On a Condensation Product of Acetone and Aldehydammonia,

by

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Some time ago A. Hantzsch[1] obtained, by the condensation of acetone and aldehydammonia, a complex mixture of basic substances boiling between 150° and 360°, from which he could only separate collidine which was formed as a direct condensation product of aldehydammonia. I have, likewise, attempted to carry on for the last four years the same line of investigation, in a somewhat different manner and have succeeded in separating a basic substance besides collidine from that complex mixture. The results of the author's experiments have already been communicated to the Tokyo Chemical Society in June, 1888. In September of the same year E. Durkopf[2] published the results of his researches on the same subject, in which he gives an account of a basic substance which was formed by the condensation of acetone and aldehydammonia. His compound is, however, probably isomeric with that obtained by the present author, as both compounds are similar in some respects and have the same molecular formula.

In the author's experiments, a mixture of 1500 grams of acetone and 750 grams of aldehydammonia was continually heated at 120°-130° for 25 hours in a cast iron digester over an oil bath. When the digester was opened, its contents were found to be a dark brown

1. Ber. d. deut. chem. Gesel. 14, 1637.
2. „ „ „ „ „ 21, 2713.

liquid of thick oily consistency, with a strong ammoniacal odour. The whole was transferred to a retort and subjected to distillation over a water bath, by which means a greater part of the unchanged acetone was removed. The remainder of the liquid was then distilled over an oil bath to get rid of the remaining traces of acetone and the water formed in the reaction, until the temperature reached 120°. The retort was then heated above the last temperature over a direct flame, but a very small quantity of an oily liquid distilled over until the temperature attained 170°. From 170° to 230°, however, a large quantity of a pale yellow oil, and above 230° some thick syrupy liquid distilled over. The residue in the retort was of a dark brown resinous matter.

On subjecting the liquid boiling between 170° and 230° to fractional distillation, an amber-coloured oil which boils at 173°-176° was separated. It soon turns brown in contact with air, even slightly in the process of distillation. The oil has a strong stupifying odour somewhat resembling that of conine. When inhaled, it causes a headache. It is poisonous ; for a drop of it will instantly kill a large frog. It gives white fumes with hydrochloric acid, and combines with common mineral acids with the evolution of heat. It is slightly soluble in cold water, but on warming, it precipitates.

As it soon changes in contact with air, it was thought best to convert into a platinum double salt, which is more stable. To do this the oil was dissolved in dilute hydrochloric acid, and on adding platinum chloride to the solution, a double salt was precipitated as a yellow crystalline powder. The precipitate was again dissolved in hot water in which it is moderately soluble, and from the solution on cooling, large reddish-yellow feather-shaped crystals of the double salt were deposited. On repeating several times the crystallization of the double salt from the hot water, the pure salt—for such it was judged

to be from its appearance—was obtained. The crystals, after being dried over sulphuric acid, were analysed.

I. 0.3754 gram of the double salt on combustion gave 0.1502 gram H_2O and 0.414 gram CO_2.

II. 0.3755 gram of the double salt gave 0.1419 gram H_2O and 0.4245 gram CO_2.

III. 0.4451 gram of the double salt gave 0.1778 gram H_2O and 0.4636 gram CO_2.

IV. 0.3364 gram of the double salt gave 0.149 gram H_2O and 0.3488 gram CO_2.

V. At first the double salt was reduced by sodium amalgam and then the chlorine estimated in the usual manner ; upon which 0.3248 gram of the double salt gave 0.4243 gram AgCl.

VI. 0.295 gram of the double salt, when burnt with soda lime, gave 0.212 gram $2NH_4Cl.PtCl_4$.

The double salt, on ignition, gave the following amount of platinum :

I. 0.1974 gram the double salt gave 0.0594 gram Pt.
II. 0.3756 „ „ „ „ „ 0.1137 „ „
III. 0.2244 „ „ „ „ „ 0.0680 „ „
IV. 0.2569 „ „ „ „ „ 0.0769 „ „
V. 0.2020 „ „ „ „ „ 0.0611 „ „

	I.	II.	III.	IV.	V.	VI.
Carbon...	...30.07	28.39	30.81	28.27	—	—
Hydrogen ...	4.44	4.48	4.19	4.91	—	—
Nitrogen ...	—	—	—	—	4.51	—
Chlorine ...	—	—	—	—	—	32.24

	I.	II.	III.	IV.	V.
Platinum ...	...30.06	30.27	29.76	29.76	30.24

	Mean (found).	Calculated as $(C_8H_{13}N.HCl)_2PtCl_4$.
Carbon	...29.38...	... ...29.19
Hydrogen ...	... 4.50...	... ... 4.25
Nitrogen	... 4.51...	... ... 4.25
Chlorine	...32.24...	... ...32.38
Platinum... ...	...30.00...	... ...29.93
	100.63	100.00

