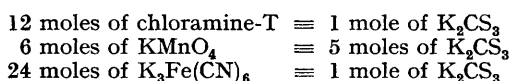


Oxidimetric Determination of Thiocarbonate Sulphur with Chloramine-T, Potassium Ferricyanide and Potassium Permanganate

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Oxidimetric methods for determining the concentration of aqueous solutions of potassium thiocarbonate by using chloramine-T, potassium ferricyanide and potassium permanganate are discussed. The chloramine-T method is based on the reaction of potassium thiocarbonate with a known excess of chloramine-T in alkaline medium at 60° C and back-titration of the unreacted chloramine-T against a standardised solution of sodium thiosulphate, with starch as indicator. Twenty-four equivalents of the oxidant per mole of potassium thiocarbonate are consumed, showing that the three sulphur atoms of thiocarbonate are oxidised to sulphate. When ferricyanide is used twenty-four equivalents of the oxidant per mole of potassium thiocarbonate are also consumed in an alkaline medium at 60° C. However, in acidic medium, potassium permanganate is found to oxidise the three sulphur atoms of thiocarbonate to elemental sulphur. The following molar relationships are established—



BECAUSE of the important analytical applications of potassium thiocarbonate reported lately in the literature,^{1,2,3,4,5} an investigation of efficient and rapid chemical procedures for the determination of thiocarbonate sulphur present in aqueous samples of the reagent was considered necessary. A gravimetric method⁶ in which thallium(I) nitrate is used for the quantitative precipitation of thiocarbonate sulphur and titrimetric procedures involving iodimetric, as well as iodatometric, oxidation of the thiocarbonate contents of samples have been reported.⁷ Iodic acid alone was found to react with the three sulphur atoms of the thiocarbonate; iodine and potassium iodate each oxidised one of the sulphur atoms, the other two forming carbon disulphide. The iodimetric and gravimetric methods^{8,9,10} available relate only to the determination of sulphide sulphur and not to thiocarbonate sulphur. The results obtained by the present method are not only quantitative, but have confirmed that three moles of hydrogen sulphide per mole of potassium thiocarbonate are available in reacting solutions under optimum conditions.

As chloramine-T is able to break the C-S, N-S and S-S bonds in a variety of sulphur compounds,^{11 to 17} oxidising all of the sulphur quantitatively to the sulphate form, it was of interest to investigate the reaction between chloramine-T and potassium thiocarbonate. The active constituent of chloramine-T is the hypochlorite ion, which is obtained by hydrolysis of chloramine-T. Chloramine-T is preferred to hypochlorite because of its relatively high stability. The oxidation of thiocarbonate sulphur was studied in both acidic and alkaline media, and a simple titrimetric procedure for the determination of potassium thiocarbonate has been developed by making use of the oxidation in alkaline medium.

Potassium ferricyanide has also been studied as an oxidant for thiocarbonate sulphur in hot alkaline medium. An investigation of the use of this oxidant was necessary because, being a weak oxidant, it is more selective than others. Moreover, oxidation of various organic and inorganic sulphur compounds in alkaline medium has been reviewed by Sant,¹⁸ but no reference to thiocarbonate sulphur in this respect is found in the literature. However, recently Deshmukh¹⁹ has standardised potassium thiocarbonate amperometrically by using ferricyanide as oxidant, with osmium tetroxide as catalyst, and has reported that only one third of the thiocarbonate sulphur reacted at room temperature.

Furthermore, evaluation of thiocarbonate sulphur in acidic medium has been carried out with potassium permanganate, a strong oxidant that reacts quantitatively with the hydrogen sulphide liberated by the thiocarbonic acid produced in acidic solutions of potassium thiocarbonate.

CHLORAMINE-T METHOD

REAGENTS—

Chloramine-T, 0.1 N—This solution was kept in amber-coloured bottles and standardised iodimetrically.²⁰

Sodium thiosulphate, 0.1 N—This was prepared from analytical-reagent grade material and standardised against potassium iodate.

Starch solution, 1 per cent., aqueous.

Potassium thiocarbonate, 2 M—An aqueous solution was prepared by the direct method, and, after standardisation,⁶ was used to prepare suitable dilutions. Other reagents used were of analytical-reagent grade.

PROCEDURE—

Transfer 10 ml of 0.02 M potassium thiocarbonate into a 250-ml conical flask containing 50 ml of standard chloramine-T solution, made alkaline with 5 ml of M sodium hydroxide. Heat to 60° C for half an hour by immersing the flask in a hot water bath. Cool to room temperature, acidify with 20 ml of 5 N sulphuric acid and add 25 ml of 10 per cent. potassium iodide solution. Titrate the liberated iodine with standard sodium thiosulphate solution. The amount of chloramine-T consumed by potassium thiocarbonate is thus obtained from the titre value. Calculate the thiocarbonate sulphur content of the sample from the relationship—

$$1 \text{ ml of } N \text{ chloramine-T} \equiv 7.75 \times 10^{-3} \text{ g of } K_2CS_3 \equiv 4.008 \times 10^{-3} \text{ g of S.}$$

Blank corrections were not necessary in these experiments. The titre values were found to be reproducible, and the results of a few representative experiments are given in Table I.

