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Reaction of Xanthates with *t*-Amines. VI. The Reaction Mechanism

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It was previously reported that xanthate reacted with *t*-amine to give quaternary ammonium salt at room temperature, and dithiolcarbonates at elevated temperatures. Precise study showed that these reaction products are formed by the following three reactions: the alkylation of *t*-amine with xanthate affords quaternary ammonium salt and the reaction of xanthate with quaternary ammonium salt yields dithiolcarbonate, while there is transesterification between thiolesters and quaternary ammonium salt. The rate constants and equilibrium constants of these reactions were calculated.

Xanthates are known to react with ammonia, prim-, and *s*-amines to give thioncarbamates and mercaptans:[1)]

$$\mathrm{ROCS_2R' + HNR''_2 \rightarrow ROCSNR''_2 + R'SH}$$

However, no work has yet been reported on the reaction of xanthates with *t*-amines. In previous papers[2)] the present author has reported that xanthates react with *t*-amines at room temperature to give quaternary ammonium salts, and at elevated temperatures (70—80°C) to yield dithiolcarbonates and a small amount of ammonium salts. For example, *n*-propyl methylxanthate reacts with triethylamine thus:

$$\begin{aligned}&\mathrm{MeOCS_2}\,n\text{-}\mathrm{Pr} + \mathrm{Et_3N} \rightarrow\\ &\quad \mathrm{Et_3\overset{\oplus}{N}(Me)\overset{\ominus}{S}COSMe} + \mathrm{Et_3\overset{\oplus}{N}(Me)\overset{\ominus}{S}COS}\,n\text{-}\mathrm{Pr}\\ &\quad + \mathrm{MeSCOSMe} + \mathrm{MeSCOS}\,n\text{-}\mathrm{Pr}\\ &\quad + n\text{-}\mathrm{PrSCOS}\,n\text{-}\mathrm{Pr}\end{aligned}$$

The present paper will deal with the formation of the products obtained by the reaction of xanthates with *t*-amines by the following three successive reactions:

i) Alkylation of *t*-amines with xanthates (to give quaternary ammonium salts).

ii) The reaction of xanthates with the quaternary ammonium salts (to yield dithiolcarbonates).

iii) Transesterification between thiolesters (xanthates and/or dithiolcarbonates) and the quaternary ammonium salts.

Results and Discussion

t-Amine, a nucleophile, reacts with ordinary carboxylic esters to yield quaternary ammonium salts.[3,4)] Alkyl acylates are cleaved at their alkyl-

TABLE 1. PRODUCTS OF THE REACTIONS BETWEEN THIONESTERS AND NUCLEOPHILES

Ester	Nucleophile	Reaction condition		Product
$\mathrm{MeOCS_2Me}$[a)]	$\mathrm{Et_3N}$	80°C	*	$\mathrm{MeSCOSMe, Et_3\overset{+}{N}(Me)\overset{-}{S}COSMe}$ (7%)
	$\mathrm{Et_3\overset{+}{N}(Me)\overset{-}{S}COSMe}$	80°C	*	$\mathrm{MeSCOSMe, Et_3\overset{+}{N}(Me)\overset{-}{S}COSMe}$ (Recov.)
$\mathrm{EtOCS_2Et}$	$\mathrm{Et_3N}$	90°C	20 hr	$\mathrm{EtSCOSEt, Et_4\overset{+}{N}\overset{-}{S}COSEt}$ (5%)
$\mathrm{MeOCS_2C_6H_5}$[b)]	$\mathrm{Et_3N}$	40°C	*	$\mathrm{MeSC_6H_5}$
	$\mathrm{Et_3\overset{+}{N}(Me)\overset{-}{S}C_6H_5}$	40°C	*	$\mathrm{MeSC_6H_5, Et_3\overset{+}{N}(Me)\overset{-}{S}C_6H_5}$ (Recov.)
$\mathrm{MeOCSC_6H_5}$	$\mathrm{Et_3N}$	80°C	10 hr	$\mathrm{MeSCOC_6H_5, Et_3\overset{+}{N}(Me)\overset{-}{S}COC_6H_5}$ (6%)
	$\mathrm{Et_3\overset{+}{N}(Me)\overset{-}{S}COC_6H_5}$	80°C	5 hr	$\mathrm{MeSCOC_6H_5, Et_3\overset{+}{N}(Me)\overset{-}{S}COC_6H_5}$ (Recov.)

Mole ratio 1:1, in each reaction no solvent was used.

