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The Conversion of Some Alkylxanthates to the Corresponding Trithiocarbonates. The Nucleophilic Reaction of $^-$SCSSR

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The reaction of *O*-methyl-, ethyl-, and benzylxanthates with a catalytic amount of triethylamine in the presence of excess carbon disulfide gave the corresponding trithiocarbonate in good yields. The products were formed by the nucleophilic reaction of $^-$SCSSR with xanthates. The kinetic study showed the following order of nucleophilicity toward xanthates in DMF:

$$^-\text{SCOSMe} > {}^-\text{SCSSMe} > \text{Me}_3\text{N}$$

Dialkyl trithiocarbonates are generally prepared from mercaptans and thiophosgene$^{1)}$:

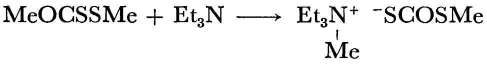
$$\text{RSH} + \text{ClCSSR}' \longrightarrow \text{RSCSSR}'$$

$$\text{RSH} + \text{CS}_2 \longrightarrow \text{KSCSSR} \longrightarrow \text{RSCSSR}'$$

$$2\text{RSH} + \text{CSCl}_2 \longrightarrow \text{RSCSSR}$$

In the course of the studies of the reaction of xanthates with tertiary amines,$^{2)}$ the present authors have found a convenient route for the preparation of trithiocarbonates from xanthates.

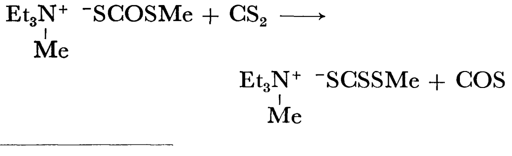
In a previous paper,$^{2)}$ the authors reported that xanthates reacted with tertiary amines to give quaternary ammonium salts at room temperature, and dithiolcarbonates at elevated temperatures. It was then shown that these reaction products were formed by the following paths. As an example, the reaction of methyl methylxanthate and triethylamine will be shown:



$$\text{MeOCSSMe} + \text{Et}_3\text{N} \longrightarrow \underset{\text{Me}}{\text{Et}_3\text{N}^+}\ {}^-\text{SCOSMe}$$

$$\text{MeOCSSMe} + {}^-\text{SCOSMe} \longrightarrow \text{MeSCOSMe} + {}^-\text{SCOSMe}$$

The salt thus formed reacted easily with carbon disulfide to yield the corresponding trithiocarbonate salt:$^{3)}$



$$\underset{\text{Me}}{\text{Et}_3\text{N}^+}\ {}^-\text{SCOSMe} + \text{CS}_2 \longrightarrow \underset{\text{Me}}{\text{Et}_3\text{N}^+}\ {}^-\text{SCSSMe} + \text{COS}$$

Results and Discussion

When O-alkylxanthates was treated with triethylamine in the presence of carbon disulfide at higher temperatures, the corresponding trithiocarbonate was obtained in a good yield (Table 1) and gaseous carbon oxysulfide was detected by vpc. Moreover, when methyl methylxanthate was reacted with triethylamine in carbon disulfide at room temperature, diemethyl trithiocarbonate and a small amount of triethylmethylammonium methyltrithiocarbonate were found. These observations seem to show that $^-$SCSSR reacts with xanthate to yield trithiocarbonate.

Table 1. The reaction of xanthates with triethylamine in the presence of carbon disulfide$^{a)}$

Xanthate	Reaction condition		Yield of trithiocarbonate(%)
	°C	hr	
MeOCSSMe	100	0.7	94
MeOCSSEt	100	0.7	93
MeOCSS*n*-Pr	100	0.7	81
EtOCSSMe	130	6	76$^{b)}$
EtOCSSEt	130	7	77
$C_6H_5CH_2OCSSMe$	100	0.5	84

a) Mole ratio, xanthate: CS_2: Et_3N=1: 2: 0.2
b) Dimethyl and diethyl trithiocarbonate were also produced.

