

Mercurimetric Estimation of Alkyl Xanthates

STIG VEIBEL and MIECZYSLAW WRÓŃSKI*

Department of Organic Chemistry, Technical University, Copenhagen, Denmark

A new, simple and rapid method for estimation of the xanthates, salts and esters of the xanthic acids, has been suggested. The sample is decomposed by dimethylamine into dimethylxanthamide and sulphide or thiolate, which are titrated with *o*-hydroxymercuribenzoate in the presence of thiofluorescein as indicator.

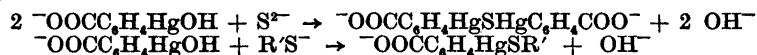
The most frequently applied methods for the determination of xanthates are based on the titration with iodine,¹ with perchloric acid,² or with silver or mercury salts using electrometric indication of the end-point.³⁻⁵ The first two methods are applicable only to pure substances and the electrometric methods are somewhat inconvenient for general use.

In order to find an analytical method suitable for selective determination of xanthates we have examined the known reaction between xanthates and ammonia, resulting in formation of xanthamide (*O*-alkyl thiocarbamate) and thiolate or sulphide. The reaction was, however, found to be too slow for analytical purposes. When, on the other hand, primary or secondary amines are used instead of ammonia, the reaction is completed in a few minutes. The use of dimethylamine is recommended because it is easily commercially available, very active, and the dimethylxanthamides produced are resistant to further decomposition and do not interfere in the titration of thiols with *o*-hydroxymercuribenzoate (HMB), $o\text{-C}_6\text{H}_4(\text{HgOH})\text{COO}^-$.

The decomposition of xanthates by dimethylamine may be considered as a nucleophilic substitution reaction, following a $\text{S}_{\text{N}}2$ scheme:



As the sulphide and thiolate ions are removed in the course of the titration, forming with HMB stable mercaptides,⁶ the reaction goes to completion:



* Present address: Department of Chemical Technology, University of Łódź, Poland.

It has been found that complete reaction is reached 1–3 minutes after the first end-point of the titration. After a longer period of time some sulphide may be formed from decomposition of dimethylxanthamide.

The decomposition of xanthic esters proceeds more rapidly than that of xanthates. Moreover, the xanthic esters are more sensitive to alkali than the salts and they can be quantitatively decomposed by heating them with an excess of HMB in 0.1 N sodium hydroxide. In this case the doubly bound sulphur is converted to sulphide, and the consumption of HMB amounts to 3 moles per mole of ester. On this basis the determination of xanthic esters is possible, but the procedure would be more complicated than the decomposition by dimethylamine, and not selective because many types of bivalent sulphur compounds are decomposed by heating with HMB in alkaline solution.⁷

The decomposition by dimethylamine can be recommended as well for the determination of esters of dithiocarboxylic acids:



EXPERIMENTAL

Reagent. A 0.05 N solution of *o*-hydroxymercuribenzoate was prepared by dissolving ca. 16 g of *o*-hydroxymercuribenzoic acid anhydride (supplied by Fabryka Odczyńników Chemicznych, Gliwice, Poland) in 200 ml of N sodium hydroxide and diluting to 1 l with water. The normality was calculated directly from the weight of the anhydride ($M = 320.71$).

The indicator solution was prepared by dissolving a small amount of thiofluorescein (supplied by FOCh) in N ammonia and adding some EDTA in order to slow down the oxidation of thiofluorescein. As the indicator will itself use up a certain amount of the titrant this amount should be determined in a blank with the same volume of indicator solution as in the experiment. The blank value should be not more than 0.03 ml of 0.05 N HMB.

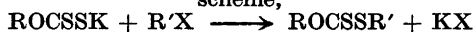
The xanthates were prepared in the usual way from alcohol, potassium hydroxide, and carbon disulphide. They were subsequently precipitated from acetone solution with ether and dried over calcium chloride.