* The reaction was quite facile at this temperature.

a) Ref. 2b.

b) Ref. 2c.

[1)] W. Walter and K. D. Bode, *Angew. Chem.*, **79**, 285 (1967).

[2)] a) H. Yoshida, S. Inokawa and T. Ogata, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 950 (1965); b) *ibid.*, **86**, 1179 (1965); c) *ibid.*, **87**, 1209 (1966); d) *ibid.*, **87**, 1212 (1966).

[3)] a) B. Willstätter and W. Kahn, *Ber.* ,**35**, 2757 (1902); b) L. P. Hammett and H. L. Pfluger, *J. Am. Chem. Soc.*, **55**, 4079 (1933); c) A. C. Pierce and M. M. Joullie, *J. Org. Chem.*, **27**, 3968 (1962).

[4)] J. H. Wernz, U.S. Pat. 3635100.

oxygen bond to afford the corresponding sulfides[5—7] by means of the action of mercaptides, while thiolacylates undergo ester interchange reactions[5,6] with mercaptides as a result of the nucleophilic attack of mercaptide ions on the carbonyl group. As has previously been reported,[2d] the alkylation of *t*-amines with xanthates resembled the Menschutkin reaction. At elevated temperatures xanthates react with *t*-amines to yield the rearranged dithiolcarbonates and a small amount of ammonium salts. As is shown in Table 1, not only xanthates but also thionesters give the rearranged thiolesters when they are treated with triethylamine or with the corresponding ammonium slats. The reactivity of alkyl thionesters decreased in the order: methyl$\gg$ethyl$>$*n*-propyl with respect to the alkyl group. When thionesters were heated under similar conditions without any amines or ammonium salts, no detectable change was observed. These preliminary experiments indicated that ammonium salts formed in the initial step attack thionesters to give thiolesters.

Alkylation of *t*-Amines with Xanthates (to give Quaternary Ammonium Salts). It has been reported that the reaction of *t*-amines with ordinary esters yields quaternary ammonium salts at elevated temperatures.[3,4] Hammett and Pfluger[3b] have reported that the rates of the methylation of trimethylamine by various esters increase with an increase in the strength of the acid. However, no work has been reported on the reaction of *t*-amines and thion- or thiol-esters. In a previous paper,[2d] the kientics of the reaction of *S*-alkyl, -aryl, and -aralkyl xanthates with various amines in benzene has been reported (Table 3). The rates of the reaction of various esters with trimethylamine are compared with those of xanthates in Table 2. The rate constants (observed or extrapolated from higher temperatures) for the quaternization of trimethylamine with methylesters in benzene at 30°C are shown in Table 3. As the table shows, thionesters are more active than the corresponding oxygen-esters. The difference in activation energy between dimethylcarbonate and dimethylthioncarbonate, and that between methyl *p*-nitrobenzoate and methyl *p*-nitrothionbenzoate, are 5.2 and 3.6 kcal/mol respectively (Table 3); therefore, the activation energy of the alkylation of trimethylamine with an ordinary ester is 4—5 kcal/mol greater than the corresponding thionester which rearranges to form the thiolester. The summation of the bond energies shows that thion-thiol rearrangement should be exothermic, amounting to

Table 2. Rate constants of the alkylation of trimethylamine with esters in benzene

Ester	Temp. (°C)	k_2 (*l*/mol·hr)
$MeOCOC_6H_4NO_2$-(*p*)	100.0	0.0109
	110.0	0.0201
	120.0	0.0338
$MeOCSC_6H_4NO_2$-(*p*)	45.0	0.0421
	50.0	0.0575
	55.0	0.0850
$MeOCSC_6H_4Cl$-(*p*)	50.0	0.00985
$MeOCSC_6H_5$	45.0	0.00325
	50.0	0.00456
	55.0	0.00657
$MeOCSC_6H_4Me$-(*p*)	50.0	0.00251
$MeOCSC_6H_4OMe$-(*p*)	50.0	0.00171
MeOCSOMe	25.0	0.0149
	30.0	0.0224
	34.9	0.0332
MeOCOOMe	100.0	0.00749
	110.0	0.0144
	120.0	0.0296
MeSCOSMe	120.0	*
$MeSCOC_6H_5$	120.0	*

* No detectable reaction was observed.

