The Determination of Micro Amounts of Polythionates. II.* A Photometric Method for the Determination of Hexathionate by Means of Its Cyanolysis[1]

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In the preceding paper[2] of this series, the methods in current use for analyzing polythionates have been reviewed. So far, there has not been any procedure for the determination of micro quantities of hexathionate. One of the present authors (T. K.)[2] has, however, reported an excellent method for the determination of a small amount of pentathionate, a method which depends upon the reaction:

$$S_5O_6^{2-}+4CN^-+H_2O= \\ S_2O_3^{2-}+SO_4^{2-}+2HCN+2SCN^-$$

followed by the photometric measurement of the thiocyanate thus formed with ferric iron. The above study establishes the feasibility of a method for the determination of hexathionate, because the higher polythionate, hexathionate, reacts more easily with cyanide to form thiocyanate.

The present authors have investigated, in detail, a photometric method for the determination of a micro amount of hexathionate, a method which is based on the reactions:

$$S_6O_6^{2-}+5CN^-+H_2O= \\ S_2O_3^{2-}+SO_4^{2-}+2HCN+3SCN^-$$

$$SCN^-+Fe^{3+}=FeSCN^{2+}$$

they have established an excellent method, finding the most suitable conditions for the reaction of hexathionate with cyanide to proceed completion by varying the cyanide amount, the pH, the reaction time, and the temperature.

In the present investigation, it was observed that hexathionate also is quantitatively converted

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* Part I: This Bulletin, **38**, 1510 (1965)

[1] Presented at the Scientific Meeting on Chemistry, Tokyo, November, 1964.

[2] T. Koh, This Bulletin, **38**, 1510 (1965).

into thiocyanate under the same conditions as are used for the determination of pentathionate.

The proposed method is sufficiently rapid, precise, and accurate to be used for the determination of a small amount of hexathionate.

Experimental

Apparatus and Materials.—Unless stated particularly, the apparatus and materials used in this investigation are the same as those described in the previous paper.[2]

Potassium Hexathionate.—This salt was prepared according to the directions of Goehring and Feldmann.[3] The hexathionate obtained was then recrystallized twice with 2 N hydrochloric acid and dried at room temperature for 6 days.

In order to obtain pure hexathionate, it is of great importance to recrystallize the raw hexathionate as fast as possible, because it undergoes thermal decomposition easily, even in a strong acid solution. In the present study, much purer hexathionate could be obtained than that described in the literature (96%).[3]

The water content physically adsorbed on the hexathionate was estimated to be 1.2% by the Karl Fischer method.

The Purity of the Potassium Hexathionate.—The purity of this salt was estimated by determining the total potassium and sulfur contents as follows.

The potassium hexathionate was decomposed into potassium sulfate by heating it at around 800°C; $K_2S_6O_6 \rightarrow K_2SO_4$. The potassium was determined by weighing[4] the potassium sulfate thus formed.

As for the sulfur, the hexathionate was oxidized[4,5] by bromine in an alkaline medium on heating and, the sulfate ion content formed was determined by the usual gravimetric method. Tables I and II show that the results obtained are within the limits of experimental error and that this potassium hexathionate is pure enough for the purposes of this study.

TABLE I. DETERMINATION OF K FOR THE POTASSIUM HEXATHIONATE* USED IN THE PRESENT STUDY

Sample taken mg.	As $K_2S_6O_6$ mg.	Found as K_2SO_4 mg.	K found for $K_2S_6O_6$ %	K calcd. for $K_2S_6O_6$ %
179.2	177.0	83.7	21.23	21.33
237.0	234.1	111.7	21.41	

TABLE II. DETERMINATION OF S FOR THE POTASSIUM HEXATHIONATE* USED IN THE PRESENT STUDY

Sample taken mg.	As $K_2S_6O_6$ mg.	Found as $BaSO_4$ mg.	S found for $K_2S_6O_6$ %	S calcd. for $K_2S_6O_6$ %
212.0	209.4	796.1	52.22	52.48
173.4	171.3	651.0	52.20	

* Water content was estimated to be 1.2%.

