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The Action of Cyanide on Selenopentathionate and Telluropentathionate

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In aqueous solutions, cyanide reacts with pentathionate ions to give thiosulphate, sulphate and thiocyanate[1, 2]:

$$S(S_2O_3)_2^{--} + 2\ CN^- + 2\ OH^- = S_2O_3^{--} + 2\ SCN^- + SO_4^{--} + H_2O \qquad (1)$$

We have found that selenopentathionate*[3] reacts with cyanide in an analogous way, as follows:

$$Se(S_2O_3)_2^{--} + 2\ CN^- + 2\ OH^- = S_2O_3^{--} + SeCN^- + SCN^- + SO_4^{--} + H_2O \qquad (2)$$

In presence of an excess of potassium cyanide, both reactions are rapid and quantitative. The first of the reactions forms the basis for the cyanide method[2, 4] for the iodometric analysis of pentathionate. Correspondingly, the second one may, in dilute solutions, be used for the iodometric analysis of selenopentathionate.

The mechanism of the reaction of cyanide with pentathionate has been discussed elsewhere[4], on the basis of the kinetic results of Foresti[5] and the general reactivity of pentathionate as a monosulphur di(thiosulphate). So far, no kinetic experiments have been made on the reaction of cyanide with selenopentathionate. However, in view of the similarity of the two reactions, it seems reasonable to assume that the mechanism is the same in both cases. Thus, the first step is probably a nucleophilic displacement, on divalent selenium, of thiosulphate by cyanide.

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* The prefix "mono" is omitted, since the monoseleno and monotelluro compounds are the only selenium- or tellurium-substituted pentathionates known.

Heuer[6], in his studies on the Norris and Fay reaction between selenious acid and potassium thiosulphate, isolated crystalline mixtures which perhaps contained potassium selenopentathionate, beside other selenopolythionates and polythionates. He said (Ref. 6 p. 31) that selenopentathionate seemed to react with cyanide to give selenosulphate. The salt did not (Ref. 6 p. 35) react to give thiosulphate, and thus (Ref. 6 p. 44) not according to Eq. (2). However, Heuer did not investigate the pure salt. Actually, no selenosulphate is formed, as can be shown by means of formaldehyde, since this reagent immediately liberates selenium from selenosulphate[7].

Telluropentathionate *[8] does not react with potassium cyanide. Instead, due to the alkalinity of the cyanide solutions, a rapid and complete hydrolysis takes place, as in presence of hydroxyl ions alone[8]:

$$2\ \mathrm{Te(S_2O_3)_2^{--}} + 6\ \mathrm{OH^-} = 4\ \mathrm{S_2O_3^{--}} + \mathrm{Te} + \mathrm{TeO_3^{--}} + 3\ \mathrm{H_2O} \qquad (3)$$

In this respect, the tellurium derivative differs markedly from the corresponding sulphur and selenium compounds.

Experimental

The behaviour of selenocyanate towards iodine. In sodium hydrogencarbonate buffer, potassium selenocyanate is oxidized by an excess of iodine, to give selenite and iodine cyanide[9]:

$$\mathrm{SeCN^-} + 3\ \mathrm{I_2} + 6\ \mathrm{OH^-} = \mathrm{SeO_3^{--}} + \mathrm{ICN} + 5\ \mathrm{I^-} + 3\ \mathrm{H_2O}$$

In neutral solutions, selenocyanate is only partly oxidized by iodine[10], to give selenocyanogen, $\mathrm{(SeCN)_2}$, or the brown-coloured triselenocyanate, $\mathrm{(SeCN)_3^-}$.

The following experiment shows that in dilute aqueous solutions, in presence of acetic acid and sufficient amounts of potassium iodide, potassium selenocyanate is not attacked by small amounts of iodine: To a mixture of 10 ml of 0.01 *M* potassium selenocyanate, 10 ml of 5 % potassium iodide, 10 ml of 10 % acetic acid, and starch, was added one drop of 0.01 *N* iodine. A distinct and stable starch-iodine colour appeared. In absence of potassium iodide, more than 1 ml of 0.01 *N* iodine was consumed, to produce, in the solution, a brownish yellow colour, probably due to the triselenocyanate ion, $\mathrm{(SeCN)_3^-}$. On addition of potassium iodide to the reaction mixture, iodine was regenerated, in accordance with an equilibrium which, tentatively, may be formulated thus:

$$3\ \mathrm{SeCN^-} + \mathrm{I_3^-} \rightleftharpoons \mathrm{(SeCN)_3^-} + 3\ \mathrm{I^-}$$

The finding that a species is indifferent to iodine in presence of potassium iodide, does not, however, exclude the possibility that an oxidation of the compound may be induced through the simultaneous oxidation of thiosulphate by iodine, as has been demonstrated earlier[4] in the case of thiosulphonates, sulphinates, and dialkylthiophosphates. In fact, larger amounts of potassium iodide and acetic acid are required in order to prevent such

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* See footnote on the foregoing page.

an induced oxidation of selenocyanate. Some control titrations, performed under the same conditions as later used for the iodometric analysis of selenopentathionate by means of cyanide, are reported in the following paragraph.