Table 3. Rate constants of the alkylation of trimethylamine with esters in benzene at 30°C

Ester	k_2 (*l*/mol·hr)	Relative rate	E_a (kcal/mol)	ρ (°C)
MeOCS·SMe[a)]	0.0731	1	12.1	
MeOCS·OMe	0.0112[c)]	1/6.5	14.6	
MeOCO·OMe[b)]	0.0000078[c)]	1/9400	19.8	
$MeOCS\cdot SC_6H_5$[a)]	0.353	4.8		+1.65 (30)
$MeOCS\cdot SCH_2C_6H_5$[a)]	0.129	1.8		+0.82 (30)
$MeOCSC_6H_5$[b)]	0.00119	1/61	13.1	+1.44 (50)
$MeOCSC_6H_4NO_2$-(*p*)[b)]	0.0153	1/4.8	12.9	
$MeOCOC_6H_4NO_2$-(*p*)[b)]	0.0000652	1/1120	16.5	

a) Ref. 2d.
b) Rate constant extrapolated from higher temperatures in Table 2.
c) The half value of the observed rate constant.

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5) W. R. Vaughan and J. B. Baumann, *J. Org. Chem.*, **27**, 739 (1962).

6) G. S. Sasin, P. R. Schaeffer and R. Sasin, *ibid.*, **22**, 1183 (1957).

7) J. C. Sheehan and G. D. Daves, Jr., *ibid.*, **29**, 2006 (1964).

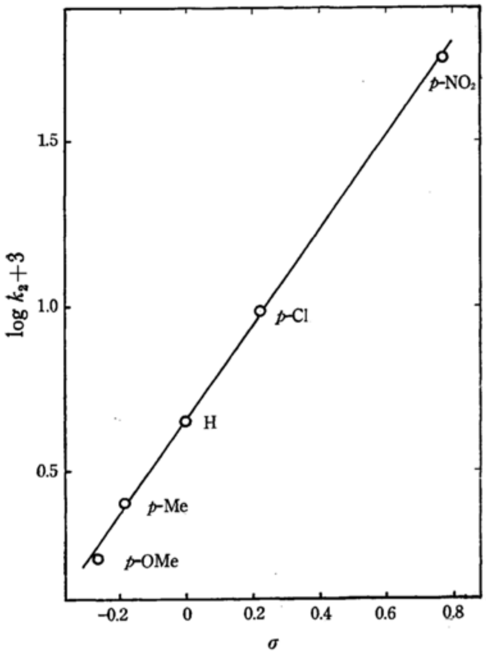

Fig. 1. Hammett plot of methyl thionbenzoates with trimethylamine in benzene at 50°C.

nearly 20 kcal/mol.[8] O'Connor and Nace[9a] have reported that the activation energies for the pyrolysis of the ethylcarbonate and methylxanthate of cholesterol are 41.0 and 32.9 kcal/mol respectively. This difference in activation energy (8.1 kcal/mol) is in good agreement with that between dimethyl carbonate and methyl methylxanthate for alkylation (7.7 kcal/mol. Table 3). The substitution of an electron-accepting group for the carbonyl carbon of the esters leads to an increase in the rate of alkylation (positive ρ values in Table 3). The ρ factor is $+0.467$ for the pyrolysis of *S*-benzyl cholesterylxanthates,[9a] and $+0.82$ for the alkylation of trimethylamine with *S*-benzyl methylxanthates. The difference may be due to the fact that the former is a cyclic *cis* intramolecular elimination reaction,[9c] and the latter, an S_N2. The smaller reactivity of dimethyl thioncarbonate than that of methyl methylxanthate may be due to the electron-releasing resonance effect of the methoxy group.[10]

Thus, the greater reactivity of xanthates may be based on the decreased activation energy due to the electron-accepting mercapto group and to thion-thiol rearrangement.

The Reaction of Methyl Methylxanthate (I) with Tetramethyl Ammonium Dithiocarbonate $\mathbf{Me_4\overset{\oplus}{N}\overset{\ominus}{S}COSR}$ (II). The reaction product between I and trimethylamine gave no rearranged product in benzene. On the other hand, it gave dimethyldithiolcarbonate under homogeneous conditions in dimethylformamide (DMF) or dimethylsulfoxide (DMSO), even at room temperature. The rate constants of the following reactions in DMF at 30°C were determined by measuring the rates of the disappearance of I (the transesterification, described in the following section, was disregarded):

$$\mathrm{Me_3N + MeOCS_2Me \xrightarrow{k_2} Me_4\overset{\oplus}{N}\overset{\ominus}{S}COSMe} \qquad (1)$$

$$\mathrm{Me_4\overset{\oplus}{N}\overset{\ominus}{S}COSMe + MeOCS_2Me \xrightarrow{k_2'} Me_4\overset{\oplus}{N}\overset{\ominus}{S}COSMe + MeSCOSMe} \qquad (2)$$