The Standard Hexathionate Solution.—The standard solution, a 1.0×10^{-3} M concentration of hexathionate, was prepared by dissolving 185.6 mg. of the potassium hexathionate (water content: 1.2%) in redistilled water and by then diluting it to 500 ml. This stock solution proved to be stable; even after two months, no measurable change was found by the present method when it was kept at 5±2°C in a refrigerator. The working standard solutions were prepared by then diluting this stock solution properly.

Procedure. — A standard hexathionate solution of 10.0 ml. is placed in a 25 ml. volumetric flask. To this solution are added first 4.0 ml. of the buffer solution of pH 7.4, and then 2.6 ml. of 0.05 M sodium cyanide, whereupon the pH of the solution is brought to 8.6.

The volumetric flask is kept in the thermostat at 40±1°C for 30 min.; hexathionate is thus converted into thiocyanate quantitatively. Then 3.0 ml. of a 1.5 M ferric nitrate - perchloric acid solution is added. After the flask has been filled to the mark with redistilled water, its contents are mixed well. The absorbancy of the solution of the ferric-thiocyanate complex thus formed is measured at the wavelength of 460 mμ, using distilled water as a reference.

Results and Discussion

Calibration Curves.—The solutions containing various amounts of hexathionate and thiocyanate were treated by the procedure mentioned above; the experimental results are plotted in Figs. 1 and 2.

As can be seen in Figs. 1 and 2, the absorbancy and concentration were in a good linear relationship. When one ion of hexathionate undergoes cyanolysis, three ions of thiocyanate are formed. Consequently, if the hexathionate is pure enough and if it is, moreover, converted into thiocyanate quantitatively, the sensitivity of hexathionate should be just three times as high as that of thiocyanate when plotted by the mole concentration for hexathionate and thiocyanate. In fact, Fig. 1 shows that the calibration curve for hexathionate is three

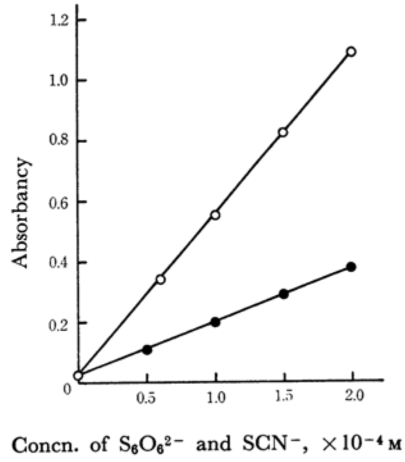

Fig. 1. Calibration curves.
○ Hexathionate ● Thiocyanate

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[3] M. Goehring and U. Feldmann, *Z. anorg. Chem.*, **257**, 223 (1948).

[4] F. Martin and L. Metz, *Z. anorg. u. allgem. Chem.*, **127**, 83 (1923).

[5] C. Mishima, *Bull. Tokyo Inst. Tech.*, No. 1, 27 (1951).

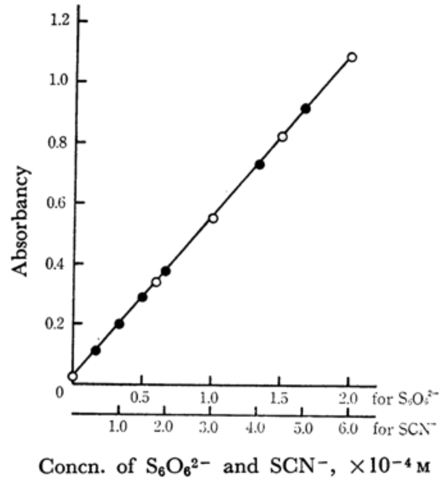

Fig. 2. Calibration curves.
○ Hexathionate ● Thiocyanate

times as sensitive as that for thiocyanate. As can also be seen in Fig. 2, the calibration curve of hexathionate exactly coincides with that of thiocyanate when the scale of the thiocyanate concentration is made one-third of that of the hexathionate concentration, demonstrating that the stoichiometric reaction has occurred.