(1) To a mixture of 10 ml of approx. 0.01 *N* sodium thiosulphate and 10 ml of 0.01 *M* potassium selenocyanate, volume 40 ml, were added 2 ml of 1 *M* potassium cyanide, 1 ml of 40 % formaldehyde, 2 g of potassium iodide, 50 ml of water, 20 ml of 10 % acetic acid, and 10 ml of starch solution, and the mixture was titrated with 0.01094 *N* iodine: 9.30 ml, 9.29 ml. (2) Without selenocyanate and potassium iodide: 9.29 ml, 9.30 ml. (3) With 20 ml of 0.01 *N* sodium thiosulphate and 20 ml of 0.01 *M* potassium selenocyanate, otherwise as (1): 18.59 ml, 18.61 ml. (4) With 10 ml of selenocyanate: 18.59 ml, 18.57 ml. (5) Without selenocyanate and potassium iodide, otherwise as (3) and (4): 18.58 ml, 18.59 ml of 0.01094 *N* iodine.

In the above experiments, in presence of 2 g of potassium iodide, the iodine-thiosulphate reaction was not complete unless 50 ml of water were added, as described, before the addition of acetic acid. Thus, Exp. (1) performed without 50 ml of water: 9.20 ml of 0.01094 *N* iodine were consumed. Exp. (2) without 50 ml of water, and in presence of 2 g of potassium iodide: 9.21 ml, 9.20 ml. Even when the solutions were thus diluted, the presence of 2 g of potassium iodide (containing no iodate) seemed to depress the thiosulphate-iodine titer to a slight degree. *E. g.*, Exp. (5) in presence of 2 g of potassium iodide: 18.54 ml, 18.54 ml. Also, as has been noted earlier [4], formaldehyde and acetic acid, especially when potassium iodide is present, markedly retard the reaction between thiosulphate and iodine. The fact that concordant results are obtained in Exps. (1)—(5) may thus be due to a compensation of small errors.

In more concentrated solutions, *e. g.*, when using 0.1 *N* thiosulphate and 0.1 *N* iodine, a simultaneous oxidation of selenocyanate cannot be prevented by use of potassium iodide and acetic acid.

Selenopentathionate and cyanide. The following procedure was accordingly adopted for the iodometric analysis of selenopentathionate by means of cyanide, Eq. (2).

10—20 ml of approx. 0.01 *M* selenopentathionate are diluted to 40 ml. 2 ml of 1 *M* potassium cyanide are added, and the solution is allowed to stand for 5 minutes. Then 1 ml of 40 % formaldehyde, 2 g of potassium iodide, 50 ml of water, and 20 ml of 10 % acetic acid are added, and the solution is titrated with 0.01 *N* iodine (using starch as an indicator).

The following example illustrates the method. 1.0980 g (approx. 2.5 millimole) of potassium selenopentathionate, $K_2Se(S_2O_3)_2 \cdot 1\frac{1}{2}\ H_2O$, were dissolved to 250 ml in a volumetric flask. 10 ml samples were pipetted out and analyzed as described above: 9.81 ml, 9.84 ml, 9.82 ml of 0.01094 *N* iodine. 20 ml samples: 19.69 ml, 19.64 ml, 19.66 ml of 0.01094 *N* iodine. Average values, 9.82 ml and 19.66 ml; theoretically, according to Eq. (2): 9.83 ml and 19.65 ml, respectively. A 10 ml sample, analyzed for selenious acid according to Norris and Fay after oxidation by means of potassium bromate [3]: 46.54 ml—7.24 ml = 39.30 ml of 0.01094 *N* iodine, which corresponds to 9.83 ml (one fourth of the Norris and Fay value) per 10 ml after Eq. (2), or to 19.65 ml per 20 ml sample.