The rate equations are:

$$\mathrm{d}[\mathrm{X}]/\mathrm{d}t = -k_2[\mathrm{X}][\mathrm{A}]-k_2'[\mathrm{S}][\mathrm{X}]$$
$$\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k_2[\mathrm{X}][\mathrm{A}]$$

The concentrations are related thus:

$$[\mathrm{S}]+[\mathrm{A}]=[\mathrm{A}_0]$$
$$[\mathrm{S}]+[\mathrm{X}]+[\mathrm{T}]=[\mathrm{X}_0]$$

where [X], [A], [S], and [T] indicate the concentrations of I, trimethylamine, II (R=Me), and dimethyl dithiolcarbonate respectively, and where [A_0] or [X_0] indicate the initial concentration. Put [X_0]=[A_0]; then, upon integration:

$$\left.\begin{aligned} x &= [(\kappa-1)/\kappa]\alpha + (1/\kappa)\ln\alpha + 1/\kappa \\ \tau &= \int_\alpha^1 \frac{\mathrm{d}\alpha}{\alpha[(\kappa-1)\alpha+\ln\alpha+1]} \\ \tau &= -\ln x \qquad (\kappa=1), \end{aligned}\right\} \qquad (3)$$

where $\tau=[\mathrm{A}_0]k_2't$, $\kappa=k_2/k_2'$, $x=[\mathrm{X}]/[\mathrm{X}_0]$, and $\alpha=[\mathrm{A}]/\mathrm{A}_0]$. x and τ, as functions of α for various κ's, can be calculated by Eq. (3); and x plotted against τ in Fig. 3.

The reaction (2) is pseudo-first-order, and the apparent first-order rate constant is proportional to the concentration of II (R=Me) (Fig. 2). The slope of the line gives k_2'. Equimolar reactions of I with trimethylamine proceed; data typical of those shown in Table 8 are plotted in Fig. 3, where they give $\kappa=0.19$. The results, summarized in Table 4, indicate that, toward I, MeSCOS$^-$ is a stronger nucleophile than trimethylamine by a factor of 5. As has been shown previously (Table 1), xanthates react with triethylamine to yield dithiolcarbonates at elevated temperatures. At lower temperatures crystalline quaternary ammonium salts have little reactivity, while at elevated temperatures they melt and dissolve in the reagent and react with xanthates. Trimethylamine reacts

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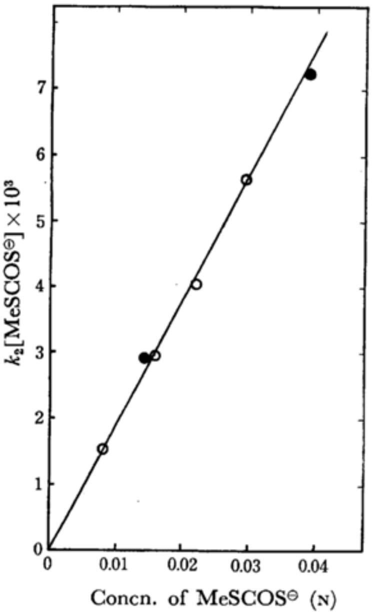
[8] C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

[9] a) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **74**, 5454 (1952); b) *ibid.*, **75**, 2118 (1953); c) R. F. W. Bader and A. N. Bourns, *Can. J. Chem.*, **39**, 348 (1961).

[10] A. W. Baker and G. H. Harris, *J. Am. Chem. Soc.*, **82**, 1923 (1960); C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962), p. 10.



iFg. 2. The relation between the appararent first-order rate constant and concentration of I for reaction (2).

○: $\text{Me}_4\overset{+}{\text{N}}\overset{-}{\text{S}}\text{COSMe}$ ●: $\text{Et}_3\overset{+}{\text{N}}(\text{Me})\overset{-}{\text{S}}\text{COSMe}$

30 times faster with I in DMF than in benzene (Table 4). This increase in rate agrees with the reported value[11] for the Menschutkin reaction (25.6). The rearrangement of thionesters to thiolesters has been reported by many workers, almost all of them concerned with intramolecular reactions (for example, the Schönberg rearrangement[12] or the thermal rearrangement of xanthates[13]). It was confirmed that the reactions of thionesters (such as xanthates and thionbenzoates) with *t*-amines to form thiolesters are second-order and that the initially-formed thiolate ions (monoalkyl dithiolcarbonate and thiolbenzoate ions) react as strong nucleophiles with thionesters to give rearranged thiolesters.