The xanthic esters were taken from the collection of chemicals at this Department. The purification was carried out by recrystallisation or distillation. The *p*-bromophenacylestere were prepared by the procedure suggested by Berger and Uldall.⁸

Table 1. Titration of potassium alkyl xanthates (procedure 1).

Xanthate prepared from	Taken, mg			Found, mg			Average recovery
	1	2	3	1	2	3	%
Methanol	41.0,	43.7,	58.3	40.6,	43.1,	57.4	98.7
Ethanol	36.0,	78.8,	59.0	36.2,	79.0,	58.8	100.2
1-Propanol	45.8,	24.9,	57.8	45.8,	25.1,	58.0	100.5
2-Propanol	93.8,	43.2,	50.5	92.5,	42.3,	49.8	98.5
1-Pentanol	82.5,	60.7,	42.3	82.6,	60.8,	42.8	100.5
Benzyl alcohol	44.3,	87.7,	70.8	44.3,	87.5,	70.6	99.8

Table 2. Titration of xanthic esters ROCSSR' (procedure 2) prepared according to the scheme,



R	R'X	Taken, mg		Found, mg		Average recovery %
Ethyl	Allyl chloroacetate	59.7,	119.5	60.5,	120.0	100.4
		179.5		179.5		
Ethyl	Ethyl bromide	36.5,	73.0	36.6,	72.6	99.7
		109.5		109.0		
Ethyl	Bromosuccinic acid monoamide	96.5,	145.0	98.0,	147.0	101.2
		48.3		49.0		
Ethyl	Chloroacetic acid	63.5,	127.0	63.0,	125.0	99.0
		190.0		188.0		
Ethyl	Methyl chloroacetate	32.7,	65.4	33.2,	65.5	100.7
		98.0		98.2		
Methyl	Ethyl chloroacetate	24.0,	48.0	24.2,	47.8	100.3
		72.0		71.7		
Ethyl	Butyl bromide	35.3,	70.5	35.4,	70.3	100.2
		100.6		100.5		
Ethyl	<i>p</i> -Bromophenacyl bromide	96.3,	86.6	96.5,	87.0	100.3
		154.2		155.5		
Pentyl	<i>p</i> -Bromophenacyl bromide	84.2,	106.8	84.2,	107.5	100.3
		115.0		115.5		
Benzyl	<i>p</i> -Bromophenacyl bromide	72.6,	176.8	72.6,	175.5	99.7
		86.4		86.6		
(Thiobenzoylthio)acetic acid		59.5,	119.0	59.2,	119.0	99.7
		178.0		177.0		

1. *Procedure for xanthates.* Dissolve the sample in 5 ml of 40 % aqueous dimethylamine, heat for 30 sec on a steam bath and titrate with 0.05 N HMB in the presence of thiofluorescein as indicator until the blue colour disappears. Wait 3 min and titrate again to the final end-point. One mole of xanthate corresponds to two moles of HMB.

2. *Procedure for xanthic esters.* Dissolve the sample in 10 ml of ethanol, add 2 ml of 2 N ammonium chloride, 5 ml of 40 % dimethylamine and titrate with HMB as described above. For *p*-bromophenacylestere use 1 ml of dimethylamine and wait one minute. One mole of xanthic esters corresponds to one mole of HMB.

DISCUSSION

Tables 1 and 2 show that the suggested method is well applicable for xanthates, xanthic esters, and esters of dithiocarboxylic acids. Moreover the method is suitable for the analysis of different types of sulphur compounds in the presence of each other, *e.g.* sulphide and xanthate. The sulphide can be titrated separately with HMB in 0.1 N sodium hydroxide solution using dithizone as indicator.⁶ In a second sample the sulphide plus xanthate can be determined by the dimethylamine method.

The method allows the determination of the equivalent weight of xanthates and xanthic esters with a precision of ordinarily $\pm 0.5\%$. When a g of substance use up b ml of HMB of normality n the equivalent weight is given by

$$E_{\text{xanthate}} = 2a \times 1000/bn; E_{\text{xanthic ester}} = a \times 1000/bn$$

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