Methyl methylxanthate reacted vigorously with a catalytic amount of KSCSSMe to give dimethyl trithiocarbonate. Even ethyl-, *n*-propyl-, and *i*-propylxanthates gave trithiocarbonates. *i*-Propylxanthate was recovered in about an 80% yield by a 20-minute reac-

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1) H. C. Godt, and R. E. Wann, *J. Org. Chem.*, **26**, 4047(1961).
2) H. Yoshida, This Bulletin, **42**, 1948 (1969).
3) H. Yoshida, *Nippon Kagaku Zasshi*, **89**, 883 (1968).

Table 2. The reaction of xanthates with KSCSSMe in the presence of carbon disulfide[a)]

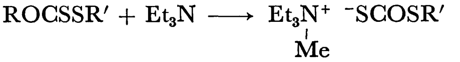
Xanthate	Reaction condition		Yield (%)		
	°C	min	MeS-CSSMe	MeS-CSSR	RS-CSSR
MeOCSSMe	130	1	93		
EtOCSSMe	130	15	26	47	22
n-PrOCSSMe	130	20	25	49	20
i-PrOCSSMe	130	240	28	41	13
EtSCSSMe	130	20	27	49	23

a) Mol ratio, xanthate: CS_2: KSCSSMe=1: 2: 0.2. DMF was added as a homogeneous solvent by about 20 wt %.

tion at 130°C, while heating for about 4 hours gave trithiocarbonates in a good yield. The results are summarized in Table 2. The order of reactivity of xanthates (Me>Et>*n*-Pr≫*i*-Pr) seems to show the reaction proceeds *via* the nucleophilic attack of $^-$SCSSMe on the *O*-alkyl group of xanthates.

When ethyl methyl trithiocarbonate was heated at 130°C with KSCSSMe, crossed products, dimethyl and diethyl trithiocarbonates, were found (Table 2, the bottom line). Without KSCSSMe, however, no crossed product was found under similar reaction conditions. Thus, the crossed products were supposed to be yielded by the transesterification catalysed by the mercaptide ion,[2)] which was itself formed by the thermal decomposition of $^-$SCSSMe.

Thus, the reaction of xanthate with triethylamine in the presence of carbon disulfide may be simplified as follows:



$$\text{ROCSSR}' + \text{Et}_3\text{N} \longrightarrow \text{Et}_3\underset{\displaystyle \text{Me}}{\underset{|}{\text{N}^+}}\ {}^-\text{SCOSR}' \qquad (1)$$

$$^-\text{SCOSR}' + \text{CS}_2 \longrightarrow {}^-\text{SCSSR}' + \text{COS} \qquad (2)$$

$$\text{ROCSSR}' + {}^-\text{SCSSR}' \longrightarrow \text{RSCSSR}' + {}^-\text{SCOSR}' \qquad (3)$$

$$\text{ROCSSR}' + {}^-\text{SCOSR}' \longrightarrow \text{RSCOSR}' + {}^-\text{SCOSR}' \qquad (4)$$

The first reaction is the alkylation of triethylamine with xanthate to yield a quaternary ammonium salt, which was then changed to the corresponding trithiocarbonate salt (reaction (2)). The reactions (3) and (4) are the nucleophilic attack of $^-$SCSSR′ and $^-$SCOSR′ on xanthate to yield trithio- and dithiolcarbonate respectively. Since no dithiolcarbonate was detected in the reaction, the reaction (2) may be said to proceed faster than the reactions (3) and (4).

In order to clarify the mechanism, the reaction of $^-$SCSSMe with xanthate was investigated kinetically in DMF. The rate constant was first-order with xanthate and was independent of the concentration of carbon disulfide. These results show that the reaction (2) proceeds much faster than the reactions (3) and (4). As Fig. 1 shows, the apparent first-order rate consttants (k_1') are proportional to the concentration of $^-$SCSSMe. The slope of the line gives a second-order rate constant, k_2. The data are summarised in Table 3.

