CCLXXIII.—*Ferric Thiocyanate.*

By Kenneth Claude Bailey.

It is generally assumed that the blood-red substance produced by the interaction of ferric chloride and potassium thiocyanate, and extracted by ether from its aqueous solution, is ferric thiocyanate. Kruss and Moraht (*Ber.*, 1889, **22**, 2054) obtained double salts, to which they attributed the formulæ $9KSCN,Fe(SCN)_3,4H_2O$ and $3KSCN,Fe(SCN)_3,nH_2O$, by crystallisation from aqueous mixtures, but these salts were decomposed by moist ether, and could not account for the colour extracted by that solvent.

Clarens's suggestion (*Buli. Soc. chim.*, 1923, **33**, 988) that the substance obtained in presence of an excess of ferric chloride is a dithiocyanate has been combated by the author (*Proc. Roy. Irish Acad.*, 1924, **37**, *B*, 2, 6).

Tarugi stated (*Gazzetta*, 1904, **34**, ii, 326; *Annali Chim. Appl.*, 1925, **15**, 416; 1926, **16**, 281) that the red compound was a per oxidised ferrous salt, $FeHC_3N_3S_3O_3$, but his conclusions from hi earlier work were disputed by Bongiovanni (*Gazzetta*, 1907, **37**, i, 472). Although Tarugi reaffirmed these conclusions in his later work, it was deemed desirable to repeat his experiments and examine point by point the most striking arguments which he adduced in support of his formula.

According to his directions, therefore, an excess of freshly prepared ferric hydroxide was dissolved in aqueous thiocyanic acid, the solution saturated with sodium chloride and extracted with ether, and the extract filtered and dried, where desirable, over anhydrous sodium sulphate. The results obtained were identical with those given by an ethereal extract of ferric chloride and potassium thiocyanate (excess).

(1) A little of the fresh ethereal solution was added to water, and then gave a deep blue colour with potassium ferrocyanide and only a yellow colour with ferricyanide (Tarugi obtained a greenish colour and a blue colour, respectively). After being kept for some time, the solution gave a blue colour with ferricyanide, showing slow reduction of part of the iron to the ferrous condition.

(2) When dilute nitric acid was added to a strong solution of potassium thiocyanate, and the mixture shaken with ether, a red extract was obtained which was strongly acid. This result can hardly be attributed to oxidation as asserted by Tarugi, for a similar extract was obtained when hydrochloric acid was substituted for nitric acid, and the substance extracted was almost certainly thiocyanic acid (compare Bailey, *loc. cit.*; Werner and Bailey, J., 1926, 2970).

(3) A solution of ferric sulphate was prepared containing 5·58 g. per litre of iron and excess of acid. If no excess acidity had been present, 30 c.c. of *N*/10-sodium hydroxide should have sufficed to precipitate all the iron in 10 c.c. and give a neutral solution. About 69 c.c. were actually needed; 10 c.c. of the ferric solution contained, therefore, the equivalent of about 39 c.c. of *N*/10-acid in excess. When similar titrations were performed with solutions containing potassium thiocyanate and potassium oxalate, very indefinite results were obtained by the use of phenolphthalein, the indicator employed by Tarugi. Neutral litmus paper gave consistent results and was employed throughout.

Another source of error lay in the fact that the iron was not completely precipitated from solutions containing thiocyanate and oxalate until a fair excess of alkali was present, and there was a danger of adsorption of the alkali by the precipitated hydroxide. To avoid this, the solution was boiled, and 68 c.c. of *N*/10-alkali were added. The solution was filtered, the filter-paper washed, and further alkali added to ensure complete precipitation. The solution was again filtered, and the solution and washings were back-titrated with *N*/10-sulphuric acid. This procedure was followed even in the case of the plain ferric sulphate solution, to ensure uniformity of results, for each filtration necessarily incurs loss. The following results were obtained :

10 C.c. of ferric sulphate solution required 69·1 c.c. of *N*/10-sodium hydroxide.

10 C.c. of ferric sulphate solution + 60 c.c. of *N*/10-potassium thiocyanate (*i.e.*, 6 mols.) required 69·3 c.c.

10 C.c. of ferric sulphate solution + excess of concentrated potassium thiocyanate + potassium oxalate until solution was pale yellow required 69·1 c.c.

