

IX.—*Thiocarbamide Hydrochloride.*

By HENRY P. STEVENS, M.A., Ph.D.

THIOCARBAMIDE hydrochloride is stated by Glutz (*Annalen*, 1870, 154, 40) to be obtained from thiocarbamide stannochloride by removal of the tin and concentration of the resulting aqueous solution, as a crystalline substance which could be purified by recrystallisation from alcohol. It was not analysed, nor was its melting point given, and the only evidence brought forward by Glutz to show that it was thiocarbamide hydrochloride is the fact that with platinic chloride it gave a double salt, and with silver nitrate a mixed precipitate of silver chloride and the silver compound of thiocarbamide.

Reynolds (*Annalen*, 1869, 150, 232) was unable to prepare the hydrochloride, whilst Claus (*Annalen*, 1875, 179, 131) states that, like Reynolds, he had been unable to prepare the hydrochloride *directly*, but had often obtained the pure salt by Glutz's method, in spite of which assertion, however, no analysis is given nor is the salt in any way further characterised. It is therefore a matter of doubt whether thiocarbamide hydrochloride has hitherto been isolated in a pure state.

On investigating the question, it was found that identical products were obtained by Glutz's method and by bringing together aqueous solutions of thiocarbamide and hydrochloric acid in the calculated proportion.

The white, crystalline substance produced on evaporation of the solutions on the water-bath is very soluble in alcohol, and when fractionally recrystallised from this solvent, it yields, in addition to some unchanged thiocarbamide, well-formed, prismatic crystals having an ill-defined melting point and containing an amount of chlorine too small for such a compound as  $\text{CS}(\text{NH}_2)_2 \cdot \text{HCl}$ . Repeated crystallisation from alcohol, instead of purifying the compound, lowered the percentage of chlorine without, at the same time, yielding any free thiocarbamide.

Eventually the hydrochloride was obtained pure by the following method. Thiocarbamide was dissolved in more than sufficient of the most concentrated, warm, aqueous hydrochloric acid to convert the whole into hydrochloride. On allowing the solution to stand, the hydrochloride separated out in thick, massive crystals. The mother liquor was poured off from the crystals, which were then redissolved by gently warming in the smallest possible quantity of hydrochloric acid, from which, on standing, the greater part again separated. It is difficult to dry the crystals without slight loss of hydrogen chloride; they may, however, be obtained in a pure state by pouring off the mother liquor, washing them rapidly with cold alcohol on the filter pump, and drying them over calcium chloride. On analysis:

- I. 0.1212 gave 0.1546 AgCl. Cl = 31.54.  
 II. 0.2374 ,, 0.3017 AgCl. Cl = 31.42.  
 $\text{CH}_5\text{N}_2\text{ClS}$  requires Cl = 31.38 per cent.

As thiocarbamide in aqueous solution has a neutral reaction with respect to litmus, the whole of the chlorine can be accounted for as hydrochloric acid by titration with decinormal ammonium hydroxide solution. Thus, in analysis II, the substance was titrated, before precipitation, with silver nitrate and gave Cl = 31.46 per cent.

The salt, when exposed to air, rapidly effloresces with the loss of some hydrogen chloride, of which about one-half can be removed by prolonged exposure in a vacuum over strong sulphuric acid and potassium hydroxide. When heated, it softens gradually and melts below  $100^\circ$ . It is extremely soluble in water or alcohol. If silver nitrate be gradually added to a solution of the hydrochloride, the precipitate first formed redissolves immediately in the excess of the hydrochloride solution, and on allowing the clear liquid to stand, fine, needle-shaped crystals separate out which melt at  $172^\circ$  and on oxidation with nitric acid yield silver chloride. They appear to be identical with the compound  $2\text{CS}(\text{NH}_2)_2, \text{AgCl}$  (m. p.  $170-171^\circ$ ) obtained by Reynolds (*Trans.*, 1892, 61, 252) by dissolving silver chloride in a hot alcoholic solution of thiocarbamide.

Thiocarbamide forms additive compounds with alkyl iodides and bromides on standing in the cold or heating in sealed tubes (Claus, *Annalen*, 1875, 179, 145; Berntsen and Klinger, *Ber.*, 1878, 11, 492, &c.); but no statement, however, is to be found with regard to its behaviour with the alkyl chlorides. On treating a solution of thiocarbamide in alcohol with ethyl chloride, freed from hydrochloric acid by bubbling through water with calcium carbonate in suspension, no appreciable action took place even on warming the solution. Nevertheless, it was possible that ethyl chloride, formed in the solution itself by the action of hydrochloric acid on the alcohol, might prove more reactive, and this was eventually found to be the case.

An alcoholic solution of thiocarbamide hydrochloride, prepared by dissolving thiocarbamide in about ten times its weight of alcohol in which the necessary amount of hydrogen chloride had been dissolved, was boiled for several days in a reflux apparatus on a water-bath. The solution was evaporated down twice with fresh quantities of alcohol to remove any slight excess of hydrochloric acid. The product, a thick, unpleasant smelling oil, solidified completely on standing and stirring with a glass rod. Like thiocarbamide hydrochloride, it was extremely soluble in water or alcohol, but insoluble in other solvents provided they were dry, and on this account much difficulty was experienced in finding a suitable solvent for its recrystallisation. Eventually the product was dissolved by gently warming and shaking in glacial acetic

## METHOD FOR DETERMINING SMALL QUANTITIES OF CARBONATES. 81

acid, a few drops of water or alcohol being added to promote solution. Dry ether, insufficient in amount to cause any permanent precipitation, was then added in small quantities at a time to the cold solution, and the whole set aside to stand; a crop of crystals formed which was filtered off, and the mother liquor treated with more ether. In this manner, by a process of fractional crystallisation, the new substance was obtained in a state of purity. It is more soluble than thiocarbamide hydrochloride in the mixture of glacial acetic acid and ether, and separates when pure from the same solvent in long, slender prisms. It melts gradually just below  $100^{\circ}$ . The aqueous solution of the salt is neutral to litmus, but the whole of the chlorine is precipitated as silver chloride by silver nitrate in dilute nitric acid solution. Chlorine estimations showed that it is an additive product of thiocarbamide and ethyl chloride, or, from another point of view, that it is ethyl- $\psi$ -thiocarbamide hydrochloride.

0.2097 gave 0.2122 AgCl. Cl = 25.02.

0.2183 ,, 0.2227 AgCl. Cl = 25.22.

$C_3H_9N_2ClS$  requires Cl = 25.20 per cent.

This hydrochloride behaves similarly to the hydriodide obtained by direct combination of thiocarbamide and ethyl iodide.

It follows, therefore, that thiocarbamide hydrochloride cannot be recrystallised from alcohol, as it reacts with it to give ethyl- $\psi$ -thiocarbamide hydrochloride.

CHEMICAL LABORATORY,  
ST. THOMAS' HOSPITAL, S.E.

---