LXXIX.—*Reduction of Perthiocyanic Acid.*

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THE atoms forming the molecule of perthiocyanic acid have been assumed to be arranged in a simple ring from the observation that it yields thiourea and carbon bisulphide on reduction. As, however, the properties of the substance render it probable that its molecule is larger than that represented by the formula $\text{H}_2\text{N}_2\text{C}_2\text{S}_3$, which is the simplest possible, the conclusion that in this complex molecule all the structural units have a similar atomic arrangement is only valid if the amounts of thiourea and carbon bisulphide obtained on reduction approach the theoretical; otherwise, if small yields only are obtained, it simply proves that, in some part of the molecule, this grouping occurs, the structure of the remainder being perhaps indicated by the other substances produced in the action. Glutz, who first effected the reduction (*Annalen*, 1870, 154, 40), unfortunately gives but little information beyond the fact that these two substances are formed together with hydrogen sulphide. He does not describe fully the methods by which the reduction was effected, nor does he give any indication of the yields of the three products. Moreover, he purified the acid in a most unsuitable way by dissolving it in a hot solution of ammonia, and reprecipitating by hydrochloric acid. The action of alkalis on perthiocyanic acid is not yet properly understood, but the first action undoubtedly results in the precipitation of free sulphur, which, on heating, redissolves. This renders it very doubtful whether the substance used by Glutz was really pure perthiocyanic acid.

The reduction of perthiocyanic acid has therefore been carefully carried out in various ways in order to determine the exact amounts of

carbon bisulphide and thiourea obtainable, and the nature and amount of any other products of the action. When perthiocyanic acid is reduced by tin and hydrochloric acid, carbon bisulphide and thiourea are produced in almost theoretical amount.

Only very small quantities of hydrogen sulphide and carbon dioxide are produced in addition, these being doubtless formed by the hydrolysis of a small portion of the perthiocyanic acid under the influence of the strong hydrochloric acid.

Amorphous phosphorus, iodine, and water can also be advantageously employed, but other reducing agents are not so suitable. Although thiourea and carbon bisulphide are generally first formed, secondary actions occur, and the yields obtained are not good.

Reduction of Perthiocyanic Acid by Tin and Hydrochloric Acid.

This is by far the best method of reducing perthiocyanic acid; the action goes quietly and almost quantitatively, the mode of procedure being the following.

Twenty grams of perthiocyanic acid placed in a two-litre flask are moistened with 30 c.c. of water, and 50 grams of granulated tin and 100 c.c. of strong hydrochloric acid are added; the flask is then attached to a condenser, to which are fixed two long, connected U-tubes immersed in ice. Any gas escaping from these is passed through a series of flasks containing an alkaline solution of arsenious oxide. On being heated until the liquid boils gently, the perthiocyanic acid turns somewhat red, and is rapidly reduced, carbon bisulphide being given off, accompanied by some hydrogen sulphide and small quantities of carbon dioxide.

The action is rather violent at first, but soon moderates, and is over in about 5 minutes. The carbon bisulphide collects in the U-tubes, from which it can be removed and weighed, the sulphuretted hydrogen and carbon dioxide being absorbed by the alkaline solution of arsenious oxide. On adding acid to the latter liquid, arsenious sulphide is precipitated, and carbon dioxide liberated. The arsenious sulphide is dried and weighed, and the carbon dioxide is passed into standard sodium hydroxide, precipitated with barium chloride, and the amount estimated by difference. The thiourea remains in the flask, along with the excess of tin and hydrochloric acid, as the stannous double salt which crystallises out in long, slender needles on cooling, and by recrystallisation from a little hot water can be obtained in well-formed white crystals melting not very sharply at 115°.

The thiourea is most conveniently obtained from this by adding a slight excess of sodium hydrogen carbonate, heating for a time, and filtering. After evaporating the filtrate to dryness, the thiourea can be extracted with alcohol, and completely freed from sodium chloride by evaporating the alcoholic extract to dryness and again taking up with alcohol. This process is repeated as long as necessary, but the thiourea is obtained practically pure after three extractions; and, after recrystallisation from water, melts at 171° . The thiourea can also be obtained by diluting the solution of the tin double salt, precipitating the tin by sulphuretted hydrogen, and evaporating the residue to dryness. On recrystallisation from water, the thiourea is obtained pure in large, brilliant crystals. This method, although the simplest, is rather tedious, as the tin is not very easily precipitated completely at one operation.

The reduction of the perthiocyanic acid takes place almost quantitatively, according to the equation $\text{H}_2\text{N}_2\text{C}_2\text{S}_3 + 2\text{H} = \text{CSN}_2\text{H}_4 + \text{CS}_2$.

The yield of thiourea is about 99–99.5, and of carbon bisulphide usually about 90–95, per cent. of the theoretical. The amounts of hydrogen sulphide and carbon dioxide formed vary with the amount of acid used and the rapidity with which the action is conducted; they correspond approximately in amount, and are, no doubt, mainly formed by the hydrolysis of a small portion of the perthiocyanic acid under the influence of the strong acid.

The lower yield of carbon bisulphide, however, is, without doubt, mainly due to its volatility; however carefully the receivers may be cooled, a certain amount of carbon bisulphide vapour is sure to be carried over by the escaping gases, especially at first, when the action is very vigorous.

Action of Stannous Chloride on Perthiocyanic Acid.