Some experiments were made in more concentrated solutions. 4.2618 g (approx. 10 millimole) of potassium selenopentathionate hemitrihydrate were dissolved to 100 ml in a volumetric flask. 10 ml samples were pipetted out and diluted to approx. 200 ml, and 10 ml of 1 *M* potassium cyanide were added. After 5 minutes, 5 ml of 40 % formaldehyde, 2 g of potassium iodide, and 20 ml of 10 % acetic acid were added, and the mixture was titrated with 0.1020 N iodine: 11.14 ml, 11.12 ml. Using 4 g of potassium iodide: 10.44 ml, 10.50 ml, 10.40 ml. Theoretically, 10.23 ml of 0.1020 N iodine. The values are thus too high. On standing, the titrated solutions became red (selenium being liberated from the selenocyanate). To the three last samples, before selenium appeared, was added barium chloride, and the barium sulphate thus precipitated was filtered off, dried and weighed: 0.2436 g, 0.2407 g, 0.2501 g; theoretically, according to Eq. (2): 0.2435 g $BaSO_4$.

Telluropentathionate and cyanide. 0.4376 g (approx. 1 millimole) of sodium telluropentathionate, $Na_2Te(S_2O_3)_2 \cdot 2\ H_2O$, was dissolved to 250 ml in a volumetric flask. 25 ml samples were pipetted out, diluted to 40 ml, and 2 ml of 1 M potassium cyanide were added. Tellurium immediately appeared. After 5 minutes, 1 ml of 40 % formaldehyde was added, and the tellurium was filtered off (the filtrate remained clear and colourless, also if the formaldehyde was added after the filtration, instead of before). 10 ml of 10 % acetic acid and a few crystals of potassium iodide were added to the filtrate, and the mixture was titrated with 0.01132 N iodine: 17.78 ml, 17.77 ml, 17.79 ml; theoretically, according to Eq. (3): 17.81 ml. A 25 ml sample of the sodium telluropentathionate solution was titrated directly with iodine as described earlier[8]: 35.60 ml and (the formed tetrathionate being analyzed by means of the sulphite method) 8.91 ml of 0.01132 N iodine; theoretically, 35.62 ml and one fourth of this value, respectively.

Similar results were obtained in more concentrated solutions, using 0.1 N iodine. In one case, the tellurium, appearing on addition of potassium cyanide, was dried and weighed. Thus, 0.4156 g of sodium telluropentathionate dihydrate, dissolved in 200 ml of water, and 10 ml of 1 M potassium cyanide added, gave, when filtered after 5 minutes, 62.1 mg of tellurium; theoretically, according to Eq. (3): 61.1 mg. On addition of acetic acid to the filtrate, tellurous acid separated out.

NOTE ON TELLUROCYANATE AND ANALOGOUS TELLURO ANIONS

The fact that the cyanide ion does not react with telluropentathionate reflects upon the poor ability of tellurium, as compared with sulphur and selenium, to give compounds with the cyanide group, and with analogous sulphur- and selenium-bonding groups or ions like sulphite and phosphite.

A survey of the literature fails to reveal descriptions of salts of tellurocyanic acid. Inferring from the lower stability of selenocyanates as compared with thiocyanates, tellurocyanates should, even in solutions, be fairly unstable. Nor are such solutions easily prepared. *E. g.*, hot aqueous solutions of potassium cyanide attack tellurium only to a slight degree[11]. Tellurium dissolves very slowly in solutions of potassium cyanide in liquid ammonia; however, no definite compound could be isolated[12]. Solutions of potassium tellurocyanate have been employed by Birckenbach and Kellermann[13] for measurement of the decomposition potential of the tellurocyanate ion, but the salt itself is not described in the article. According to patents[14], potassium tellurocyanate reacts with aliphatic halides to give the corresponding organic tellurocyanates; however, no such examples are included in the patents. In fact, the only compound of tellurium with the cyanide group, yet described in literature, appears to be the tellurium dicyanide, $Te(CN)_2$, of Cocksedge[15].

No tellurosulphates, whether inorganic or organic, are known. Thus, tellurium is not affected by sodium sulphite solutions. As for tellurophosphates, no such compounds are described in literature. However, according to unpublished experiments by the author, finely divided tellurium does dissolve, on gentle heating, in ethanol solutions of potassium diethylphosphite, to give potassium diethyltellurophosphate, $(C_2H_5O)_2OPTeK$. It is of interest to note that the diethylphosphite takes up tellurium more readily than does potassium cyanide under the same conditions. Potassium diethyltellurophosphate, which may be isolated as colourless, hygroscopic needles, rapidly darkening in moist air, is less stable than the corresponding thio and seleno salts[16], *e. g.*, dilute acids liberate tellurium from its solutions, and so does iodine.

SUMMARY

Selenopentathionate reacts with potassium cyanide to give one equivalent of thiosulphate, as does pentathionate.

Telluropentathionate does not react with potassium cyanide; instead, a hydrolysis takes place, to give two equivalents of thiosulphate.

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