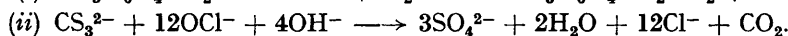
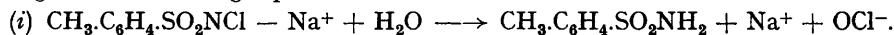
TABLE I

RESULTS OF THE DETERMINATION OF SULPHUR IN POTASSIUM THIOCARBONATE WITH CHLORAMINE-T IN ALKALINE MEDIUM AT 60° C

Volume of 0.02 M potassium thiocarbonate added, ml	Volume of 0.1 N chloramine-T consumed, ml	Number of equivalents of oxidant per mole of potassium thiocarbonate used	Sulphur present, mg	Sulphur found, mg	Difference, mg
10	47.98	23.99	19.20	19.23	+0.03
10	47.84	23.92	19.20	19.18	-0.02
5	24.02	24.02	9.60	9.63	+0.03
5	24.00	24.00	9.60	9.62	+0.02
3	14.38	23.96	5.76	5.76	0.0
3	14.40	24.00	5.76	5.77	+0.01

DISCUSSION

It is evident from the results shown in Table I that the reaction of chloramine-T with alkaline potassium thiocarbonate at 60° C is such that the three sulphur atoms undergo oxidation. For the complete oxidation of sulphur in potassium thiocarbonate to the sulphate ion twenty-four equivalents of oxidant per mole of potassium thiocarbonate would be needed according to the following equations—



Thus, 12 moles of chloramine-T \equiv 1 mole of K_2CS_3 .

Experiments carried out in acidic medium revealed incomplete oxidation, even at a higher temperature. This was caused by the partial oxidation of potassium thiocarbonate to elemental sulphur which, once formed, resists further oxidation by chloramine-T. The

sulphur precipitated during these experiments in acidic media was observed to be suspended in solution.

Oxidation in alkaline medium at room temperature (20° C) also did not proceed to completion, and separation of elemental sulphur was clearly observed as a white turbidity. However, when the temperature was raised to 60° C this turbidity vanished and the oxidation of the entire sulphur was found to be quantitative. The finely divided sulphur reacts with hot alkali,²¹ forming sulphide, sulphite and thiosulphate, all of which can be oxidised to sulphate by chloramine-T.

FERRICYANIDE METHOD

REAGENTS—

Potassium ferricyanide, 0.1 N—This was prepared by dissolving analytical-reagent grade material in redistilled water and standardised by titrating against standard sodium thio-sulphate solution.

Sodium thiosulphate, 0.1 N.

Starch solution, 1 per cent., aqueous.

Sulphuric acid, 5 N.

Zinc sulphate, 0.5 M—This was prepared by dissolving an analytical-reagent grade sample in redistilled water.

Potassium thiocarbonate, 2 M.

PROCEDURE—

In a series of experiments to determine the optimum conditions for the complete oxidation of thiocarbonate sulphur with ferricyanide, carried out at room temperature, the time of reaction was varied and the amount of potassium thiocarbonate used kept constant. The excess of ferricyanide was determined by back-titrating against standardised thio-sulphate solution. The reaction was slow at room temperature, the number of equivalents of oxidant per mole of potassium thiocarbonate increasing from 2.60 to 8.06 in 45 minutes at 5-minute intervals. However, in the second set of experiments the reactants were heated to 60° C and the reaction was found to be completed within 15 to 20 minutes.

RECOMMENDED PROCEDURE—

Introduce a measured aliquot of the test solution containing not more than 17 mg of sulphur into a measured excess volume of standard 0.1 N ferricyanide, previously made alkaline with 5 N sodium hydroxide so that its alkalinity is about 3 N. Heat to 60° C for 15 to 20 minutes by immersing the flask in a hot water bath. Cool to room temperature, and titrate the excess of ferricyanide against standardised thiosulphate after acidifying with 5 N sulphuric acid, adding 25 ml of 10 per cent. potassium iodide solution and an excess of zinc sulphate solution so that all of the resulting ferrocyanide can be precipitated as zinc ferrocyanide. Use starch as the indicator. Calculate the thiocarbonate sulphur content of the sample from the relationship—

$$1 \text{ ml of } N \text{ ferricyanide} \equiv 7.75 \times 10^{-3} \text{ g of } K_2CS_3 \equiv 4.008 \times 10^{-3} \text{ g of S.}$$

The results of a few representative experiments are given in Table II.

