bright redness it breaks up into hydrogen and more condensed hydrocarbons. He con believes, he says, "that this condensation produces at first acetylene

\[ 2 \text{C}_2\text{H}_4 = \text{C}_4\text{H}_2 + 3 \text{H}_2 \]

Methane, acetylene

and that the latter then condenses, forming rise to naphthalene

\[ 5\text{C}_4\text{H}_2 = \text{C}_{20}\text{H}_8 + \text{H}_2 \]

naphthalene.

Berthelot thus appears to have been the first Chemist who really knew what Condensation was; at any rate he was the first to furnish important contributions to the explanation of processes which was in later years to bear such an fruitful harvest. He was closely followed by Baeyer, who in the following year 1867, published his paper "Uber Condensation und Polymerie." In this paper Baeyer draws an important distinction between Condensation and Polymerisation; a distinction which it is
well to bear in mind. He defines a true
Condensation as the union of molecules,
by means of the molecules being linked
together by carbon atoms, and often
accompanied by the separation of water,
ammonia, hydrogen etc., whereas in a
case of Polymerisation the molecules
are united together through the medium
of other elements such as oxygen, nitrogen
etc. It will perhaps be well to consider this
difference more fully before passing on to
Condensation. By the action of many water
abtracting agents, for example, Sulphuric
and Hydrochloric acids, Chloride of Zinc etc.,
allyldehydes undergo Polymerisation. The
explanation or mechanism of the change was
given by Baeyer. It seems to be a general
rule that two hydroxyl groups cannot remain
united to the same carbon atom; there are
however some exceptions of which Chloral
hydrate is one. The body having the
constitution

\[
\text{CH}_3 - \text{C} = \text{O} - \text{H}
\]

does not exist, or if formed at all it very
readily splits off a molecule of water and
yields common aldehyde.

\[
\text{CH}_3 - \text{C} = \text{O} - \text{H} = \text{CH}_3 - \text{C} = \text{O} + \text{H}_2\text{O}
\]

On the other hand if two molecules of the
hypothetical hydrate of aldehyde lose
two molecules of water in the same way
we get a polymerised product, that is
toward, after the splitting off of the water, the "reets" unite through the medium of the oxygen atom thus:

\[
\text{CH}_3 - \text{CH} - \text{O} - \text{CH} - \text{CH}_3
\]

This can be regarded as the union of two molecules of aldehyde. In the same way, polymer formic aldehyde would give an isomer having the constitution \( \text{H} - \text{CH} - \text{O} - \text{CH} - \text{H} \).

Bayer also points out that the same form of double binding exists in the substance Girard obtained by the reduction of Carbon disulphide, namely, \( \text{H} - \text{CH} - \text{S} - \text{CH} - \text{H} \).

Although we have no reason to believe that the molecular weights of the above compounds are not correct yet the explanation of the polymerisation given by Bayer remains unaltered. The vapour density of para-aldehyde, for example, has been determined and this corresponds to the formula \( \text{C}_2\text{H}_4\text{O}_3 \), which means that the probable constitution is

\[
\text{CH}_3 - \text{CH} - \text{O} - \text{CH} - \text{CH}_3
\]

or that it is formed from three molecules of aldehyde. The constitution of meta-aldehyde is not yet known. The vapour density of formic para-aldehyde cannot be determined owing to dissociation, but if sulphurized...
hydrogen is led into its aqueous solution the same body which Girard obtained by the reduction of carbon disulphide separate and at this point methylene is formed from the paraaldehyde and methyl is formed from the paraaldehyde we may suppose that a substitution of sulphur for oxygen has taken place therefore that formaldehyde is formed from three molecules of aldehyde and not from two as Baeyer supposed.

The proof that in these polymers the molecules are not linked together by carbon atoms is found, firstly, in the readiness with which they can be converted again into the simple molecules (secondly) in their specific volume, refractive index, whereby the closely resemble the ethers, and (thirdly) in their behaviour to reducing agents, phosphorus pentachloride &c.

