

## 165. Methylenechloroamine.

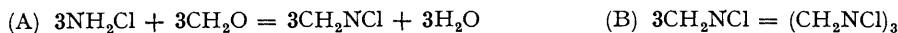
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Methylenechloroamine, prepared by the action of monochloroamine on formaldehyde, first isolated by Cross, Bevan, and Bacon, has been shown to be identical with *N*-trichlorotrimethylenetriamine obtained from hexamethylenetetramine and hypochlorite isolated by Delépine. The formation of the trimeric form in solution from monochloroamine and formaldehyde has been followed cryoscopically.

CROSS, BEVAN, and BACON (*J.*, 1910, **97**, 2404) prepared methylenechloroamine of empirical formula  $\text{CH}_2\text{NCl}$  by allowing monochloroamine and formaldehyde to react in aqueous solution, obtaining molecular weights of 133, 132.7, and 131.7 [Calc. for  $(\text{CH}_2\text{NCl})_2$ : 127] from f. p. measurements in benzene. Delépine (*Compt. rend.*, 1899, **128**, 108) obtained a compound  $(\text{CH}_2\text{NCl})_3$  from formaldehyde-ammonia and hypochlorous acid, and later (*Bull. Soc. chim.*, 1911, **9**, 1025) showed that hypochlorite reacts with aqueous solutions of hexamethylenetetramine to form *N*-dichloropentamethylenetetramine, but in the presence of acetic acid gives *N*-trichlorotrimethylenetriamine which has the same composition as Cross, Bevan, and Bacon's compound.

In the present work the compound resulting from monochloroamine and formaldehyde has been further examined. Molecular-weight determinations in benzene and in nitrobenzene using Roberts and Bury's method (*J.*, 1923, **123**, 2040) all gave values *ca.* 190 corresponding to the formula  $(\text{CH}_2\text{NCl})_3$ . The solids prepared (i) by this method and (ii) by the action of hypochlorite on hexamethylenetetramine in the presence of acetic acid decomposed before melting at about 75°. Samples of each were submitted to Dr. F. J. Turner of the Department of Geology, University of Otago, who reported that they were crystallographically identical. The optic axial angle,  $2V$ , for sample (i) had values 76, 78, 75, 76, 78, 79, and for sample (ii) 73, 82, 76, 78, 80. Optic sign +.

The rate of formation of the methylenechloroamine,  $\text{CH}_2\text{NCl}$ , from monochloroamine and formaldehyde and of its polymerisation to the trimeric form have been followed cryoscopically. This is possible since



reaction (A) in water is attended by a disappearance of 3 solute molecules and reaction (B) by a further disappearance of 2 solute molecules. The initial reaction takes place at temperatures near 0° in under 5 minutes, whereas the polymerisation is complete in about 1 hour, as shown by plotting freezing points of the aqueous mixture of formaldehyde and monochloroamine against time.

Cryoscopic measurements using acetaldehyde were in accord with the view that 1 mol. of chloroamine reacts with 1 mol. of acetaldehyde to form an analogous chloroamine,  $\text{CH}_3\text{CH:NCl}$ . The freezing point rose slightly above the value for the monomeric compound, indicating some polymerisation, but later fell rapidly, indicating decomposition. The compound isolated from acetaldehyde-ammonia and hypochlorite was similarly unstable, deflagrating when dry (cf. Delépine, *Compt. rend.*, 1897, **125**, 951), and we could not make molecular-weight determinations.

## EXPERIMENTAL.

*Materials.*—Monochloroamine was prepared as in "Inorganic Syntheses," **1**, 59. The solution (0.5M) was stabilised by adding a small quantity of ammonia (0.005N) which caused a negligible depression of the freezing point. The molar concentration given cryoscopically exceeds that of monochloroamine, estimated iodometrically, owing to the presence of ammonium chloride unavoidably formed by the decomposition  $3\text{NH}_2\text{Cl} = \text{NH}_4\text{Cl} + \text{N}_2 + 2\text{HCl}$ . Formaldehyde was prepared by heating paraformaldehyde in water, and the molar concentration obtained cryoscopically agreed with that obtained by oxidation with hydrogen peroxide in the presence of excess of standard sodium hydroxide and back titration with standard acid.

Methylenechloroamine was prepared for molecular-weight determinations by the method of Cross, Bevan, and Bacon (*loc. cit.*); it separated after approximately 15 minutes in feathery crystals, and, after being dissolved in chloroform and dried, it was deposited in long, shining needles (purity 95—99.5% by titration). When prepared by Delépine's method from hexamine and hypochlorite acidified with acetic acid, the solid was deposited first as feathery crystals and behaved similarly on recrystallisation from chloroform.

