148. *The Interaction of Ammonium and Alkylammonium Sulphides with Aqueous Formaldehyde.*

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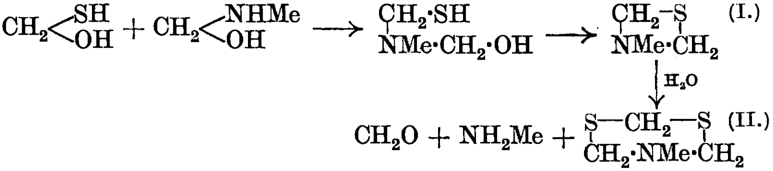
IN the hope of obtaining further information regarding the reaction between ammonium sulphide and formalin (Le Fèvre and Macleod, J., 1931, 474), the interactions of substituted ammonium sulphides with formaldehyde in dilute aqueous solution at 0° have been studied. Addition of aqueous methylamine saturated with hydrogen sulphide to formalin solution produced immediately a white precipitate, C_3H_7NS (I); the filtrate slowly deposited a substance which was shown to be the "methylthioformaldin," $(CH_2)_3S_2NCH_3$ (II), of Wohl (*Ber.*, 1886, **19**, 2345). The compound (I) was converted into (II) by aqueous acetone, and the mother-liquor reacted as if it contained methylamine and formaldehyde only. Thus the formulations (I) and (II) are not improbable.



$$CH_2\begin{smallmatrix}SH\\OH\end{smallmatrix} + CH_2\begin{smallmatrix}NHMe\\OH\end{smallmatrix} \longrightarrow \begin{matrix}CH_2{\cdot}SH\\ NMe{\cdot}CH_2{\cdot}OH\end{matrix} \longrightarrow \begin{matrix}CH_2-S\\ NMe{\cdot}CH_2\end{matrix} \quad (I.)$$

$$\xrightarrow{H_2O} CH_2O + NH_2Me + \begin{matrix}S-CH_2-S\\ CH_2{\cdot}NMe{\cdot}CH_2\end{matrix} \quad (II.)$$

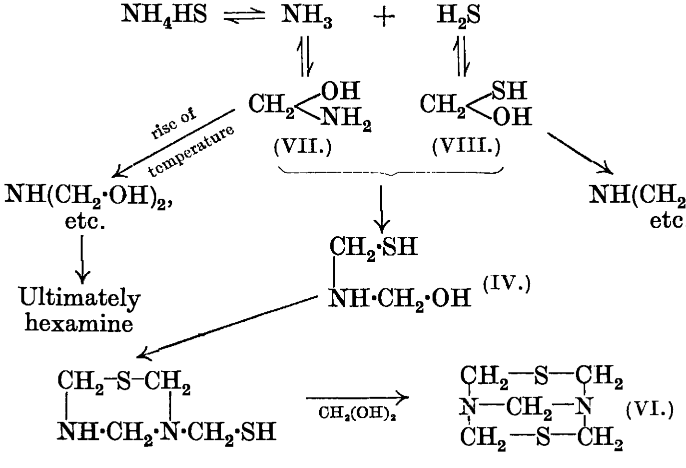
Addition of a well-cooled ethylamine solution saturated with hydrogen sulphide to excess of formaldehyde solution afforded a colourless oil, which was analysed as its *hydrochloride* and corresponded in composition to the methyl analogue (I). Both the compounds from the substituted amines, but not the thialdine (II), were rapidly hydrolysed by hot mineral acid, giving trithioformaldehyde, the amine salt, and formaldehyde.

Aqueous aniline similarly afforded with hydrogen sulphide and formalin an oily substance, which, like the white amorphous compound obtained from hydrazine hydrate and the oils obtained from dimethyl- and diethyl-amine sulphides, gave trithioformaldehyde on hydrolysis with hot hydrochloric acid. From piperidine, however, a well-crystallised compound, $C_{12}H_{26}ON_2S$, was obtained. Since here the initially formed substance, $C_5H_{10}N{\cdot}CH_2{\cdot}OH$, could not produce a compound of the type (I), it is possible that, by interaction with hydrogen sulphide, dipiperidinomethyl sulphide, $(C_5H_{10}N{\cdot}CH_2)_2S$ (III), was formed, and isolated as the monohydrate.

