Thesis
for the degree of D.Sc.

"On a new general method for the preparation of the Primary Monamines"

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In the winter of 1873-74 having occasion to acquire a quantity of methylamine I tried a number of the best methods, but owing to the difficulties encountered the amount of methylamine procured was not very large. The very small yield obtained, as the result of considerable time & trouble in the preparation, suggested the idea that there was room for a process which should give a yield better proportioned to the labour expended. Since then I have always kept that idea before me, though by no means confirming my work to carrying it out, but rather returning to it in the intervals of more regular work. After several failures a process has at last suggested itself, which gives with little trouble & material comparatively large yields.

The process of working this out and the results obtained are as follows
In the summer of 1674 Dr. Leets and myself tried to obtain methylamine by the decomposition of oxalate of methyl

\[ \text{CuH}_2 + 2 \text{CuCH}_3 \]

hoping that the reaction would take place in such a manner as to leave the

\[ \text{CuH}_2 \]

and \( \text{CuCH}_3 \)

free to combine with one another so that methylamine would be produced, but in no instance did that occur.

The reactions with the following substances were tried:

- Caustic Potash
- Sodium Cyanide
- Dry distillation by itself
- Strong sulphuric acid
- Strong hydrochloric acid

With caustic potash, the reaction was apparently

\[ \text{CuH}_2 + \text{KOH} = \text{CuOK} + \text{H}_2 \text{O} \]

\[ \text{CuCH}_3 + \text{KOH} = \text{CuOK} + \text{CH}_3 \text{OH} \]

exalate of potassium, ammoniac and methyl alcohol being produced.
When distilled with stilled lime a most curious breaking up took place in molecule giving the following reaction

\[ \text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \]

Hydrocyanic acid, water, carbonate of calcium and methyl alcohol being produced to getters with other products which were not recognized or investigated. When distilled alone it somewhat more similar decomposition took place yielding some of the above product but without giving the desired product.

From the experience derived later repeated one of the above experiments using quick lime instead of stilled lime but with no beneficial results.
In the following winter in Berlin I tried one or two experiments with oxamide.

Oxamide was heated in a sealed tube with iodide of methyl in order to see if the ammonia combined as it was would act less powerfully in the iodide of methyl, so as to avoid making the secondary and tertiary monoamines, yet remain sufficiently active to act at all. Even when heated in a sealed tube to 200° C there was no action but at 250° C a small quantity of the oxamide was acted on, the H₂ and completely out of the compound of the methylamine formed, which however was produced in exceedingly small quantity, only sufficient to allow it to be recognized by its smell when set free by caustic potash.
Id. I was aware at the time that the reaction had been tried before. I reasoned that if

\[ \text{Cu} + \text{H}_2 \rightarrow \text{CuH} \]
\[ \text{Cu} + \text{H}_2 + \text{KOH} \rightarrow \text{CuOK} + \text{H}_2 \]

ammonia + caustic potash giving oxalate of potassium + free ammonia that

\[ \text{Cu} + \text{H}_2 \rightarrow \text{CuK} + \text{H}_2 \]
\[ \text{Cu} + \text{H}_2 + \text{KOH} \rightarrow \text{CuK} + \text{H}_2 \]

should give

\[ \text{CuOK} + \text{H}_2 \]
\[ \text{CuOK} + \text{H}_2 \]

Methylate of potassium oxalate should give

etherate of potassium + methylamine accordingly I prepared, not methylate of potassium oxalate. It was more easily prepared pure, ethylate of amine, carefully drying the alcohol by several
distillations over small pieces of sodiun fusing only the inside of a bar of sodium in order that no carbonic soder might be introduced. The ethylate of sodiun so produced was used at once heated with oxime in a flask with inverted condenser, but not a trace of ethyl ammo was obtained from the gas evolved which was collected in hydrochloric acid.
In the end of the following winter in New York, starting from a new basis prepared some methyl sulphate of ammonium. Boiled it with caustic potash, collecting the evolved gas in hydrochloric acid expecting that the reaction would take place thus:

\[ \text{C}_4\text{H}_3\text{SO}_4 + 2\text{K}_2\text{CO}_3 = \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + 2\text{K}_2\text{C}_4\text{H}_3 \]

Methyl sulphate of ammonium & caustic potash would give: Sulphate of Potassium, water & Methyl amine.