No increase in free acidity due to the reduction of iron to the ferrous condition was observed, and the only plausible explanation of Tarugi's statement, that such increase occurs, is that an error was introduced by the use of phenolphthalein, or by adsorption of sodium hydroxide by the precipitate.

Tarugi suggested that the decolorisation of the red solution by potassium oxalate was due to reduction of the red peroxidised compound by the oxalate. If this were the case, an amount of potassium oxalate equivalent to the original red compound should be oxidised during the reaction.

Quantitative estimations showed that no oxalate disappeared during the operation, and that twenty times as much oxalate was necessary for approximate decolorisation as should have sufficed for reduction of the peroxidised compound supposed to be present. This result was consistent with the disappearance of the red colour by double decomposition, but not with reduction of a peroxidised compound at the expense of the oxalate.

(4) Some fresh, red, ethereal solution was decolorised by potassium oxalate. Ammonia was added and the precipitate was quickly filtered off, washed with air-free water, and dissolved in hydrochloric acid; the solution gave an intense blue colour and precipitate with ferrocyanide, but only a greenish-yellow solution with ferricyanide. Tarugi's result (that the iron is precipitated in the ferrous condition) is only intelligible on the supposition that the ferric oxalate solution was exposed to sunlight, which would probably cause formation of some ferrous oxalate.

(5) Some of the ethereal solution was treated with oxalate, calcium chloride, and ammonia, as directed by Tarugi. The precipitate, as before, contained ferric iron and no ferrous iron. To the neutralised filtrate one drop of very dilute ferric chloride solution was added. A red colour, readily extracted by ether, was produced. Tarugi obtained a red colour not extracted by ether. This result may be easily explained. If the solutions employed are fairly dilute, the filtrate is a very dilute solution of thiocyanate, and even one drop of concentrated ferric chloride produces an excess of the latter reagent. The red colour is then only extracted with diffi-

culty. By using concentrated solutions of the other reagents and a dilute solution of ferric chloride, a mixture is obtained in which the thiocyanate is in excess, and the colour is readily extracted (see Durand and Bailey, *Bull. Soc. chim.*, 1923, **33**, 653; Bailey, *loc. cit.*).

(6) To water freed from air by boiling, some ammonia was added in a separating funnel, and red ethereal solution till the funnel was quite full. After shaking, the precipitate was allowed to subside, and had the typical appearance of ferric hydroxide; it was rapidly and repeatedly washed with air-free water, and dissolved in a little acid. The resulting solution gave no blue colour with ferricyanide. The supernatant liquid was tested for thiocyanate as under (5), with similar results.

(7) The ethereal solution gave a blue colour with benzidine, but a similar result was obtained with ferric chloride and benzidine. This reaction, therefore, does not prove the peroxidised nature of the red compound.

(8) An attempt was made to crystallise the red compound from its ethereal solution, dried over anhydrous sodium sulphate. This solution, however, when kept in a desiccator, changed in composition even before depositing solid, and a solution which originally gave only a yellow colour with ferricyanide soon gave a blue colour, showing conversion of iron into the ferrous state. After the solution had evaporated almost completely, the residue remained moist for about a week. This red liquid was acid in reaction, and doubtless contained free thiocyanic acid. A large proportion of the iron in the solid residue, although not all, was in the ferrous condition.

Philip and Bramley (J., 1913, **103**, 795) observed reduction of ferric thiocyanate in aqueous solution :

$$8Fe(CNS)_3 + 6H_2O = 8Fe(CNS)_2 + 7HCNS + CO_2 + H_2SO_4 + NH_3.$$

It seems possible that a similar reduction of ferric thiocyanate to ferrous thiocyanate with production of thiocyanic acid is taking place here. In view of the undoubted and rapid alteration of the red product, it seems unlikely that an analysis of any substance crystallised from the ethereal solution in a desiccator (Tarugi found Fe, 20·59; S, 34·37. Calc. for $FeHC_3N_3S_3O_3$: Fe, 20·07; S, 34·40%) can give results sufficiently trustworthy to establish a formula such as that proposed by Tarugi.

Summary.

Many of the experiments described by Tarugi have been carefully repeated. No evidence was obtained to support his conclusion that the red compound formed by dissolving ferric hydroxide in an

aqueous solution of thiocyanic acid is $FeHC_3N_3S_3O_3$. The results all indicate that the compound is ferric thiocyanate.

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