Composition of the Ammonium Sulphide–Aqueous Formaldehyde Precipitate (Le Fèvre and Macleod, *loc. cit.*).—The constitutions of the above compounds derived from methyl- and ethyl-amines make it reasonable to suppose that the original ammonium sulphide–formaldehyde precipitate might be formed *via* some intermediate such as (IV). After crystallisation from dimethylaniline, it melts at 200° and has the composition $C_5H_{10}N_2S_2$ (V). It is very slightly soluble in most of the common solvents, but gives in dilute mineral acids solutions from which trithioformaldehyde soon crystallises. The yield of thioaldehyde is slightly less than half the weight of the substance hydrolysed; therefore the molecular weight of the latter must be $(2 \times 46)_n$, which, when $n = 2$, is in fair agreement with the above formula. From chloroform solutions of the substance, impure specimens of an unstable, hygroscopic, crystalline hydrochloride, m. p. 110° (decomp.), bromo-derivative, gummy methosulphate, and methiodide, m. p. 70—72° (decomp.), were obtained by addition of the appropriate reagent.

Formula of the Substance, m. p. 200°.—The instability of the previously mentioned derivatives rendered the verification of a structural formula for (V) difficult. In view of (1) the similarity between (I) and (V) and their rapid hydrolysis to trithioformaldehyde, in contradistinction to the slow hydrolysis of the thialdine (II), and (2) the general tendency for formaldehyde derivatives to undergo polymerisation, the formula (VI) is advanced for (V). The yield of (V) falls off almost linearly with increase of the temperature of admixture of the formaldehyde and ammonium sulphide. This should be the case if, with increase of temperature, further combination of formaldehyde with (VII) and (VIII) occurred, as suggested in the scheme below, to give compounds which are so complex as to be unable to condense to yield (IV). Support is forthcoming from the following experiment to illustrate the inhibiting effect of complex molecules. Two equal volumes of 40% formalin were taken. One was diluted with 3 volumes of water, a deficiency of ammonia solution (*d* 0·88) added, the mixture cooled, and hydrogen sulphide passed into it; a white gummy precipitate was soon formed. The other undiluted formaldehyde solution was cooled and treated with the ammonia evolved by boiling the same volume of aqueous ammonia as used before; hydrogen sulphide now produced an opalescence only after being passed for a much longer time than in the first case. Whereas in the first solution the ammonia had formed the intermediates (IV), (VII), and (VIII) (compare Werner, J., 1917, **111**, 844), in the second solution it existed largely as trihydroxytrimethylamine (Henry, *Centr.*, 1903, i, 439) and thus could not directly lead to (VI).

A chloroform solution of (VI) absorbed two atoms of bromine immediately and two more less rapidly. Further absorption was slow. This observation is not irreconcilable with formula (VI), for hexamethylenetetramine, the symmetrical formula of which (Duden and Scharff, *Annalen*, 1895, **288**, 218) has been confirmed by Gonell and Mark (*Z. physikal Chem.*, 1923, **107**, 181) by *X*-ray methods, takes up directly only two or four atoms of bromine or iodine (Horton, *Ber.*, 1888, **21**, 2000; Legler, *ibid.*, 1885, **18**, 3350) and combines with only one molecule of alkyl halide or a half molecule of alkylene dihalide (Wohl, *Ber.*, 1886, **19**, 1843; Delépine, *Bull. Soc. chim.*, 1897, **17**, 293). The scheme indicating the formation of the compound (VI) is as follows :



EXPERIMENTAL.

Interaction of Methylamine, Hydrogen Sulphide, and Formaldehyde. —Aqueous methylamine (170 c.c. of 30% solution), diluted with 350 c.c. of water, was saturated with hydrogen sulphide at 0°, and run during ½ hour into a stirred mixture of 40% formaldehyde (200 c.c.), ice, and water (400 c.c.). After an hour, the white precipitate (I) was collected, washed with hot water, and dried in the air (yield, 67 g.; m. p. 108—115°, decomp. 169—175°). It was readily soluble in chloroform, pyridine, acetic acid, carbon tetrachloride, ether, benzene, and ligroin, and crystallised from acetone in thick needles, m. p. 138—139° (Found: C, 40·5; H, 7·7; N, 15·8*; S, 36·2. C_3H_7NS requires C, 40·4; H, 7·8; N, 15·7; S, 36·0%). With hydrogen chloride in benzene solution (200 parts), it gave a gummy hydrochloride, an aqueous solution of which slowly deposited trithioformaldehyde.

