[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

The Silver Xanthates

BY R. F. MAKENS

This paper presents a study of some of the reactions of the silver xanthates, and a simple, accurate method, which developed during the course of the investigation, for the analysis of the alkali metal xanthates. Since the analysis of the xanthates is an integral part of the study of the silver xanthates, the method of analysis is presented first.

The Analysis of Xanthates.—The procedure is as follows. Dissolve approximately 0.5 g. of the xanthate in 100 ml. of water and slowly add from a buret slightly more than 1 gram mole of 0.1 N silver nitrate per mole of xanthate present, stirring the solution constantly. Add 30 ml. of 10% ferric nitrate solution, and run in immediately from a buret enough standardized potassium thiocyanate solution to produce a distinct color. Back-titrate the excess thiocyanate with silver nitrate until the red color disappears. Check the titration several times, if desired, by adding successive portions of potassium thiocyanate and silver nitrate.

Portions of several potassium xanthates were purified according to DeWitt and Roper,[1] and were analyzed for sulfur by the Carius method. After their purity was established, they were titrated with silver nitrate as outlined above. The results are shown in Table I.

TABLE I

THE ANALYSIS OF XANTHATES BY TITRATING WITH SILVER NITRATE

Xanthate	% of calcd. value Test 1	Test 2	Av.
Potassium ethyl	99.83	99.85	99.84
Potassium *n*-amyl	99.84	100.08	99.96
Potassium *n*-hexyl	100.08	99.71	99.89
Potassium *n*-nonyl	99.99	100.16	100.07

If, in making the determination outlined above, any large excess of silver nitrate is allowed to remain in the solution, a secondary reaction occurs which causes a darkening of the precipitate and consumes an excessive amount of silver. Any secondary reaction is prevented by removing immediately the excess silver with potassium thiocyanate. Furthermore, if the reaction mixture is allowed to stand for several hours, the silver will be removed quantitatively unless three or more atoms of silver are present per mole of xanthate.

The Study of the Black Precipitate.—The black precipitate formed when a large excess of silver ion reacts with potassium ethyl xanthate was analyzed. The presence of silver sulfide was shown through x-ray examination by the Hull method. A colorless gas was evolved when a portion of the black precipitate was acidified with hydrochloric or sulfuric acid. The composition of the evolved gas was determined by decomposing a portion of the black precipitate with dilute sulfuric acid, and testing the gas according to Mulliken.[2] No evidence was found of mercaptans, sulfides or carbon disulfide. The gas was identified as carbonyl sulfide according to C. Bender,[3] by precipitating in barium hydroxide solution and testing the filtrate for sulfides. The sulfuric acid solution was then distilled, and ethyl alcohol was identified in the distillate by the formation of iodoform and by the molybdic acid test of E. Merck.[4] The residue in the distilling flask proved to be silver sulfate and silver sulfide. The original black precipitate, therefore, yields silver sulfide, an ethoxy group, carbonyl sulfide, and silver ions not originally present as silver sulfide. No appreciable amount of alcohol or acetone soluble material is present in the original black precipitate. A quantitative examination of the black precipitate was made to determine the proportionate number of moles of each constituent present in the decomposition products.

The amount of carbonyl sulfide was determined by decomposing the black precipitate in a Bunsen carbon dioxide apparatus with hydrochloric acid according to Blasdale.[5] Magnesium perchlorate was substituted for the usual drying agent. The material remaining in the flask was filtered through a fritted glass crucible; the filtrate was made basic with sodium hydroxide and distilled. (The sodium hydroxide precipitated a little silver oxide which was filtered off and added to the

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[1] C. C. DeWitt and Edwin E. Roper, THIS JOURNAL, **54**, 444 (1932).

[2] S. P. Mulliken, "Identification of Pure Organic Compounds," F. H. Gilson Company, 1922, Vol. IV, p. 13.

[3] C. Bender, *Ann.*, **148**, 138 (1868).

[4] E. Merck in Allen's "Commercial Organic Analysis," P. Blakiston's Son and Company, Philadelphia, Pa., 1923, p. 142.