Table 4. Second-order rate constants of the reaction of methylxanthate wite nucleophiles

Nucleophile	Solvent	Temp. (°C)	Rate const. (l/mol·min)	Ratio
Me_3N	Benzene	30	k_2 0.0012	1
Me_3N	DMF	30	k_2 0.036	30
II (R=Me)	DMF	30	k_2' 0.186	155

Transesterification between Thiolesters and II. It is well known that transesterification occurs when an ester is heated with alcohol in the presence of acid or base. Although some works[5-7,14] have reported the transesterification of thiolesters, the kinetics or equilibrium has not been investigated. The reaction between II and thiolesters in benzene (heterogeneous conditions) produced no detectable change, but the mixture of II and thiolesters in DMF or DMSO came to equilibrium in a few

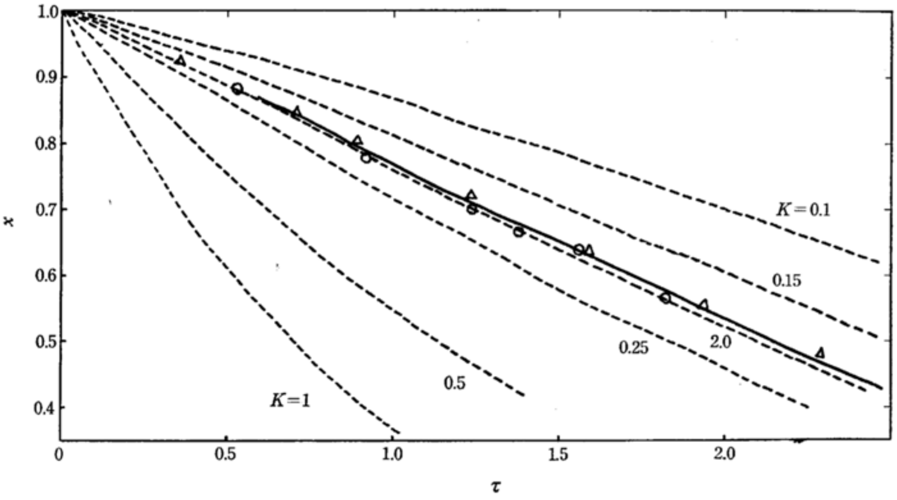


Fig. 3. The relation between τ and x.
△: $[A_0]=[X_0]=0.0466$N ○: $[A_0]=[X_0]=0.0344$N

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[11] E. L. Eliel, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley & Sons Inc., New York (1956), p. 70.

[12] H. R. Al-Kajimi, D. S. Tarbell and D. Plat, *J. Am. Chem. Soc.*, **77**, 2479 (1955); D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).

[13] T. Taguchi, Y. Kawazoe, K. Yoshihara, H. Kanayama, M. Mori, K. Tabata and K. Harano, *Tetrahedron Letters*, **1965**, 2717.

[14] H. Yoshida, S. Inokawa and T. Ogata, This Bulletin, **39**, 2055 (1966).

TABLE 5. REACTION PRODUCTS OF THE ALKYLTHIOLCARBONATES WITH II

Ammonium salt	Thiol ester $\mathrm{R'S\overset{X}{\overset{\parallel}{C}}SR'}$ R'	X	Mole ratio	Reaction condition	Products (mol%) II R	R'	$\mathrm{RS\overset{X}{\overset{\parallel}{C}}SR}$	$\mathrm{RS\overset{X}{\overset{\parallel}{C}}SR'}$	$\mathrm{R'S\overset{X}{\overset{\parallel}{C}}SR'}$	K
II (R=Me)	Et	O	2 : 1	a	56	44	19	50	31	0.621
II (R=Et)	Me	O	2 : 1	a	43	57	30	51	19	0.578
II (R=Me)	Et	S	2 : 1	a	55	45	20	49	31	0.641
II (R=Et)	Me	S	2 : 1	a	45	55	29	50	21	0.658
II (R=Me)	*n*-Pr	O	2 : 1	a	58	42	18	49	34	0.515
II (R=Me)	*i*-Pr	O	2 : 1	a	62	38	14	50	36	0.380
II (R=Me)	*s*-Bu	O	2 : 1	a	67	33	10	51	39	0.316
$\mathrm{Me_4NSCSSMe}$	Et	O	2 : 1	b						
II (R=Me)	*n*-$\mathrm{PrOCS_2Et}$		1 : 1	a	56	44	*n*-$\mathrm{PrOCS_2Me}$(45)	*n*-$\mathrm{PrOCS_2Et}$(55)		0.610
EtSK	*n*-$\mathrm{PrOCS_2Me}$		1 : 1	a			*n*-$\mathrm{PrOCS_2Me}$(44)	*n*-$\mathrm{PrOCS_2Et}$(56)		

a) 50°C for 15 min.
b) No detectable change was observed after 12 hr at 50°C.

