CCCXXXII.—*The Reaction between Thallic Chloride and Potassium Thiocyanate.*

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While making a study of the tests for thallium in presence of iron, titanium and zirconium, the author observed that solutions of thallic chloride and potassium thiocyanate became deep yellow when mixed. The colour quickly faded and a yellow or white solid was then precipitated. The yellow colour appeared and faded, but no solid was precipitated, in the presence of sulphuric acid. The solid proved to be thallous thiocyanate. The reduction of thallic salts by thiocyanates has been observed previously (Abegg's "Handbuch," III, i, 417. Compare the corresponding reduction of ferric and cupric salts; Philip and Bramley, J., 1913, **103,** 795; 1916, **109,** 597). Attempts to isolate thallic thiocyanate by means of ether or other organic solvent were unsuccessful.

It was noticed that the mixed solutions emitted a strong odour of hydrogen cyanide. The liquid also contained sulphate and was strongly acid. If hydrogen cyanide and sulphuric acid are the only products of the oxidation of the thiocyanate radical by the thallic salt, the simplest equation to represent the reaction would be $3TlCl_3 + 4KCNS + 4H_2O = 3TlCNS + 4KCl + HCN + 5HCl + H_2SO_4$.

The correctness of this equation was tested by experiments in which the sulphate and the total acid were estimated. After a solution containing a known quantity of thallic chloride has been treated with sufficient potassium thiocyanate, the sulphate formed can be determined by adding excess of barium chloride solution to the filtrate after removal of the thallous thiocyanate. The hydrochloric and sulphuric acids can be determined after filtration of the thallous thiocyanate, by titration with standard sodium carbonate solution and methyl-orange. Hydrocyanic acid is such a weak acid (dissociation constant 0·097) that it does not interfere with the titration. In the actual procedure, two solutions of thallic chloride containing 5 g. and 10 g. of the salt per 100 c.c. were prepared. In 10 c.c. of each of these solutions, the quantity of thallic salt present was determined by precipitation as thallous iodide (Found : 0·4714 and 0·9736 g. TlI respectively). Other 10 c.c. portions of the same solutions were then treated with an excess of *N*/5-potassium thiocyanate solution and the amounts of sulphate and free mineral acids formed were determined by the methods mentioned above (Found : $BaSO_4$, 0·1050 and 0·2131 g.; Na_2CO_3 equiv. to free mineral acid, 0·1671 and 0·3430 g. Calc. from the equation given above : $BaSO_4$, 0·1107 and 0·2290 g.; Na_2CO_3, 0·1760 and 0·3639 g.). The total acidity developed and the quantity of sulphate produced are very nearly in agreement with the requirements of the equation formulated above.

If, instead of potassium thiocyanate solution being added to one of thallic chloride, the reverse procedure is followed, a known volume of the latter solution being gradually added to an excess of potassium thiocyanate solution, the results obtained are in better agreement with the equation. The precipitate formed in this case is colourless, not yellow.

$TlCl_3$ in 10 c.c. of soln.	TlI obtained.	$BaSO_4$ found.	$BaSO_4$ calc.	Na_2CO_3 required.	Na_2CO_3 calc.
0·800 g.	0·7598 g.	0·1768 g.	0·1786 g.	0·2815 g.	0·2840 g.
1·600 g.	1·520 g.	0·3505 g.	0·3574 g.	0·5591 g.	0·5680 g.

From the above results it is obvious that under favourable conditions the reaction between thallic chloride and potassium thiocyanate may take place quantitatively according to the equation given. The author is investigating the reaction in greater detail with the object of evolving a volumetric or gravimetric method of determining thallium in the higher state of oxidation.

The precipitate obtained when solutions of thallic chloride and potassium thiocyanate are mixed responds in aqueous solution to the tests for thallous and thiocyanate ions. In order, however, to establish the constitution of the salt, the precipitate was dried at 100°, and after a weighed portion had been dissolved in hot water, the thallium in solution was precipitated as thallous iodide. The weight of thallous iodide obtained from both the yellow and the white precipitate was about 3% higher than that calculated by multiplying the weight of the precipitate by the ratio TlI/TlCNS. The following table gives the results obtained for four samples thus analysed.

Ppte., dried at 100°.	TlI obtained.	TlI calc.	Diff. (approx.) %
Yellow, 0·420 g.	0·548 g.	0·533 g.	2·7
Yellow, 0·250 g.	0·327 g.	0·317 g.	3·1
White, 0·420 g.	0·546 g.	0·531 g.	2·7
White, 0·675 g.	0·873 g.	0·850 g.	2·6

The cause of this difference has not yet been investigated. It may be that the slightly increased weight of thallous iodide is due to contamination of the thallous thiocyanate with thallous chloride, in which case the weight of thallous iodide actually obtained will be greater than that calculated from the ratio TlI/TlCNS.

Summary.

(1) By the interaction of thallic chloride and potassium thiocyanate in aqueous solution, hydrocyanic, hydrochloric, and sulphuric acids are produced, the formation of sulphuric acid being due to the fact that a part of the thallic chloride acts as an oxidising agent.

(2) The reaction takes place very nearly in accordance with the equation given on p. 2434.

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