But to return to condensation: unfortunately there is still some difference of opinion as to the exact signification of this word. It has already been pointed out that Baeyer proposed to include under the term Condensation Products, all bodies which were formed from two or more molecules when these were linked together by means of the carbon atoms. If we adopt this definition then, according to Ladenburg, we will speak of condensation where "true synthetics" might profitably be employed. He has therefore proposed to restrict the term Condensation to cases where the union is between the same kind of molecule or between those which are chemically similar. The chief objection to this definition, as Baeyer himself points out, is
Chemically similar. It means of course that only such processes shall be considered as condensations as the formation of Benzene from Acetylene, Dynamic aldehyde from Benzaldehyde, acetone, aldehydes, Picolin + Collidine from Acrolein + aldehydes ammonia, etc; the action in the first class cases being between molecules of the same substances in the other between similar molecules. Most chemists at the present day regard Perkins and other analogous reactions as condensations, but if we accept the definition, limitations then we must exclude these from our list of condensations.

It remains now to examine some of the interesting so-called mechanisms of condensations. Let us first take Berthelot's synthesis of Benzene. Acetylene is represented thus:

\[ \text{CH}_2 = \text{CH}_2 \quad \text{or} \quad = \text{CH} - \text{CH} = \]

and on being passed through a heated tube three molecules unite probably in this way:

\[ \text{CH}_2 = \text{CH}_2 + \text{CH}_2 = \text{CH} \quad \rightarrow \quad \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \]

Giving rise to the Benzene ring. The double bonds between the alternate carbon atoms can also be represented.

When Marsh gas is submitted to the same treatment, Benzene is also formed. We may consider, as Berthelot suggests, that the marsh gas breaks up into acetylene and hydrogen, and that Benzene is produced by the condensation of the acetylene thus:

\[ 2 \text{CH}_4 = \text{C}_2\text{H}_2 + 3 \text{H}_2 \]

\[ + 3 \text{C}_2\text{H}_2 = \text{C}_6\text{H}_6 \]

or we may consider that the process takes place all at once, where six molecules of
marsh gas furnish one molecule of Benzene and nine molecules of Hydrogen. Thus.

These can be represented thus:

\[
\text{Benzene} = \text{Diphenyl} + \text{H}_2
\]

\[
\text{Anthracene} + 3 \text{H}_2
\]

Especially interesting is the condensation of Acetone to Menthylene. This hydrocarbon was discovered in 1837 by the late Sir Robert Kane, who obtained it by the action of sulphuric acid on acetone. Bäcker in his first attempt to explain its constitution considers it as belonging to the fatty series and supposes it to be formed by the loss of three molecules of water, thus:

In a postscript to the same paper, however, he states that owing to some researches of Tiltjé on the oxidation of methylaline which had just been published, his explanation is...
probably not correct, in so much that the oxygen atom of one molecule does not unite with a hydrogen atom from each of the \( \text{CH}_3 \) groups of another molecule but with two hydrogen atoms from one group. This being the case, its formation should be represented thus:

\[
\text{CH}_2 = \text{CH}_2 + 3 \text{H}_2 \text{O} \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2
\]

or still more clearly:

\[
\text{H}_3 \text{C} = \text{C} - \text{H}_3 + 3 \text{H}_2 \text{O}
\]

That this is the constitution that the above mechanism is right is rendered highly probable by many other considerations which need not be introduced into this paper.

Aldehydes were amongst the first bodies which furnished condensation products, two classes of which are known. The first class is obtained by the process called "aldol condensation" in which a simple union of molecules is ensurred without the separation of water, i.e., the second class is obtained by "aldehyde condensation," in which there is a separation of some other molecule. Wurtz and Claisen have shown that when acetic aldehyde is allowed to stand sometime with dilute hydrochloric acid, a simple union of aldehyde molecules takes place. Alrolo is produced:

\[
\text{CH}_3 \text{COH} + \text{CH}_3 \text{COH} = \text{CH}_3 - \text{CH} - (\text{OH}) - \text{CH}_2 - \text{COH}
\]

This is the simplest example of an aldol condensation. If this alrod or if aldehyde itself however is heated
with Chloride of Zinc, water is abstracted and crotonaldehyde is formed. This may be regarded as the type of aldehyde condensation:

\[ \text{CH}_3\cdot\text{CH} = \text{CH} \cdot \text{COH} + \text{H}_2\text{O} \]

It is to be noticed that the (OH) disappears with a hydrogen atom from the CH_2 group next to it or representing the action with aldehyde itself:

\[ \text{CH}_3\cdot\text{CH} = \text{CH} \cdot \text{COH} + \text{H}_2\text{O} \]

