XVII.—*The Preparation of Monomethylamine from Chloropicrin.*

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The products of the reduction of chloropicrin seem to vary with the nature of the reducing agent. With stannous chloride and hydrochloric acid, cyanogen chloride is produced (Raschig, *Ber.*, 1885, **18**, 3326). The occasional formation of traces of ammonia was noticed by this chemist, but as a rule, after removing the tin by means of hydrogen sulphide, the product was found to be free from ammonium chloride and the hydrochlorides of hydroxylamine and methylamine. Iron filings and acetic acid (Geisse, *Annalen*, 1859, **109**, 282) or tin and hydrochloric acid (Wallach, *ibid.*, 1877, **184**, 51) give rise to monomethylamine,

$$CCl_3{\cdot}NO_2 + 12H = CH_3{\cdot}NH_2 + 3HCl + 2H_2O.$$

Since chloropicrin may easily be obtained in large quantities, it appeared desirable more closely to investigate its reduction, owing to the importance of monomethylamine in synthetic organic chemistry. It would be inferred from Geisse's paper that the base he obtained was free from ammonia, whilst Wallach states that his product was comparatively very pure and the yield good.

By employing fine iron filings and hydrochloric acid, we have found that the composition of the reduction product depends on the conditions of the experiment. The use of iron and hydrochloric acid in the theoretical quantities (six atomic proportions of iron and nine molecular proportions of acid to one of chloropicrin) in such a way as to prevent the formation of ferrous or ferric hydroxides gave a product rich in ammonium chloride. If chloropicrin is shaken with iron filings and water, the mixture becomes extremely hot and a vigorous reaction sets in, which, however, gradually slackens if no acid is added. By adopting the method employed in the reduction of aromatic nitro-compounds or of nitromethane and nitroethane (Krause, *Chem. Zeit.*, 1916, **40**, 810), the reaction proceeds satisfactorily in the presence of only about one-fortieth of the theoretical amount of hydrochloric acid, and a practically theoretical yield of methylamine hydrochloride is obtained. This usually contains about 4 per cent. of ammonium chloride, but in some of our experiments the quantity of this impurity has been still further reduced. The best results have been obtained by slowly adding the chloropicrin to a well-stirred mixture of iron filings and acidified water. The gradual addition of iron filings to a mixture of acidified water and chloropicrin did not seem to be very satisfactory, so far as could be seen from the few experiments made in this direction. Some reductions carried out by gradually adding chloropicrin to boiling alkaline ferrous hydroxide failed to confirm the results of Geisse (*loc. cit.*), who states that by this method no ammonia is produced. We obtained a product containing about 20 per cent. of ammonium chloride.

The details of a typical large-scale experiment may be briefly outlined. Five hundred grams of fine iron filings were gradually shaken into a large earthenware jar containing 2500 c.c. of water and 60 c.c. of concentrated hydrochloric acid. In this way, the filings were thoroughly moistened and the tendency to clogging was diminished. The jar was fitted with a stirrer and placed in a little cold water; 250 grams of chloropicrin were then gradually added in the course of one-and-a-quarter hours. Too rapid addition of the chloropicrin caused the mixture to froth over. Owing to the large amount of hydrated oxide of iron produced, the stirring was as efficient as possible, otherwise chloropicrin escaped reaction through being enclosed in masses of iron filings or oxide.

The temperature rose considerably, and was maintained at about 50°, when the odour of chloropicrin was found to have disappeared after about three hours. The mixture was then gradually added to a boiling solution of sodium hydroxide contained in a large iron can, into which steam was blown. The methylamine was absorbed in hydrochloric acid, the solution evaporated, and the residue dried at 110° until constant weight was attained. The crude, dry hydrochloride was obtained in this way in a yield of 95·5 per cent., and contained 53·1 per cent. of chlorine, corresponding with an ammonium chloride content of only 3·5 per cent.