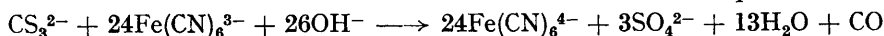
TABLE II

RESULTS OF THE DETERMINATION OF SULPHUR IN POTASSIUM THIOCARBONATE WITH FERRICYANIDE IN ALKALINE MEDIUM AT 60° C

Volume of 0.06 M potassium thiocarbonate added, ml	Volume of 0.1 N ferricyanide consumed, ml	Number of equivalents of oxidant per mole of potassium thiocarbonate used	Sulphur present, mg	Sulphur found, mg	Difference, mg
1	14.38	23.96	5.76	5.76	0.0
1	14.40	24.00	5.76	5.77	+0.01
2	28.76	23.96	11.52	11.52	0.0
2	28.78	23.98	11.52	11.53	+0.01
3	43.20	24.00	17.28	17.32	+0.04
3	43.22	24.01	17.28	17.33	+0.05

DISCUSSION

It was seen from the results that the reaction between ferricyanide and potassium thiocarbonate is time consuming. It takes about 45 minutes to oxidise only one of the three sulphur atoms to sulphate at room temperature, after which the titre value remains constant. However, the reaction at 60° C is rapid, and the three sulphur atoms of the thiocarbonate are oxidised to sulphate, as seen in Table II. The reaction of ferricyanide with potassium thiocarbonate in alkaline medium at 60° C can be expressed—



Thus, 24 moles of ferricyanide \equiv 1 mole of K_2CS_3 .

Before titrating the excess of ferricyanide, sufficient zinc sulphate must be added to precipitate all the ferrocyanide as zinc ferrocyanide. Otherwise, the end-point would not be sharp because of the formation of Prussian blue, the presence of which has been verified by making the solution alkaline (colour fades).

POTASSIUM PERMANGANATE METHOD

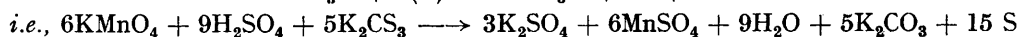
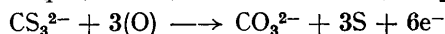
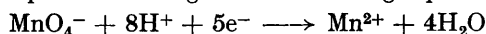
PROCEDURE—

Transfer 10 ml of 0.1 N potassium permanganate solution to a 250-ml conical flask and add 10 ml of 0.1 N sulphuric acid. Introduce, gradually, freshly prepared potassium thiocarbonate solution from a microburette with a bent nozzle, keeping the tip of the nozzle beneath the liquid surface. Continue adding until the colour of the potassium permanganate is discharged. Repeat the observations with different amounts of potassium permanganate. Calculate the potassium thiocarbonate sulphur content of the sample solution from the relationship—

$$1 \text{ ml of } N \text{ KMnO}_4 \equiv 31.006 \times 10^{-3} \text{ g of } \text{K}_2\text{CS}_3 \equiv 16.03 \times 10^{-3} \text{ g of S.}$$

DISCUSSION

The results in Table III show that the reaction of potassium thiocarbonate with acidified potassium permanganate is such that the three sulphur atoms of thiocarbonate undergo oxidation to elemental sulphur according to the following equations—



Thus, 6 moles of $\text{KMnO}_4 \equiv$ 5 moles of K_2CS_3 .

The results of titrimetric evaluation with permanganate are accurate for 0.006 to 0.06 M concentrations of potassium thiocarbonate. The volume of permanganate taken should be such that not more than 8 mg of sulphur are precipitated out after the complete reaction.

TABLE III

RESULTS OF THE DETERMINATION OF THIOCARBONATE SULPHUR WITH POTASSIUM PERMANGANATE IN THE PRESENCE OF 0.05 TO 0.1 N SULPHURIC ACID

Volume of 0.05 N potassium permanganate taken, ml	Titre of 0.03 M potassium thiocarbonate, ml	Number of equivalents of oxidant per mole of potassium thiocarbonate used	Sulphur present, mg	Sulphur found, mg	Difference, mg
5	1.38	6.03	4.00	3.97	-0.03
5	1.40	5.95	4.00	4.03	+0.03
10	2.80	5.95	8.12	8.06	-0.06
10	2.82	5.91	8.12	8.12	0.0
15	4.46	5.60	12.18	12.84	+0.66
15	4.44	5.63	12.18	12.78	+0.60

The fact that the three sulphur atoms of thiocarbonate are oxidised by permanganate and no trace of carbon disulphide separated was confirmed by the negative result of a colorimetric test.²² In this test a drop of the solution should produce a stable, pink colour if acetone

and elemental sulphur are present together with free carbon disulphide. The reaction of permanganate with potassium thiocarbonate in alkaline medium at room temperature was also studied, and it was found that only one sulphur atom of thiocarbonate had undergone oxidation to sulphate, while the other two formed carbon disulphide. Furthermore, results at 60° C are not reproducible.

To ensure that the liberated hydrogen sulphide undergoes oxidation, potassium thiocarbonate is added to the permanganate, dropwise, from a burette.

CONCLUSIONS

The results are quantitative, and suitable dilution of more concentrated solutions of potassium thiocarbonate is necessary to obtain accurate results. Under optimum conditions the three sulphur atoms of the thiocarbonate are oxidised, thus giving a rapid method for determining and identifying thiocarbonate from other sulphur compounds.

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