The Effect of the Amount of Sodium Cyanide.—The preliminary experiments led the authors to the conclusion that pH has a great effect on the cyanolysis and that hexathionate, just like pentathionate,2) undergoes a partial alkaline decomposition as a result of the higher pH caused by the addition of the cyanide.

As will be described below, it was observed that the optimum pH for the reaction of hexathionate with cyanide is over the range of 7.8 to 8.9 under the conditions of the preceding procedure. 0.5 ml. of 0.025 M sodium cyanide and 0.5 to 4.0 ml. of 0.05 M sodium cyanide were employed, and in all cases the solution was buffered to the optimum pH value. The resulting effect of the amount of sodium cyanide on the cyanolysis is shown in Fig. 3.

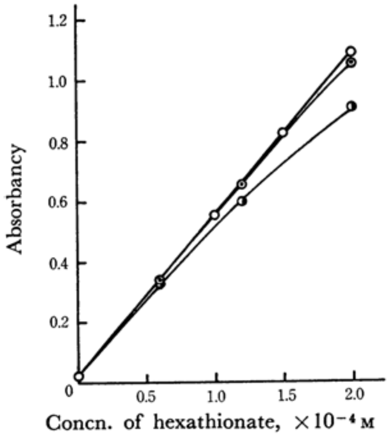

Fig. 3. Effect of sodium cyanide amount. The pH was adjusted to the range from 7.8 to 8.9 in all cases.

Cyanolysis time: 30 min. at 40°C
◑ 0.025 M NaCN 0.5 ml. (I)
⊙ 0.05 M NaCN 0.5 ml. (II)
○ 0.05 M NaCN 1.0, 2.0, 2.6 and 4.0 ml. (III)

The calibration curves with 0.5 ml. portions of 0.025 and 0.05 M sodium cyanide solutions do not form straight lines (see I and II), indicating that hexathionate is not quantitatively converted into thiocyanate because of insufficient amounts of cyanide. It can be concluded from Fig. 3 that 1.0 ml. of a 0.05 M sodium cyanide solution is sufficient for the quantitative conversion of hexathionate into thiocyanate, and that the amount of sodium cyanide does not have any effect on the method, so long as it is sufficient and the pH is adjusted to an optimum value.

The Effect of pH.—At higher pH levels, hexathionate undergoes an alkaline decomposition besides cyanolysis; therefore, the procedure should be carried out below a pH value of 8.9. Figure 4 shows the dependence of the rate of cyanolysis on the pH of the solution at 20°C.

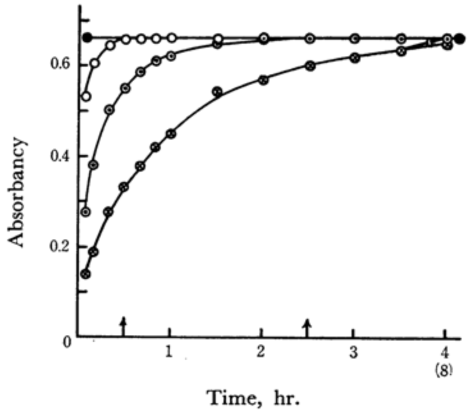

Fig. 4. Effect of pH on the rate of cyanolysis at 20°C.
● 3.6×10^{-4} M SCN^-
○ pH 8.7 (I)
⊙ pH 8.0 (II) } 1.2×10^{-4} M $S_6O_6^{2-}$
⊗ pH 7.5 (III)

The maximum absorbancy, which corresponds to the complete and stoichiometric reaction of hexathionate with cyanide, is reached in 30 min. at pH 8.7; it then remains constant (see I), while the reaction at pH 8.0 goes to completion in two hours and a half (see II). On the other hand, the reaction at pH 7.5 does not go to completion even within 4 hr.; however, it goes stoichiometrically to completion in 8 hr. (see III).