That ammonium chloride is actually produced during the reduction of chloropicrin was shown by treating cold concentrated aqueous solutions of the crude hydrochlorides with gaseous hydrogen chloride. The precipitated solid was collected, carefully freed from adhering hydrochloric acid, and analysed, when it was found to be almost pure ammonium chloride. The analyses of the crude methylamine hydrochloride were checked in some instances by an estimation of the platinum in the platinichloride. The hydrochlorides were evaporated with an excess of chloroplatinic acid solution, and the dry residue was extracted with absolute alcohol, whereby only platinum tetrachloride is removed. The possibility of a partial separation of the platinichlorides of the two bases would thus appear to be excluded.

Summary of Results.

Section A.—In the following experiments, the quantity of acid was very small, and the amount of iron theoretically required for the liberation of 12 atomic proportions of hydrogen (supposing sufficient acid had been present) was employed. The temperature was usually allowed to rise to about 50—70°.

Experiment.	1.	2.	3.	4.	5.	6.
Chloropicrin, grams	500	250	250	25	25	25
Iron, grams	1000	500	500	50	50	50
Water, c.c.	3500	2500	2500	200	200	200
Hydrochloric acid, c.c.	100	60	60	12	32	10
Crude hydrochloride, grams	190	98	94	9·5	10·0	9·5
Theoretical weight, grams	205	102·5	102·5	10·2	10·2	10·2
Cl in crude hydrochloride.....	53·3	53·1	53·6	52·9	52·8	53·1
Hence percentage NH_4Cl	5·0	3·5	7·0	2·0	1·5	3·5
Pt in crude platinichloride.....	41·53	41·43	—	—	—	41·33
Hence percentage NH_4Cl	6·5	2·75	—	—	—	1·10

NH_4Cl requires Cl = 66·5. $(NH_4)_2PtCl_6$ requires Pt = 43·96.
$CH_3{\cdot}NH_3Cl$ requires Cl = 52·6. $(CH_3{\cdot}NH_3)_2PtCl_6$ requires Pt = 41·36 per cent.

Section B.—In the experiments described in this section, the quantity of acid employed was much larger (up to 9 molecular proportions, not including the three formed during the reduction), and the iron as in *A*. The chloropicrin and the acid were both added gradually to the iron filings. The percentage of ammonium chloride is seen to have increased considerably.

Experiment.	1.	2.	3.
Chloropicrin, grams	25	25	50
Iron, grams	50	50	100
Water, c.c.	100	50	100
Hydrochloric acid, c.c.	200	150	300
Yield of dry hydrochloride, grams	9	6·5	15·0
Theoretical weight, grams	10·2	10·2	20·5
Cl in crude hydrochloride	58·0	60·9	60·5
Hence percentage NH_4Cl	40·0	60·0	60·0

Section C.—In these experiments, the chloropicrin was gradually added to a boiling alkaline ferrous sulphate solution. A considerable amount of ammonia was formed.

Experiment I.—Chloropicrin, 25 grams; ferrous sulphate, 550 grams; sodium hydroxide, 300 grams; water, 1800 c.c.

Dry hydrochloride, 7 grams. Theory, 10·2.

Analysis in samples of about 0·2 and 0·1 gram: Cl = 56·0, 55·2. Mean = 55·6, whence NH_4Cl = 22 per cent.

Experiment II.—Quantities as in above.

Dry hydrochloride, 9 grams.

Analyses in samples of about 0·5 gram: Cl = 54·8, 54·8, 54·6. Mean = 54·7, whence NH_4Cl = 15 per cent.

Interaction of Methylamine and 1:2:4-*Trinitrobenzene.*

With 1:2:4-trinitrobenzene, the alcoholic solution of the base gave an almost immediate deposit consisting of yellow needles melting at 175—176°, and at 176° after one crystallisation. The formation of 2:4-dinitromethylaniline (m. p. 176—177°) by this method does not seem to have been described.

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