[5] W. C. Blasdale, "Fundamentals of Quantitative Analysis." D. Van Nostrand Company, New York, 1928, p. 105.

former precipitate.) The amount of alcohol in the distillate was determined by oxidation with permanganate according to Rozman.[6]

The precipitate in the fritted glass crucible from the carbonyl sulfide separation was extracted with dilute ammonium hydroxide to constant weight, and the amount of silver in the ammonium hydroxide extract was determined. The remaining silver sulfide was analyzed for silver and sulfur. The results of several analyses are shown in Table II, in which each sample represents a separate precipitate.

TABLE II

PERCENTAGE OF EACH PRODUCT FROM THE BLACK PRECIPITATE

	Sample I	Sample II	Sample III
Ag^{+a}	19.85	18.33	21.26
C_2H_5O—	8.10	7.58	8.83
COS	11.06	10.46	11.78
Ag_2S + free sulfur	60.49	63.01	57.14
Total	99.50	99.38	99.01

[a] This refers to silver not present as silver sulfide.

TABLE III

MOLES OF EACH PRODUCT FROM THE BLACK PRECIPITATE PER MOLE OF CARBONYL SULFIDE

	Sample I	Sample II	Sample III
Ag^{+a}	0.9991	0.9756	1.0060
C_2H_5O—	.9766	.9664	1.0006
Ag_2S	1.3232	1.4485	1.1670

[a] This refers to silver not present as silver sulfide.

As a further verification of the assumption that only carbonyl sulfide is evolved on the addition of hydrochloric acid, and also as a check upon the other analyses, Carius combustions were made on portions of samples II and III.

TABLE IV

TOTAL PERCENTAGE SULFUR FOUND IN THE BLACK PRECIPITATE

	Sample II	Sample III
By Carius method	14.37	14.36
Calcd. from Table II	14.11	14.24

It is therefore justifiable to calculate the gas evolved as carbonyl sulfide.

Discussion of Results

The results shown in Tables II and III indicate in the black precipitate the presence of a compound which must be a combination of silver ion, carbonyl sulfide, and an ethoxy group, namely, silver ethyl mono-thiocarbonate.

The variability of the ratio of moles of the silver ethyl mono-thiocarbonate to moles of silver sulfide can probably be best explained by the following three reactions. The first reaction

$$AgNO_3 + KSC(S)OC_2H_5 \longrightarrow AgSC(S)OC_2H_5 + KNO_3$$

has been shown to take place by Reychler.[7] Since the final products are silver sulfide and silver ethyl mono-thiocarbonate and since from the data they appear to be approaching a ratio of 1 mole of silver sulfide to 1 mole of mono-thiocarbonate, the second reaction may be written

$$2AgNO_3 + AgSC(S)OC_2H_5 \longrightarrow Ag_2S + 2HNO_3 + AgSC(O)OC_2H_5$$

This reaction is evidently followed by a slow hydrolysis of the silver mono-thiocarbonate similar to that found by Bender[3] for the potassium salt. He has shown that when an aqueous solution of potassium ethyl mono-thiocarbonate is warmed, the reaction is

$$2KSC(O)OC_2H_5 + HOH \longrightarrow K_2CO_3 + COS + C_2H_5OH + H_2S$$

When silver ion is present the reaction should precipitate silver sulfide instead of evolving hydrogen sulfide, and since the solution is acid (*p*H about 4.5) the carbon dioxide should be evolved and the following reaction should take place

$$AgSC(O)OC_2H_5 + HOH \longrightarrow CO_2 + COS + Ag_2S + C_2H_5OH$$

When silver mono-thiocarbonate is treated with strong hydrochloric acid and warmed, as was done in the analysis, the reaction evidently proceeds in a somewhat different manner

$$AgSC(O)OC_2H_5 + HCl \longrightarrow AgCl + COS + C_2H_5OH$$

Summary

1. A method is proposed for the analysis of xanthates by precipitating the silver xanthate and back-titrating the excess silver with potassium thiocyanate.

2. The precipitate formed when excess silver is present contains silver ethyl mono-thiocarbonate, silver sulfide and a trace of sulfur.

3. Equations are given to account for the products formed.

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(6) B. Y. Rozman, *Zhur. Prikladnoi Khim.*, **2**, 191 (1929).

(7) A. Reychler, *Bull. soc. chim. Belg.*, **37**, 166 (1928).