# LVIII.—*The Preparation of Dichlorocarbamide.*

By Frederick Daniel Chattaway.

The author has recently shown (*Proc. Roy. Soc.*, 1908, *A*, **81**, 381) that when a solution of carbamide in water is acted on by chlorine, two of its hydrogen atoms are replaced by halogen, and dichlorocarbamide, NHCl·CO·NHCl, is formed.

If the chlorine is passed rapidly into a sufficiently concentrated solution, dichlorocarbamide crystallises out in thin, colourless plates, as it is much less soluble in water than the parent substance. The yield, however, is not good, even if the operation is carried out at a low temperature and as rapidly as practicable, the amount of dichlorocarbamide obtained thus never exceeds 25 per cent. of the quantity which should be furnished by the carbamide used, and is frequently much smaller, especially if the duration of the experiment has been unduly prolonged.

The loss is due mainly to hydrolysis of the dichlorocarbamide, which is much accelerated by the hydrogen chloride formed in the reaction:

$$NH_2\cdot CO\cdot NH_2 + 2Cl_2 = NHCl\cdot CO\cdot NHCl + 2HCl.$$

In this hydrolysis and the subsequent action of chlorine on the primary products, nitrogen chloride is formed, and can be recognised by its characteristic odour and the extraordinarily irritating quality of its vapour. As this nitrogen chloride is not only liberated during the passage of the chlorine, but is frequently found soaking the crystals of dichlorocarbamide when they are collected, the preparation of the latter may be a very disagreeable, although in no way a dangerous, operation.*

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* A very exaggerated idea of the danger of carrying out any operation in which nitrogen chloride is produced appears to be widely held, chiefly owing to Faraday's graphic description of a slight accident which befell him when experimenting with the substance before its properties were properly understood. In clean vessels and at the ordinary temperature considerable quantities of nitrogen chloride can be made either by the slow hydrolysis of dichlorocarbamide in aqueous solution, or by passing chlorine into an aqueous solution of an ammonium salt, without the slightest risk if ordinary precautions are taken. I have found it most convenient to prepare liquid nitrogen chloride by passing a slow stream of chlorine into a 20 per cent. solution of ammonium acetate through a tube reaching not quite to the bottom of the vessel. The nitrogen chloride then collects in a layer beneath the liquid, and can be washed by decantation and manipulated in quantities of 5 c.c. or thereabouts without risk. To render it perfectly safe, however, it may be diluted with two or three times its volume of chloroform, unless the presence of the latter is inadmissible.

Nitrogen chloride is very volatile in a current of air, and if the vapour only is needed, this can rapidly be drawn off and led through any desired solution by

If the hydrogen chloride set free in the reaction be removed as it is formed, so that the liquid is never strongly acid, this hydrolysis is to a large extent prevented, and a yield of dichlorocarbamide approaching the theoretical can be obtained, the loss under such conditions being chiefly due to the solubility of the compound in water.

The substance which has been found most effective for this purpose is zinc oxide. By the following procedure more than 75 per cent. of the theoretical yield of pure, dry, well-crystallised dichlorocarbamide can be obtained.

Six grams of carbamide are dissolved in 50 c.c. of distilled water, and 10 grams of finely divided zinc oxide are added. The mixture is cooled to $-5^\circ$ or thereabouts in a freezing mixture, and a rapid stream of chlorine passed through the liquid. If the operation is carried out in a small flask, and this is well shaken in the freezing mixture during the passage of the gas, the temperature does not rise above zero. The zinc oxide quickly dissolves, and a clear liquid results, from which in a very short time crystals of dichlorocarbamide begin to separate. When the liquid has become a thick pulp from the separated solid, and crystals appear no longer to separate, the dichlorocarbamide is rapidly collected by the aid of a pump, washed twice with 5 c.c. of ice-cold distilled water, and then several times with dry chloroform. The latter, in which dichlorocarbamide is only very slightly soluble, removes most of the adhering moisture. Ten grams of dichlorocarbamide are invariably obtained thus as a soft, white, crystalline powder. This yield is 77·5 per cent. of the theoretical.

The crystalline dichlorocarbamide thus obtained is pure, save for a scarcely recognisable amount of zinc chloride retained by the traces of mother liquor. For many purposes, the solid, simply filtered off or dried thus with chloroform, may be employed. The last traces of moisture can be removed by exposure in a vacuum for a short time over phosphoric oxide. A specimen thus obtained and dried gave the following numbers on analysis:

0·3389 liberated $\text{I} = 104{\cdot}2$ c.c. $N/10$-iodine. Cl as $:\text{NCl} = 54{\cdot}49$.

$CH_2ON_2Cl_2$ requires Cl as $:\text{NCl} = 54{\cdot}96$ per cent.

In order to ascertain how far the loss still observed is due to hydrolysis and how far to the dichlorocarbamide formed remaining dissolved in the mother liquor, an estimation of the solubility of the compound in water at 0° was made. An excess of dichloro-

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bubbling a stream of air through the water or ammonium acetate solution containing the liquid nitrogen chloride in suspension. In working with nitrogen chloride the effects of its vapour on the eyes and lungs, which are very painful and do not pass off for days, are far more to be feared than an explosion.

carbamide was shaken for an hour with distilled water in a thermostat at 0°. A known weight of solution was then filtered off, and the amount of dissolved dichlorocarbamide was estimated by adding excess of hydriodic acid and titrating the iodine liberated by standard thiosulphate. It was found that 100 grams of water at 0° dissolve 4 grams of dichlorocarbamide.

This determination of the solubility cannot lay claim to very great accuracy; indeed, this is impossible, since hydrolysis slowly goes on during the time taken by the operation, and at the end of the hour's shaking nitrogen chloride can be recognised by its odour, but still it is sufficiently exact for the purpose. Since from six grams of carbamide 10 grams of dichlorocarbamide can be obtained by the procedure above described, the difference between this amount and the theoretical yield of 12·9 grams, that is, 2·9 grams, has to be accounted for. Of this, 2·4 grams are held in solution in the mother liquor, assuming that the solubility of dichlorocarbamide in a dilute solution of zinc chloride does not differ markedly from its solubility in water; only about half a gram, therefore, undergoes hydrolysis during the process.

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