minutes at room temperature. Table 5 shows that the amount of ammonium salts produced depends on thiol groups and not on the structure of the thiolesters (*i.e.*, xanthate, trithiocarbonate, and dithiolcarbonate).

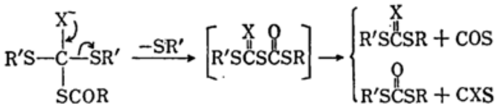
The following equilibrium can be derived from Table 5:

$$\mathrm{Me_4\overset{\oplus\ominus}{N}SCOSMe} + \mathrm{(Ester)\text{-}SR} \rightleftarrows \mathrm{Me_4\overset{\oplus\ominus}{N}SCOSR} + \mathrm{(Ester)\text{-}SMe}$$

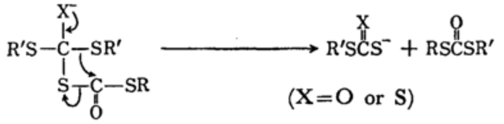
$$K = [\mathrm{Me_4\overset{\oplus\ominus}{N}SCOSR}][\mathrm{(Ester)\text{-}SMe}]/[\mathrm{Me_4\overset{\oplus\ominus}{N}SCOSMe}][\mathrm{(Ester)\text{-}SR}]$$

The slope of the straight line obtained by plotting $\log K$ *vs.* σ^* for R ($\rho^* = +2.2$) is shown in Fig. 4. The positive ρ^* value indicates that the equilibrium of the reaction depends on the relative basicities of $\mathrm{RSCOS^-}$.[15]

The explanation that these reaction products are formed by an S_N2 attack of $\mathrm{RSCOS^-}$ on the carbonyl carbon of the thiolester seems improbable, since the reaction of dialkyl trithiocarbonate (X=S) and II gave no trithiocarbonate ion ($\mathrm{RSCS_2^-}$), while this ion should be formed in any reaction by mechanism (A) or (B):



(A)



(B)

(X=O or S)

The reaction of methyl *n*-propylxanthate with potassium ethylmercaptide was found to yield ethyl *n*-propylxanthate by ester interchange under similar conditions (Table 5). Thus, it seems plausible that the mercaptide ion initially formed by the reaction (C):[16]

$$\mathrm{RSCOS^{\ominus}} \rightleftarrows \mathrm{RS^{\ominus}} + \mathrm{COS} \qquad \text{(C)}$$

attacks the carbonyl carbon of the thiolesters to yield transesterification products. Thiolesters do not react with monoalkyl trithiocarbonate. The

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[15] Although free acids RSCOSH are not known, their $\mathrm{p}K_a$ values should give postive ρ^* for R groups considering the data of xanthic acids [V. Hejl and J. Pecher, *Chem. Zvensti*, **21**, 261 (1967); *Chem. Abstr.*, **67**, 85514 (1967); H. Majima, *Chem. Abstr.*, **56**, 2201f (1962)] and mercaptans [D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940); M. M. Kreevoy, E. T Happer, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *J. Am. Chem. Soc.*, **82**, 4899 (1960)].

[16] Although in a literature [Houben-Weyl "Methoden der Organischen Chemie" 9, Georg Thieme Verlag, Stuttgart (1955), p. 807] the salt is described to be unknown, the treatment of potassium ethylmercaptide with carbonyl sulfide in DMF or in benzene was found to yield $\mathrm{EtSCOS^-K^+}$. The structure of the salt was determined by VPC analysis of the reaction product [EtSCOSMe] with methyl iodide. This finding also seems to suggest reaction (C).