But on heating the hydrochlorate so obtained with caustic potash the gas which came off was not inflammable, nor was the hydrochlorate soluble to any extent in absolute alcohol. 

For the time this method was given up, but it looked so promising that in the winter of 1876-77 in Edin.

I again tried it, modifying the method.
however by using quick lime instead of common potash on the ground that in

\[ \text{CH}_3 \text{SO}_4 + \text{KHO} \]

\[ \text{H}_2\text{H}_4 \text{O} + \text{KHO} \]

The common potash presents to each molecule (the \( \text{CH}_3 \) + \( \text{H}_2\text{O} \)) hydroxyl \( \text{OH} \) that they take it up separately forming

\[ \text{CH}_3\text{OH} \]

\[ \text{H}_2\text{H}_4 \text{O} = \text{H}_2\text{H}_3 + \text{H}_2\text{O} \]

But if quick lime be used then there is only one atom of oxygen between the two.

\[ \text{CH}_3\text{SO}_4 + \text{CaO} = \text{CaSO}_4 + \text{CH}_3\text{OH} \]

\[ \text{H}_2\text{H}_4 \text{O} = \text{CH}_3 + \text{H}_2\text{O} + \text{H}_2\text{O} \]

The result of experiment justified the assumption.
For on collecting the gas given off on heating methyl sulphate of ammonia with excess of quicklime, in hydrochloric acid, evaporating on the water bath to dryness, the hydrochlorate so obtained is to the extent of from one third to one half readily soluble in a small quantity of hot absolute alcohol & when heated with quick lime it gives off a combustible gas.

The qualitative reactions show the salt to be, or at least to contain, hydrochlorate of methylamine.

The reason why so great a proportion of the hydrochlorate obtained is chloride of ammonia is that in the reaction water is produced which combines with the quicklime to form slaked lime. Which acting on the methyl sulphate of ammonia gives methyl alcohol & ammonium water so that all the methyl present could never be obtained as methylamine.
In order to see how much hydrochloric acid of methylamine is practically obtained from a given weight of the double sulphate of methyl ammonium, I took 30 grammes of the crude methyl sulphate, crude that is to say because not purified, but taken as it is prepared by precipitating a solution of calcium methyl sulphate with a solution of carbonate of ammonia, filtering and evaporating to the crystallising point, drawing the crystals drying on paper by pressure over warm sulphuric acid in an exhausted receiver. 30 grammes of this salt containing of course some sulphate of ammonium from the cleaning of the sulphate of calcium in the solution when heated with 60 grammes of quicklime gave 13 grammes of hydrochlorate of methyl ammonium were soluble in absolute alcohol.
A portion of the crude hydroxylate was exhausted with alcohol, filtered, evaporated to dryness on the waterbath of the purified salt so obtained treated with a small quantity of boiling absolute alcohol to get rid of the last traces of chloride of ammonium. This solution was precipitated with chloride of Platinum. The precipitate washed with alcohol and dried in the waterbath then at 120°C.

(1) .591 grammes taken, after ignition left .2365 grammes Platinum equal to 40.04 %.

.667 grammes gave .0275 grammes Platinum

= 41.04 %.

At a different time:

1.0155 grammes left .2355 grammes Platinum

= 42.6 %

1.2236 grammes left .528 grammes Platinum

= 42.7 %

but these were made from hydroxylate not so thoroughly freed from chloride of ammonium.
by calculation

\[
\begin{align*}
\text{Ammonium chloro-platinum} & = 14.187% \text{ Pt} \\
\text{Methyleneimine} & = 41.68 \% \\
\text{Dimethyleneimine} & = 34.36 \% \\
\text{Trimethyleneimine} & = 37.49 \%
\end{align*}
\]

A portion of the twice purified hydrochlorate was taken for the estimation of the chlorine which was done volumetrically. 1 cc of the silver solution = 0.01 gramme chlorine.

(a) 0.051 gr. required 27.5 cc = 53.9% Cl.
    0.08 - 44.1 cc = 53.7% Cl.
    0.11825 gr. - 63 cc = 53.3% Cl.