Or with higher aldehyde, for example propyl aldehyde. We have also the condensation taking place in the same way viz the oxygen atom of one molecule disappearing with the CH_2 of the CH_2 group of the other molecule. Thus:

\[ \text{CH}_3\cdot\text{CH} = \text{CH} \cdot \text{COH} + \text{H}_2\text{O} \]

This kind of condensation is very important, e.g., we have the action of aldehyde with the ethers of malonic acid, CH_2 = CH = CH_2, and acetoacetate, etc. One of the most important condensations the so-called Perkin's Reaction has been submitted to a good deal of critical examination. The reaction is a pretty general one for producing unsaturated acids by the condensation of aldehyde with the salt of fatty acids, in the presence of some water, abstracting substance such as anhydrous acid, etc. Perkin heated together benzaldehyde, sodium acetate and acetic anhydride obtained acrylic acid. He also explained the reaction by supposing a condensation to take place first between the aldehyde and anhydride but Fitting and others have shown that this is not the case and that an
aldehyde condensation probably takes place between the aldehyde + sodium salt, with the production of a β-salt thus.

\[ \text{C}_2\text{H}_5\text{-COH} + \text{CH}_3\text{-COONa} \to \text{C}_2\text{H}_5\text{-COONa} + \text{CH}_3\text{-COH} \]

That water is then subtracted by means of the anhydrous acid.

\[ \text{C}_2\text{H}_5\text{-CH(OH)}\text{-CH}_2\text{-COOH} \to \text{C}_2\text{H}_5\text{-CH=CH-COOH} + \text{H}_2\text{O} \]

With propionic and other higher acids the H₂ of the CH₂ which is united to carbonyl is subtracted with the oxygen of the aldehyde, for example,

\[ \text{C}_2\text{H}_5\text{-COH} + \text{CH}_3\text{-CH}_2\text{-COOH} \to \text{C}_2\text{H}_5\text{-CH=CH-COOH} + \text{H}_2\text{O} \]

In the same way condensations take place between malonic + succinic acids.

The term condensation is more particularly inner condensation has been applied to another process, namely, that by which one molecule of substance changes into the molecule of another by giving up atoms which unite to form molecules of a simpler substance such as hydrogen, water, ammonia etc. The molecule thus becomes more condensed. The formation of succinic anhydride from succinic acid

\[ \text{CH}_2\text{-C}=\text{O}-\text{H} \to \text{CH}_2\text{-C}=\text{O} + \text{H}_2\text{O} \]

is considered as an inner condensation, as also is the formation of acrylic from hydroacrylic acid. By the subtraction water from aldehydes, a ketone is produced thus, "\[\text{H} - \text{C}=\text{C}-\text{H} = \text{H} - \text{C} = \text{C} + \text{H}_2\text{O} \]" the formation of aldehydes + ketones etc. from alcohols is also regarded as an inner condensation. We have also examples of the same in the formation of the lactone from the oxy-acids.
Many of these examples of inner condensation have been known for a long time, but no importance was attached to the process until the discovery of the so-called ortho-condensation. This is an inner condensation which takes place among the ortho derivatives of benzene, the characteristic of which is that the substituting groups in the ortho position are brought into direct union with each other or form a ring. This appears to be peculiar to the ortho is not to be found among the meta and para derivatives. The formation of quinone from hydroquinone may be considered an inner condensation, the hydrogen being removed by means of some oxidizing substance.

Hydroquinone is a para derivative since it does not appear to be only with ortho derivatives that a ring is formed. It seems to me that this is an additional consideration for in favour of the constitution of quinone in which the oxygen is represented as being in the ketone combination.

Very few examples of ortho condensation are to be found in the formation of phthalic anhydride from phthalic acid

\[
\text{C}_6\text{H}_4\text{O}_2\cdots\text{O}^-\text{H} \rightarrow \text{C}_6\text{H}_4\text{O}_2 \cdots \text{O}^- + \text{H}_2\text{O}
\]

in the formation of oxindole from o-amidophenylacetic acid

\[
\text{C}_6\text{H}_4\text{O}_2\cdots\text{O}^-\text{H} \rightarrow \text{C}_6\text{H}_4\text{O}_2 \cdots \text{O}^- + \text{H}_2\text{O}
\]
and in the formation of Tatin from o-amido benzoyl formic acid.

\[
\text{O} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{H} \quad = \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{H} \quad + \quad \text{H}_2\text{O} \\
\text{O} \quad \text{N} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \quad + \quad \text{H}_2\text{O} \quad \text{etc.}
\]

Very often we have cases in which outer and inner condensation take place at the same time. Let us take, as an example, the Krafft Reaction for the preparation of Quinoline.