In order to accelerate the rate of cyanolysis, the reaction temperature was raised from 20°C to 40°C and 70°C. Figure 5 shows how the pH

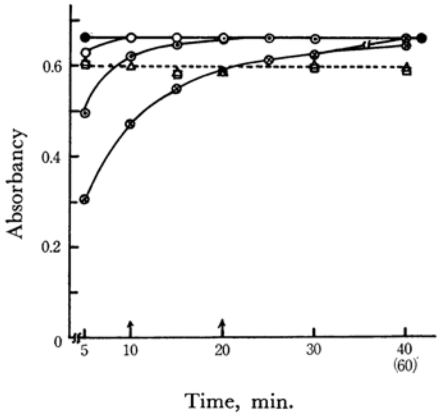

Fig. 5. Effect of pH on the rate of cyanolysis.
—●— 3.6×10^{-4} M SCN^-
—○— pH 8.7 (I) } at 40°C } 1.2×10^{-4} M $S_6O_6^{2-}$
—⊙— pH 8.0 (II)
—⊗— pH 7.5 (III)
--△-- pH 8.7 (IV) } at 70°C
--□-- pH 8.0 (IV)

of the solution affects the rate of cyanolysis at 40°C and 70°C.

At 40°C, the reaction goes well to completion and is stoichiometric in 10 min. at pH 8.7 (see I), while the reactions at pH 8.0 and 7.5 go to completion in 20 min. and 1 hr. respectively (see III). At 70°C, the thermodecomposition occurs in addition to cyanolysis, so hexathionate is not completely converted into thiocyanate (see IV).

The reaction of hexathionate with cyanide at various pH values was carried out, both at 20°C for 60 min. and at 40°C for 30 min., for the purpose of studying the effect of pH on the cyanolysis. The results are shown in Fig. 6, where the reaction at 20°C for 60 min. gives maximum absorbancies over the pH range from 8.9 to 8.3 (see I), and that at 40°C, for 30 min. over the pH range from 8.9 to 7.8 (see II). The decrease in absorbancy above the pH value of 9.0 may be attributed to the alkaline decomposition of hexathionate. The optimum pH range for the stoichiometric reaction can be extended from both 7.8 and 8.3 to a lower pH value by making the cyanolysis time longer, because the rate of cyanolysis decreases with the lowering of the pH.

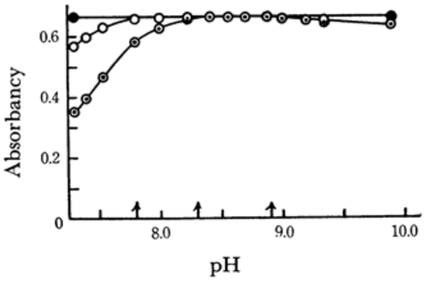

Fig. 6. Effect of pH.
● 3.6×10^{-4} M SCN^-
○ 30 min. at 40°C (II) } 1.2×10^{-4} M $S_6O_6^{2-}$
⊙ 60 min. at 20°C (I)

A similar method which is available for the determination of micro amounts of tetrathionate under the same conditions as those used here for the determination of pentathionate and hexathionate will be reported on in another paper.

Summary

A photometric method for the determination of a small amount of hexathionate has been developed, a method depending on the formation of thiocyanate equivalent to the hexathionate, and on the determination of thiocyanate with an excess of ferric iron. A buffer solution is first added to a standard hexathionate solution in order that the pH of the mixed solution after the addition of the cyanide solution may be within an optimum range; otherwise the hexathionate undergoes alkaline decomposition as a result of the higher pH value caused by the addition of the cyanide. The conditions under which the reaction of hexathionate with cyanide is rapid and proceeds well to completion, have been established by varying the cyanide amount, the pH, the reaction time, and the temperature. Hexathionate can be determined by exactly the same procedure as that used for phentathionate.

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