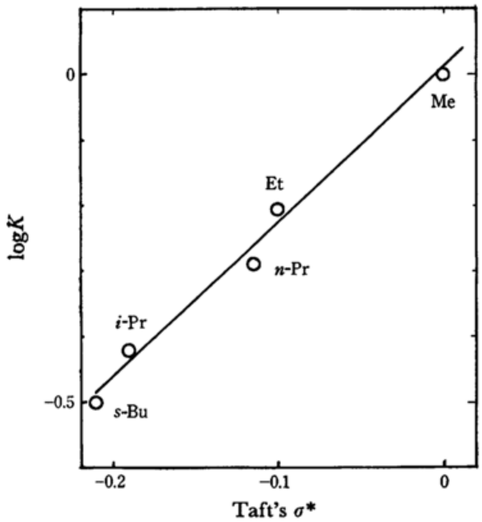

Fig. 4. The relation between Taft's σ^* and log K.

resonance energy[17] calculated by the author leads to the conclusion that the stability of the trithiocarbonate ion is greater than that of the dithiolcarbonate ion (II).

Experimental

Materials. The newly-prepared compounds are shown in Table 6, together with the previously-reported ones.[2]

Kinetic Determination in Benzene. The accurately-weighed ester was dissolved in dry benzene. The concentration of trimethylamine in benzene was determined by titration.[18] The solution (the initial concentrations of the reagents were 0.2—0.5N) was sealed in stoppered test tubes (reactions at 25—35°C) or in ampoules (above 45°C). After appropriate times, ampoules were removed from the bath and cooled; the ammonium salts produced were collected on a glass filter, washed with ether, and then weighed. First-order rate constants with respect to esters and trimethylamine are shown in Tables 1 and 2.

The structure and purity of ammonium salts were tested as previously.[2] The newly-prepared ammonium salts are shown in Table 6. The physical constants of the *S*-methylesters obtained by the reaction of ammonium salts with methyl iodide agreed with those of authentic samples (Table 6).

Kinetic Determination in DMF. The concentrations of trimethylamine in DMF were determined by potentiometric titration,[18] while the solutions of methyl methylxanthate (I) and ammonium salts were prepared by dissolving accurately-weighed amounts of the solute in dry DMF. The solutions of ammonium salt are not stable at elevated temperatures, exhibiting a slight yellow color in a few hours at 50°C. Thus, the solutions should be prepared just before use.

The reaction rate was determined spectrometrically by measuring the rate of the disappearance of I (λ_{max} =275.5 mμ, ε=9020, ethanol). In the reaction, dimethyl dithiolcarbonate (λ_{max}=248 mμ, ε=4420, ethanol) was obtained in 60—80% yields. The reaction of I with tetramethyl ammonium dithiocarbonate $Me_4NSCOSR$ (II) was of a pseudo-first-order, and the rate constants were proportional to the concentration of II (R=Me) (Fig. 2). A typical example is shown in Table 7.

The rate constant, k_2, for the reaction of trimethylamine and I in DMF is obtained by the use of the curves shown in Fig. 3, which are drawn from data typical of those in Table 8. The data are listed in Table 4.

Determination of Equilibrium Constants. An equimolar mixture of II and thiolester (accurately weighed) in DMF (a 10% solution) was sealed in a stoppered test tube filled with nitrogen, and then left for 15 min at 50°C to let it come to equilibrium. Then the mixture was divided into two equal parts. To one part was added a large amount of a mixture of dry benzene and ether 1:1 (v/v), and the resulting precipitates (ammonium salts) were washed thoroughly with the solvent. The composition of the precipitates was determined by VPC after treating them with methyl iodide. The second part was poured into cold water and extracted with ether. The ethereal extract (thiolesters), after having been dried over sodium sulfate, was analyzed by VPC. The ratio of the products is listed in Table 5.

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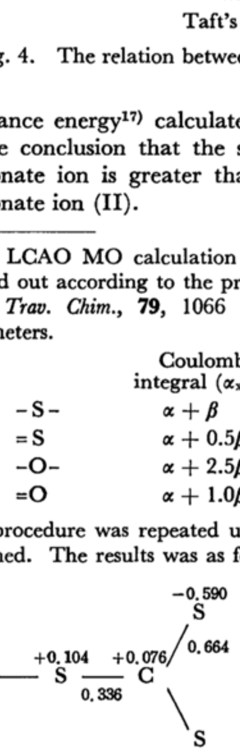
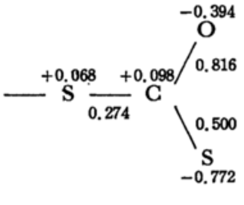
[17] LCAO MO calculation of carbonate ions were carried out according to the procedure of M. J. Janssen [*Rec. Trav. Chim.*, **79**, 1066 (1960)] using following parameters.