In this reaction a mixture of aniline and glycerine is acted on by Nitrobenzene and Sulphuric acid. The Sulphuric acid acts as the water absorbing medium and the Nitrobenzene acts in the capacity of an oxidising agent, being itself reduced to Aniline.

The first action of the Sulphuric acid is probably to convert the Glycerine into Acrolein by the abstraction of two molecules of water.

\[
\text{CH}_2\text{OH} \cdot \text{CH} = \text{OH} \cdot \text{CH}_2\text{OH} = \text{CH}_2 = \text{CH} \cdot \text{COOH} + 2\text{H}_2\text{O}
\]

A condensation then takes place between the aniline and the acrolein, thus,

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{O} \\
\text{CH} = \text{CH} = \text{CH} = \text{CH} \\
\text{H} \\
\text{O}
\end{array}
\]

An inner condensation then takes place thus,

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{O} \\
\text{CH} = \text{CH} = \text{CH} = \text{CH} \\
\text{H} \\
\text{O}
\end{array} + \text{H}_2
\]

the hydrogen being to reduce the Nitrobenzene to Aniline.

The synthesis of Indigo is also a good example of outer and inner condensation.
From considerations such as these here before referred to it will be seen that condensation is a special case of synthesis. As the multiplication of terms however requires some argument in its favor we must at last rise right of the principal feature of condensation which is the extension in the manner already described of a "carbon chain" or the branching of carbon atoms already contained in a molecule into direct or compound union; this latter expression being used to signify the introduction of the so-called "double or triple bonding" between the carbon atoms.

---

Note on the reduction of Phenylparaconic acid

Last winter I prepared Phenylparaconic acid by a slight modification of the method employed by Jayme viz. by heating together Benzaldehyde, Sodium succinate acetate anhydride and obtaining a very good yield of acid. An acid condensation probably takes place first, thus:

\[
\text{C}_6\text{H}_5\text{-COOH} + \text{CH}_2\text{-COOH} \rightarrow \text{C}_6\text{H}_5\text{-C}=\text{CH}\text{-CH}_2\text{-COOH}
\]

with the formation of Phenylsuccinic acid but this very readily loses water to give Phenylparaconic acid thus:

\[
\text{C}_6\text{H}_5\text{-C}=\text{CH}\text{-CH}_2\text{-COOH} \rightarrow \text{C}_6\text{H}_5\text{-CH}\text{-CH}_2\text{-COOH} + \text{H}_2\text{O}
\]

I then submitted this acid to the reducing action of Hydrobromic acid (boiled with powdered Condenser) and found it to undergo a complete change. After a good deal of trouble I managed to separate and purify the main product of the reaction by mean
Their calcium salts were found to be
(a) Benzyl succinic acid
(b) Phenyl butyric acid

Their formation can be represented thus:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{-CHCH}_2\text{COOH} + 2\text{H} & = \text{C}_6\text{H}_5\text{-CH}_2\text{CH}_2\text{-COOH} \\
\text{C}_6\text{H}_5\text{-CHCH}_2\text{COOH} + 2\text{H} & = \text{C}_6\text{H}_5\text{-CH}_2\text{CH}_2\text{-CH}_2\text{-COOH} + \text{CO}_2
\end{align*}
\]

so the latter may be represented as being formed from the former by the splitting off of \text{CO}_2. Thus,

\[
\text{C}_6\text{H}_5\text{-CHCH}_2\text{COOH} = \text{C}_6\text{H}_5\text{-CH}_2\text{CH}_2\text{-CH}_2\text{-COOH} + \text{CO}_2
\]

Owing to the fact that the research is not yet finished I am unable to give a more detailed account of it, but these two substances, along with a very small quantity of a neutral body which appears to be a hydrocarbon and not a lactone, are the main products of the reaction. Of these two substances, Benzyl succinic acid is produced in much larger quantity, and owing to the comparative ease with which it is obtained, this method proves to be the best method of preparation for this acid.