The mother-liquor of the substance (I) deposited, after 36 hours, a substance (12 g.) which crystallised from acetone and then had m. p. 65—66° (Found: C, 35·5; H, 6·8; N, 10·6*; S, 47·5. Calc.: C, 35·6; H, 6·7; N, 10·4; S, 47·4%), alone or mixed with "Methylthioformaldin," prepared by Wohl's method (*loc. cit.*). It formed with ethereal methyl iodide, after 30 hours, needles of the monomethiodide, m. p. 164° (decomp.) (Wohl gives 161—163°, decomp.) (Found: I, 45·9. Calc.: I, 45·85%), from an aqueous solution of which picric acid precipitated the corresponding methopicrate, m. p. 238° (after previous shrinking and charring), as yellow matted needles. The crystalline hydrochloride, prepared in well-cooled dilute benzene solution, had m. p. 193—194° (decomp.) (Wohl gives 188°, decomp.) (Found: Cl, 20·9. Calc.: Cl, 20·7%); in dilute hydrochloric acid solution, it gave precipitates with platinic chloride (see Wohl, *loc. cit.*), mercuric chloride, and concentrated ferric chloride solution.

Preparation of Wohl's "Methylthioformaldin" from Substance (I).—Attempts to prepare a methiodide from (I) resulted in a gum, from which was ultimately obtained in small yield a product, m. p. 163—164° (Found: I, 46·0%), identical (mixed m. p.) with the methiodide obtained above from Wohl's compound.

Substance (I), suspended in aqueous acetone, slowly dissolved, and the solution gradually deposited a dirty-white substance, m. p. 59—61° (raised to 65° by admixture with Wohl's compound): this, in benzene solution, gave a hydrochloride, m. p. 192—193° (decomp.), from which Wohl's "Methylthioformaldin" was regenerated by stirring with aqueous ammonia.

The preparation was satisfactorily conducted by dissolving substance (I) (5 g.) in 50 c.c. of warm acetone, adding water to the cold solution to crystallising point, and after 5 days stirring in water (5 vols.); 2·1 g. of large plates, m. p. 63—65°, were obtained (calc., 3·7 g.).

Interaction of Ethylamine, Hydrogen Sulphide, and Formaldehyde.—Ethylamine (55 c.c. of 33% aqueous solution), diluted with 250 c.c. of water, was cooled to 0° by addition of ice, saturated with hydrogen sulphide, and added quickly to 100 c.c. of 40% formaldehyde solution diluted with 200 c.c. of water, the whole being cooled in ice–salt. Hydrogen sulphide was passed into the only emulsion for a further 2 hours. After 12 hours, the product was extracted and dried (with sodium sulphate) in benzene and recovered. As it could not be distilled without decomposition, it was redissolved in benzene, mixed with light petroleum, cooled to – 10°, and treated with hydrogen chloride; a white trioxymethylene-like *hydrochloride* (31 g.) was obtained, m. p. 100—150° (Found: N, 10·4*. C_4H_9NS,HCl requires N, 10·0%), from which cold 4*N*-aqueous sodium hydroxide regenerated the base as an oil which did not solidify in ice–salt.

Interaction of Aniline, Hydrogen Sulphide, and Formaldehyde.—The usual process, applied to aniline (5 c.c.), water (300 c.c.), ice (50 g.), and formaldehyde (25 c.c. of 40% solution and 100 c.c. of water), led to a white gum which could not be crystallised. When boiled with an excess of concentrated hydrochloric acid, it gave a yellowish powder, from which, by crystallisation from acetone, trithioformaldehyde was obtained, m. p. and mixed m. p. 215—216°.

Action of Formaldehyde on Hydrazine Hydrate saturated with Hydrogen Sulphide.—A mixture of hydrazine hydrate (20 c.c. of 90% solution) and 300 c.c. of ice and water was treated with hydrogen sulphide for 2 hours and dropped during 1 hour into a mixture of formaldehyde (390 c.c. of 40% solution), and ice and water suspension (700 c.c.). After 1 hour's stirring, the white precipitate was collected, washed, and dried (32 g.). It formed an impalpable powder, soluble in ligroin, chloroform, and acetic acid. An extract of 5 g. of the substance in 200 c.c. of boiling pyridine gave, on cooling, 1 g. (residue, 3 g.) of a micro-crystalline powder, m. p. 248—250° (decomp.) (Found: C, 35·8; H, 5·7; N, 30·4; S, 22·9%), of unknown constitution.

Reactions between Dimethyl- and Diethyl-amines, Hydrogen Sulphide, and Formaldehyde.—The usual procedure was applied to (*a*) dimethylamine (100 c.c. of 33% solution), water, and ice (300 c.c.); 180 c.c. of 40% formalin and water and ice (350 c.c.), and (*b*) diethylamine (130 c.c. of 30% solution), water, and ice (500 c.c.); formaldehyde (180 c.c.) and water and ice (400 c.c.): time of addition, 1 hour. The oily products, which were extracted in light petroleum in (*a*) and in benzene in (*b*), could not be distilled without decomposition and did not give crystalline salts.