% of chlorine by calculation in Hydrochlorate
\[\text{of Methyleneimine} 52.74 \%
\]
\[\text{of Chloride of Ammon.} 63.35 \%
\]

% of the hydrochlorate of Ethyleneimine made by this process

\[
\begin{align*}
0.112 \text{ grammes required} & = 44.21 \% Cl. \\
0.107 - 47. \text{ cc} = 43.83 \% Cl. \\
0.113 - 50. \text{ cc} = 44.2 \% Cl.
\end{align*}
\]

% of chlorine in hydrochlorate
\[\text{of Ethyleneimine} = 43.55 \%\]
The same method was tried with
ethyl sulphate of Ammonia
Propyl
Isobutyl
Isamyl

under the same conditions, for the
purpose of seeing whether it was a
general method or not.

In each case the hydrochlorate when
precipitated by solution in alcohol &
evaporation to dryness, gave a combustible
gas when heated with lime & dissolved
readily in alcohol.
The chloroplatinate was, in each case
considered.

18.95 grammes of the ethylamine chloride
platinic acid gave 57.7 grammes of Platinum
equal to 70.74% calculate 70% 39.36
0.24 grammes of the benzylamine salt gave 0.87 grammes Platinum
= 36.2 % Pt, calculated 35.4 %

Grammes of the 2-benzylamine salt gave 0.87 grammes Platinum
= 36.2 % Pt, calculated 35.4 %

Grammes of the 1-benzylamine salt gave 0.87 grammes Platinum
= 33.72 % Pt, calculated 33.72 %
The yield in the case of these higher alcohols was not as good as in the case of methylamine. The process requires more care, or else the greater part of the salt splits up into ammonia and the corresponding alcohol.

It has been my intention to apply this method to:

- Phenylsulphonic acid ammonia
- Benzylsulphonic acid ammonia

in order to see if benzene would be formed, and as soon as it was in possession of these salts I shall put it to the test of experiment.

While when the diethyl methyl sulphate of ammonia is mixed with quininine and run in the distillation the gas given off smells of ammonia and of ammonia only, yet if the residue of the distillation be left when it can absorb moisture it soon smells of tri-methylamine.
Although I have not as yet pushed this method to its furthest limit, it is obvious that it becomes a general method for the preparation of the secondary and tertiary monamines. If the methylamine (or other monoamine) made at one operation be used instead of ammonia in the preparation of the methyl sulphate, the methyl sulphate of methylamine so made being heated with quinoline would give a mixture of methylamine and dimethylamine. Methyl sulphate of dimethylamine would similarly give dimethylamine and tri methylamine. In these cases however the separation of the secondary from the primary and the tertiary from the secondary monamine would not be as easy as that of ammonia from the primary monamine. It is however interesting to bring
an additional method to the only one known (Hofman's) for the preparation of these compounds.

The quaternary ammonium bases, however, could, of course, not be made in this way.

To sum up, the advantages of this method are:

- It is easy.
- It does not involve the use of costly reagents, such as cyanate of silver.
- It does not take (comparatively) much time or trouble.
- It gives a fair yield.

Its chief disadvantage lies in the extreme dilution of these ammonium salts, as this is a great disadvantage as any moisture present diminishes the yield.
Another method tried for the purpose of obtaining the mercurinnes was heating sulphate of ammonium with alcoholic potash for if

$$2\text{KHSO}_4 + (\text{NH}_4)_2\text{SO}_4 = \text{K}_2\text{SO}_4 +$$

$$+ 2\text{NH}_4\text{OH} = 2\text{NH}_3 + 2\text{H}_2\text{O}$$

Common potash + sulphate of ammonium gives sulphate of potassun. Water + ammonia might not

$$2\text{K}_2\text{H}_2\text{C}_2\text{H}_3^- + (\text{NH}_4)_2\text{SO}_4 = \text{K}_2\text{SO}_4 +$$

$$+ 2\text{NH}_4\text{OH} \text{C}_2\text{H}_3^- = 2\text{H}_2\text{O}$$

$$+ 2\text{NH}_2 \text{C}_2\text{H}_5^-.$$}

but the reaction does not appear to take place in that way. The evolved gas collected in hydrochloric acid of the which chloride tested apparently does not contain any stearinmidic.
One thing deserves notice namely, as I have before said having tried the action of a solution of some tri-ester on methyl sulphate of ammonia I obtained no methylamine, on repeating the experiment I find that it is a little but if ethyl sulphate of ammonia be substituted for the methyl sulphate there is a decidedly larger percentage of ethylamine produced than when alcohols of methylamine Besides the ethyl sulphate of ammonia is still larger proportion of dibutylamine apparently the greater the number of carbon atoms in the molecule the better the yield.