It is well known that thiolate anions have strong nucleophilicities toward tetrahedral carbons in protic solvents.[4)] Although the nucleophilicities of some thiolate anions have been investigated in DMF,[5)] no work on the thiocarbonate ion has been presented.

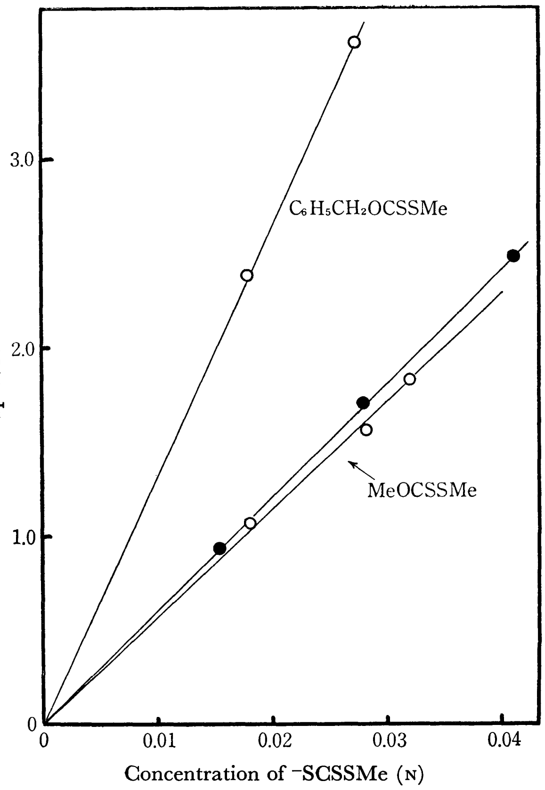


Fig. 1. The relation between the apparent first-order rate constant (k_1') and the concentration of $^-$SCSSMe for the reaction (3).
○ $Me_4NSCSSMe$ ● KSCSSMe

Table 3. Second-order rate constants for the reaction of xanthates with nucleophiles
(30°C k: l/mol·min)

Xanthate	Nucleophile	in DMF	in C_6H_6
MeOCSSMe	Me_3N[a)]	0.036	0.0012
	Et_3N[a)]		0.000097
	$Me_4NSCOSMe$[a)]	0.186	
	$Me_4NSCSSMe$	0.0573	
	KSCSSMe	0.0601	
$C_6H_5CH_2OCSSMe$	Me_3N[a)]		0.0028
	$Me_4NSCSSMe$	0.132	

a) Taken from Ref. 2.

Table 3 shows that $^-$SCSSMe and $^-$SCOSMe have larger nucleophilicities toward xanthate than trimethylamine and obviously than triethylamine has in DMF. The smaller reactivity of $^-$SCSSMe than that of $^-$SCOSMe may be attributed to the resonance stabilization of the ion.

The greater reactivity of benzylxanthate than that of methylxanthate supports the S_N2 mechanism. Once the reaction (1) proceeds, the reactions (2) and (3) recurr to give trithiocarbonate.

Experimental

All the reactions were carried out in stoppered test tubes. The reaction mixture was treated with cold aqueous hy-

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[4)] R. G. Person, H. Sobel, and J. Songstand, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

[5)] D. Cook, I. P. Evans, E. C. F. Co. and A. J. Parker, *J. Chem. Soc., B*, **1966**, 404.

drochloride and then extracted with carbon disulfide. The carbon disulfide extract was dried over calcium chloride, and was analyzed by vpc and NMR.

Materials. $Me_4NSCSSMe$ was prepared according to the previously described method.[3] KSCSSMe was prepared from methylmercaptan and carbon disulfide in a cold aqueous potassium hydroxide solution. After drying, the salt was recrystallized from acetone - ether. The purity was determined by acid-base titration.

Kinetic Run. A DMF solution containing ^-SCSSMe (0.015—0.04N), xanthate (0.05—0.08N), and carbon disulfide (0.1—0.4N) was allowd to stand in a constant-temperature bath. The rate was followed at suitable time intervals by analyzing the NMR spectrum of the S-Me groups.