Hydrolysis of the Preceding Compounds by Mineral Acid.—A solution of any one of the preceding compounds in warm dilute hydrochloric or sulphuric acid sooner or later deposited trithioformaldehyde, m. p. 216°. With concentrated hydrochloric acid at 100° as the hydrolysing agent the yield of trithioformaldehyde obtained, calculated from the weight of substance taken, was 35—40% from the methylamine derivative (I), 25% from the ethylamine derivative, 40% from either the diethyl- or the dimethyl-amine derivative, and 20% from the hydrazine derivative.

Interaction of Piperidine, Hydrogen Sulphide, and Formaldehyde.—Piperidine (15 c.c.) and water (100 c.c.) were together saturated with hydrogen sulphide and added to 40% formalin (100 c.c.) and water (200 c.c.), both mixtures being ice-cold. Crystals were soon produced (15 g., m. p. 61—62° after washing), very soluble in chloroform, benzene, pyridine, light petroleum, acetic acid, ether, and acetone. From aqueous acetone, 10 g. of white granular crystals, m. p. 56°, were obtained (Found: C, 58·6; H, 10·2; N, 11·2*; S, 13·1. $C_{12}H_{26}ON_2S$ requires C, 58·6; H, 10·6; N, 11·4; S, 13·0%). The *compound* dissolved readily in mineral acids, but did not appear to undergo hydrolysis. From a dilute hydrochloric acid solution, concentrated aqueous ferric chloride precipitated a yellow ferrichloride; picric acid afforded a light yellow picrate.

Preparation of the Substance (VI).—To ordinary ammonium sulphide (500 c.c. of approx. 16% solution), diluted with water (3,000 c.c.), formaldehyde (350 c.c. of 40 % solution) was run in, with vigorous stirring, during 12 minutes, the temperature being kept below 25°. The micro-crystalline powder produced was collected after 12 hours, washed with much water, and dried in the air; m. p. 125—145°.

Variation of the yield with temperature. The two solutions to be mixed (quantities as above) and a large reaction vessel, fitted with a stirrer and a thermometer, were brought to the same temperature in a water-bath. The mixing was then done and the highest temperature reached during the precipitation was noted (generally there was a rise of some 10°). The mean of the initial and the final temperature was taken as the temperature of the reaction.

Temp.	0°	12°	20°	42°	57°	70°	92°
Yield, g.	130	140	130	108	84	68	41

Properties. The crude substance is not very soluble in the common solvents except chloroform. It can be crystallised from chloroform, *cyclo*hexanol, and tritolyl phosphate, but best from dimethylaniline. The process is wasteful, much formaldehyde being evolved. From 40 g. of the crude material, about 7 g. of a white crystalline substance were obtained, m. p. 190° raised to 200° by further crystallisation (Found: C, 37·2; H, 6·2; N, 17·3*; S, 39·5; *M*, in camphor, 182. $C_5H_{10}N_2S_2$ requires C, 37·0; H, 6·2; N, 17·3; S, 39·5%; *M*, 162).

Action of bromine. Addition of a dilute solution of bromine in chloroform to a chloroform solution of (VI) yielded a magma of crystals which appeared to decompose on filtration. A rapidly collected specimen underwent slight melting at 80° and became a clear liquid at 135—136°. 0·1794 G. required 6·43 c.c. of bromine solution (2·9824 g. in 100 c.c.) to give a noticeable excess of bromine; whence 1 g.-mol. (162 g.) would require 173 g. of bromine (calc. for 2Br, 160 g.).

Addition of twice the above amount of bromine solution to a similar solution of (VI) caused re-solution of the white bromo-derivative. After 3 days the excess of bromine had disappeared.

Action of acids. Substance (VI) dissolved fairly easily in dilute mineral acids, but was violently oxidised by nitric acid. A solution in hot hydrochloric or dilute sulphuric acid soon deposited white needles of trithioformaldehyde, m. p. 216° (Found: S, 69·4. Calc.: S, 69·5%). The filtrate contained formaldehyde (identified, after distillation in steam, as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 165°) and an ammonium salt. The quantity of ammonia found by titration in the steam-distillate from the solution (made alkaline) corresponded to the percentage of nitrogen found in (VI) by combustion. All the nitrogen, therefore, is hydrolysable.

The substance (VI) dissolved slightly in cold glacial acetic acid (about 8·5 g. in 300 c.c.). After 5 days the solution had deposited about 3 g. of a white crystalline substance, m. p. 175—176° after recrystallisation from acetic acid (Found: N, 9·1; S, 55·5%).

The analyses, except those marked with an asterisk, are micro-analyses made by Dr.-Ing. A. Schoeller.

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