*Molecular Weights in Benzene and Nitrobenzene.*—By using weights of solute, prepared by Cross, Bevan, and Bacon's method, of 0.2—0.46 g. in 22 g. of "AnalaR" benzene, molecular weights of 198, 190, and 180 were obtained [Calc. for  $(\text{CH}_2\text{NCl})_3$ : 190.5]. To determine whether the chloroamine is trimeric under more dissociating conditions, nitrobenzene was used. This solvent has the disadvantage of being hygroscopic, but by using the salt hydrate pair, anhydrous sodium sulphate and decahydrate (2 g. in 20 g. of nitrobenzene), the water content is kept constant (Roberts and Bury, *loc. cit.*). The results obtained by using 0.07—0.58 g. of solute in 20 g. of nitrobenzene were 196.0, 203.0, 182.7, 178.0, 194.5, 194.0, 191.8; mean 191.

*Rates of Formation and Polymerisation of Methylenechloroamine.*—A 1.0M-solution of formaldehyde or of monochloroamine will depress the f. p. of water by 1.87°. Hence if an aqueous solution is 1.0M with respect to each, the f. p. of the solution should be approximately  $-3.74^\circ$ . As the reaction  $\text{NH}_2\text{Cl} + \text{CH}_2\text{O} \longrightarrow \text{CH}_2\text{NCl} + \text{H}_2\text{O}$  proceeds, the f. p. should rise to  $-1.87^\circ$ , and if the polymerisation  $3\text{CH}_2\text{NCl} \longrightarrow (\text{CH}_2\text{NCl})_3$  occurs without separation of solid, the f. p. should rise to  $-0.62^\circ$ . The further rise towards 0° as the trimer crystallises out is limited by its partial solubility, and by the presence of any decomposition products.

In the actual experiment corresponding to the table, the monochloroamine solution containing ammonium chloride as impurity had a f. p. depression of 1.40°. The concentration of the monochloroamine in solution, from its iodine titre, was 0.29M. To 20 c.c. of the monochloroamine solution, 1.20 c.c. of 4.98M-formaldehyde were added, making the concentration of monochloroamine 0.27M and of formaldehyde 0.28M. Thus the solution of monochloroamine (with its accompanying ammonium chloride) has been diluted in the ratio of 20 to 21.2 c.c., giving a depression of 1.32°, which would be increased, if no reaction occurred, by 0.52° by the presence of 0.28M-formaldehyde, giving a total f. p. depression of 1.84°. If the monomeric chloroamine is formed, the depression should clearly decrease to 1.32°, and still further

to 0.98° if the trimeric chloroamine is formed without separation as solid. The freezing points observed are given below.

Time (mins.)	.....	5	10	15	20	25	30	40	50	60	70	77	91	123
$\Delta T$	.....	1.32°	1.27°	1.23°	1.17°	1.12°	1.11°	1.07°	1.04°	1.00°	0.97°	0.94° <sup>1</sup>	0.87° <sup>2</sup>	0.86°

<sup>1</sup> Solution becoming cloudy.

<sup>2</sup> White solid separating.

It is clear that the formation of the monomeric form has been completed within 5 minutes, and that the polymerisation continues at the temperature of the experiment over the following hour.

Other runs gave similar curves, but if formaldehyde is in excess a comparatively slow side reaction occurs, as shown by a greater rise than is required for the formation of  $(\text{CH}_2\text{NCl})_3$ . This is due to the formation of hexamethylenetetramine by the reaction  $6\text{CH}_2\text{O} + 4\text{NH}_4\text{Cl} = \text{C}_6\text{H}_{12}\text{N}_4 + 4\text{HCl} + 6\text{H}_2\text{O}$ . This reaction cannot occur appreciably when equimolar amounts of chloroamine and formaldehyde are used, owing to the rapid removal of the formaldehyde as methylenechloroamine.

When the concentration of monochloroamine is in slight molar excess, the polymerisation appears to be slower. When a mixture 0.32M with respect to formaldehyde and 0.37M with respect to monochloroamine was examined, the initial rise of the f. p. corresponded to a disappearance of 0.32 mol. from the solution, *i.e.*, to the formation of monomeric methylenechloroamine. The freezing point stayed approximately constant at this level for about 15 minutes before rising.

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