A solution of stannous chloride in strong hydrochloric acid has little action on perthiocyanic acid at 100° , but at a higher temperature is capable of reducing it. When perthiocyanic acid is heated in a hard glass tube at 170° for 3 hours with an equivalent quantity of stannous chloride and an excess of strong hydrochloric acid, it is completely decomposed. There is great pressure in the tube when it is opened, and an inflammable gas smelling strongly of carbon bisulphide is given off; all the stannous chloride is found to have been converted into stannic sulphide, whilst at the bottom of the tube there is a layer of carbon bisulphide amounting to about 25 per cent. of the theoretical. On distilling off the carbon bisulphide, and filtering from the stannic sulphide, the filtrate is found to be free from thiocyanic acid, and contains nothing but ammonium chloride, the amount of ammonia obtained by distillation with potash corresponding with about 80 per

cent. of the total nitrogen in the perthiocyanic acid used. In this reaction, the perthiocyanic acid appears to be first reduced in the ordinary way to thiourea and carbon bisulphide, the thiourea is then transformed at the high temperature into ammonium thiocyanate, the thiocyanic acid liberated from this by the hydrochloric acid again reacting to form perthiocyanic acid.

Reduction of Perthiocyanic Acid by Hydriodic Acid.

Perthiocyanic acid is slowly reduced by hydriodic acid, thiourea and carbon bisulphide being produced. The hydriodic acid, however, especially if it be very concentrated, hydrolyses some of the perthiocyanic acid, considerable amounts of hydrogen sulphide and carbon dioxide being evolved, also the carbon bisulphide is partially reduced by the hydriodic acid, so that smaller yields are obtained than with tin and hydrochloric acid.

The following method gives good results. Twenty grams of perthiocyanic acid, 20 grams of amorphous phosphorus, 50 grams of iodine, and 200 grams of water are placed in a half-litre flask, and cautiously heated to gentle ebullition; the acid turns red, and is slowly reduced, carbon bisulphide distilling over, the heating being continued until it has all completely disappeared. The liquid, after dilution, is then filtered from any unchanged phosphorus, a slight excess of sulphuric acid is added to the filtrate, and the whole evaporated on a water bath, water being added from time to time until all the hydriodic acid has been expelled. The product is then dissolved, and an excess of barium carbonate added, the barium phosphate and sulphate are filtered off, and the solution of thiourea evaporated to dryness; the residue is then extracted with alcohol filtered from any small quantity of undissolved solid, and again evaporated and weighed. During the reduction, considerable amounts of hydrogen sulphide and carbon dioxide are given off which can be passed through alkaline arsenite solution and estimated as before. About 3 per cent. of the total sulphur is obtained as hydrogen sulphide. The yields of thiourea and carbon bisulphide are not so good as when the reduction is effected with tin and hydrochloric acid. The thiourea produced is about 90 per cent. of the theoretical, whilst not more than 70—80 per cent. of the theoretical quantity of carbon bisulphide can be obtained.

If perthiocyanic acid be heated in hard glass tubes at about 130° with fuming hydriodic acid, a considerable quantity of ammonium iodide is formed, and some carbon bisulphide. A small quantity of a pale yellow substance, somewhat like perthiocyanic acid in appearance, is produced in addition. This is insoluble in water, but readily crystallises from alcohol in small, yellow needles, which melt at 118° to a red liquid, and burn in the air with a blue, sulphur-like flame. The substance is readily soluble in carbon bisulphide, chloroform, and

alcohol; it is paler in colour than perthiocyanic acid, and is not affected by a solution of potassium hydroxide or hydrochloric acid, even on boiling.

This substance, which we hope to investigate further, resembles closely a compound obtained during the crystallisation of perthiocyanic acid. After repeatedly boiling the crude perthiocyanic acid when all soluble matters have been extracted, a small quantity of a brown solid residue is left; this is partially soluble in hot alcohol, and the yellow solution, on cooling, deposits crystals similar in appearance to those mentioned above. They melt at the same temperature, 118°, are soluble in alcohol, chloroform, and carbon bisulphide, and do not yield free sulphur on treatment with a solution of caustic potash.

Reduction of Perthiocyanic Acid with Sodium Amalgam.

As the action of caustic alkalis on perthiocyanic acid is a singular, and at present unexplained, one, resulting, however, in the precipitation of free sulphur, and since reducing agents have such a marked action on perthiocyanic acid, it seemed of interest to examine the action of alkaline reducing agents on it.

Perthiocyanic acid (10 parts) was suspended in water (125 parts) and a large excess of sodium amalgam added (12.5 grams of sodium and 750 grams of mercury). The acid very slowly disappeared and the solution became clear and nearly colourless, very little hydrogen being evolved and no carbon dioxide.

The liquid, after standing over the amalgam for about a fortnight, was poured off and examined. On adding excess of hydrochloric acid, large quantities of hydrogen sulphide and some carbon dioxide were evolved, and at the same time a considerable amount of perthiocyanic acid was precipitated; this apparently had been merely dissolved by the sodium hydroxide. The liquid, after filtration and expulsion of the gases, was found to contain a considerable quantity of ammonia and some thiourea.

The first action of the sodium amalgam appears to be that of a simple reduction, the perthiocyanic acid, as before, yielding thiourea and carbon bisulphide. The sodium hydroxide, however, as it is formed, dissolves some of the unreduced perthiocyanic acid, the alkaline salt thus produced being afterwards only very slowly attacked. The alkali also acts on the carbon bisulphide, forming a thiocarbonate, which, on heating, slowly decomposes into carbonate and sulphide. At the same time, part of the thiourea is decomposed, yielding sodium carbonate, sodium sulphide, and ammonia.

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