The Hydrobichromate, $(C_8H_{13}N)_2H_2Cr_2O_7$.—To the base dissolved in dilute sulphuric acid, some crystals of potassium bichromate were added and the mixture gently heated. On cooling the solution, the hydrobichromate crystallized out in large brilliant yellow prismatic plates, and upon recrystallization it was soon obtained pure. It is sparingly soluble in cold, but easily in hot water. When heated, it deflagrates and leaves a green oxide Cr_2O_3. The crystals of the hydrobichromate, after being dried over sulphuric acid, were analysed :

I. 0.3557 gram the salt gave, on combustion, 0.1853 gram H_2O and 0.5491 gram CO_2.

II. 0.2504 gram the salt, when ignited, gave 0.0831 gram Cr_2O_3.

III. 0.1886 „ „ „ „ „ „ 0.062 „ „

	Found.			Calculated as $(C_8H_{13}N)_2H_2Cr_2O_7$.
	I.	II.	III.	
Carbon	41.88	—	—	...41.31
Hydrogen	5.79	—	—	... 6.02
Nitrogen	—	—	—	... 6.02
Chromium	—	22.36	22.54...	...22.54
Oxygen	—	—	—	...24.09

The Mercury Double Chloride, $C_8H_{13}N.HCl.2HgCl_2+H_2O$.—On adding the solution of mercuric chloride to the aqueous solution of the hydrochloride of the base, fine hairy white crystals separated out in

a few minutes, and upon recrystallization from a solution in hot water, the pure double salt, for so it was judged to be from its appearance, was obtained in large brilliant scaly plates. The salt melts at 148°-149°. It partially volatilizes at above 100°. It seems to contain one molecule of the water of crystallization, but on account of its volatility its amount cannot be accurately determined by the usual method. The crystals of the double salt, after being dried over calcium chloride, were analysed :

(I.) 0.3957 gram the double salt gave 0.3941 gram AgCl.
(II.) 0.3645 „ „ „ „ „ 0.2353 „ HgS.

	Found. I.	Found. II.	Calculated as $C_8H_{13}N.HCl.2HgCl_2 + H_2O$.
Chlorine...	...24.64	— ...	... ...24.66
Mercury...	... —	55.63...	... ...55.59
Water ...	... —	— ...	... ... 2.50

The crystals of the double salt, finely pulverized, were heated over an air bath at 130° for some time, by which the powder became compact, having apparently lost its water of crystallization through partial volatilization. The salt was then analysed.

0.3887 gram the anhydrous salt gave 0.2593 gram HgS.

	Found.	Calculated as $C_8H_{13}N.HCl.2HgCl_2$.
Mercury... ...	...57.83...	... ...57.2

On comparing this analytical result with that given in the preceding analysis, we may infer that the salt contained one molecule of water.

The Gold Double Salt, $C_8H_{13}N.HCl.AuCl_3$.—This was prepared by adding an alcoholic solution of gold chloride to an aqueous solution of the hydrochloride of the base. On driving off the alcohol from the solution, the double chloride separated out as a crystalline precipitate, which consisted of microscopic yellow needles. It was

redissolved in hot water and repeatedly recrystallized. It melts under hot water to a sticky oily mass and solidifies again on cooling. The salt, dried over calcium chloride, was analysed :

0.3386 gram the salt gave 0.1452 gram Au.

	Found.	Calculated as $C_8H_{13}N.HCl.AuCl_3$.
Gold... ...	...42.88...	... ...42.54

The Hydrochloride, $C_8H_{13}N.HCl$.—On mixing concentrated hydrochloric acid and the base together, they combined energetically with the evolution of heat, and the mixture solidified. The whole mass was then dissolved in alcohol, and on concentrating the solution nearly to dryness the hydrochloride crystallized out, in an impure state, in the form of long needles. The impure salt thus obtained was purified by dissolving it in the smallest possible quantity of alcohol, and then adding ether to the alcoholic solution, by which means the hydrochloride was precipitated in fine colourless needles, as it is insoluble in ether. It is exceedingly deliquescent in air. The crystals seem to decompose under a desiccator, as they soon lose their transparency, probably giving off a part of hydrochloric acid. The crystals, dried over sulphuric acid under a desiccator, were analysed :

I. 0.1540 gram the salt gave 0.1300 gram AgCl.
II. 0.2112 „ „ „ „ 0.1819 „ „
III. 0.1500 „ „ „ „ 0.1276 „ „

	Found.			Calculated as $C_8H_{13}N.HCl$.
	I.	II.	III.	
Chlorine... ...	...20.88	21.25	21.32...	... ...22.25

The low percentage of chlorine, in the above analysis, may possibly be due to the decomposition of the salt during desiccation.

The Hydrobromide, $C_8H_{13}N.HBr$.—On adding bromine to the base dissolved in ether containing some alcohol, the hydrobromide

separated out in colourless transparent prismatic needles. The salt, dried over calcium chloride, was analysed :

0.2946 gram the salt gave 0.27 gram AgBr.

	Found.	Calculated as $C_8H_{13}N.HBr$.
Bromine...	...39.13...	... ...39.21

The Acetyl Compound, $C_8H_{12}N(CH_3CO)$.— This was prepared in the usual way, by dissolving the base in anhydrous ether and adding acetyl chloride to it. The hydrochloride of the acetyl compound thus precipitated was purified by repeated recrystallization from the mixture of alcohol and ether. It crystallizes in fine needles, in appearance very much like the hydrochloride of the base. It is very deliquescent. The free acetyl compound separates out as an oil, on adding caustic potash to its hydrochloride. The salt, dried over calcium chloride, was analysed.

0.2649 gram the hydrochloride of the acetyl compound gave 0.1906 gram AgCl.

	Found.	Calculated as $C_8H_{12}N.(CH_3CO)HCl$.
Chlorine... ...	...17.79...	... ...17.61

The Nitroso-compound, $C_8H_{12}N.NO$.—On adding pieces of solid potassium nitrite gradually to the aqueous solution of the hydrochloride of the base, a large quantity of a thick brown oily substance separated. It was extracted with ether, and shaken with water, and again extracted with ether. After repeating the same process of washing several times, the oil, dried over calcium chloride, was once distilled. It is a pale yellow oil, having the characteristic odour of nitrosamine. It gives the well-known Liebermann's nitroso-reaction ; consequently the base itself is a secondary amine.

The solution left after separating the nitroso-compound, was treated with caustic potash, by which a small quantity of an oil was

precipitated. The latter was then changed into an hydrochloride, and consequently into a double salt, with mercuric chloride. The double salt thus prepared was found to be identical with the double salt of the original base, agreeing in its crystalline form, melting point, and analytical results. The double salt, dried over calcium chloride, was analysed, and the results were as follow :

I. 0.2396 gram the double salt gave 0.2353 gram AgCl.
II. 0.2000 „ „ „ „ „ 0.1958 „ „
III. 0.3165 „ „ „ „ „ 0.2037 „ HgS.
IV. 0.3378 „ „ „ „ „ 0.2200 „ „

	Found.				Calculated as
	I.	II.	III.	IV.	$C_8H_{13}N.HCl.2HgCl_2+H_2O$.
Chlorine...	...24.30	24.22	—	—	...24.66
Mercury...	... —	—	55.47	55.50...	...55.59

It is evident, therefore, that a greater part of the base changed into a nitrosamine, and the oil separated from the solution with caustic potash was simply the base unchanged.

According to the results of analysis thus far, it is highly probable that the author's base has the formula $C_8H_{13}N$ and differs in many respects from the base isolated by Durkopf,* although they are isomeric.

The Oxidation and Decomposition of the Base.

On heating 10 grams of the base freshly distilled, with the chromic acid mixture consisting of 20 grams of potassium bichromate and 20 grams of sulphuric acid diluted with its own volume of water, the mixture gradually became green with the evolution of CO_2. The

* Durkopf's base is stated to change into collidine on treating it with KNO_2.—Ber. d. deut. chem. Gesel. 14,2713.

green solution thus formed was mixed with a large quantity of water and subjected to distillation; and in the distillate was found a considerable quantity of acetic acid and a little formic acid.

Next, the base was subjected to oxidation with a potassium permanganate solution containing 1 part of potassium permanganate to 8 parts of water. To the base a small portion of the solution was added from time to time, and it was heated over a water bath, and at each addition the solution was found immediately to decolorize, probably through the rapid breaking up of the base. The products of the oxidation were found to consist mainly of carbon dioxide and acetic acid.

On distilling the base with dilute sulphuric acid, mesityl oxide was produced as one of the decomposition products, and on further continuing the distillation, it gradually became black, evolving SO_2.

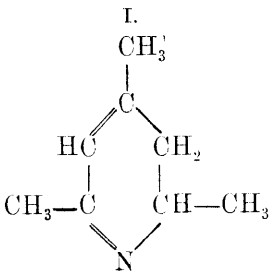
The Probable Constitution of the Base.

The condensation of aldehydammonia and acetone into the base $C_9H_{13}N$ may be represented by the following equation:

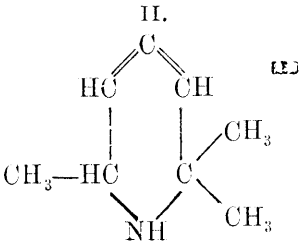
$$C_2H_7NO + 2\,C_3H_6O - 3H_2O = C_9H_{13}N.$$

Accepting the above equation as true, the formation of the base, by condensation may be possible in three ways, as may be seen in the following formulæ:

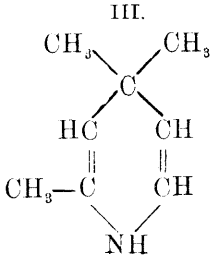
I.



II.



III.



The base would be identical, according to I, with Hantzsch's dihydrocollidine[1], and according to II, with a dehydroderivative of Heintz's vinyldiacetonamine[2]; but from the results of the experiments so far obtained, the author's base cannot be either one or the other. It is, however, very probable that it has the formula III, considering the experimental results on the behaviour of the base given in the present paper. The details of its structure will be communicated in a future paper, as further investigations are being carried on.

1. Annalen d. Chem. **215**, 1.
2. „ „ „ **178**, 326; **189**, 314; **191**, 122.

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