	Coulomb integral (α_X)	Resonance integral (β_{C-X})
−S−	$\alpha+\beta$	0.6β
=S	$\alpha+0.5\beta$	
−O−	$\alpha+2.5\beta$	1.2β
=O	$\alpha+1.0\beta$	

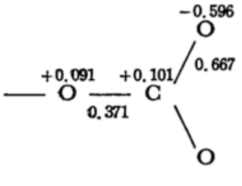
The procedure was repeated until consistent result was obtained. The results was as follows:



RE = 0.950β



RE = 0.220β



RE = 1.860β

[18] C. W. Pifer and E. G. Wallish, *Anal. Chem.*, **24**, 300 (1952).

TABLE 6. PHYSICAL CONSTANTS OF ESTERS AND TETRAMETHYL AMMONIUM SALTS

Ester	Bp °C/mmHg [mp °C]	n_D (°C)	Ref.
$MeOCSC_6H_5$	120/22	1.6118 (20)	a
$MeSCOC_6H_5$	127/18	1.5855 (20)	b
$MeOCSC_6H_4Cl$-(*p*)	[48—49]		b
$MeSCOC_6H_4Cl$-(*p*)	137—138/14 [21]		b
$MeOCSC_6H_4NO_2$-(*p*)	[71—73]		c
$MeSCOC_6H_4NO_2$-(*p*)	[97—98]		d
$MeOCSC_6H_4Me$-(*p*)	136—137/22	1.6068 (20)	e
$MeSCOC_6H_4Me$-(*p*)	133—135/13	1.5837 (20)	b
$MeOCSC_6H_4OMe$-(*p*)	[46—46.5]		b
$MeSCOC_6H_4OMe$-(*p*)	[43]		f
MeOCSOMe	119—120	1.4624 (25)	g
i-PrSCOS*i*-Pr	96.5—98/18	1.5100 (25)	h
s-BuSCOS*s*-Bu	124—125/17	1.5028 (23)	i
$Me_4\overset{+}{N}\overset{-}{S}COC_6H_5$	[113—114]		
$Me_4\overset{+}{N}\overset{-}{S}COC_6H_4Cl$-(*p*)	[153—155]		
$Me_4\overset{+}{N}\overset{-}{S}COC_6H_4NO_2$-(*p*)	[201—202]		
$Me_4\overset{+}{N}\overset{-}{S}COC_6H_4Me$-(*p*)	[144—145]		
$Me_4\overset{+}{N}\overset{-}{S}COC_6H_4OMe$-(*p*)	[126—129]		
$Me_4\overset{+}{N}\overset{-}{O}COC_6H_4NO_2$-(*p*)	[250—252]		

a) M. Matsui, *Mem. Coll. Sci. Kyoto*, **1**, 285 (1908).
b) R. Mayer, S. Scheithauser and D. Kunz, *Chem. Ber.*, **99**, 1393 (1966).
c) Found: C, 48.26; H, 3.39; N, 6.97%. Calcd for $C_8H_7NO_3S$: C, 48.72; H, 3.58; N, 7.10%.
d) A. M. Khaletskii and A. M. Yanovitskaya, *Zhur. Obschei Khim.*, **19**, 1193 (1949); *Chem. Abstr.*, **44**, 1952 (1950).
e) Y. Sakurada, *Mem. Coll. Sci. Kyoto*, [A] **10**, 73 (1927).
f) H. Gross and G. Mattey, *Chem. Ber.*, **97**, 2606 (1964).
g) M. Delepine, *Compt. rend.*, **150**, 878 (1910).
h) Found: C, 46.61; H, 8.27%. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91%.
i) Found: C, 52.25; H, 9.16%. Calcd for $C_9H_{18}OS_2$: C, 52.38; H, 8.79%.

TABLE 7. THE REACTION OF I WITH II (R=Me) IN DMF AT 30°C

Time (min)	Abs ($\lambda^{275.5}_{max}$)	Abs (λ^{248})	k (min^{-1})
0	1.046	0.044	
100	0.708	0.152	0.00405
120	0.658	0.167	0.00403
175	0.538	0.203	0.00401
230	0.441	0.235	0.00396
305	0.330	0.271	0.00404
365	0.251	0.281	0.00409
1440	0.034	(0.232)	

13.7 mg (I), 20.0 mg (II) (R=Me) in 5 m*l* DMF. Absorbance of 20 *μl* aliquot diluted with 5 m*l* ethanol in a 1 cm cell.

TABLE 8. THE REACTION OF I WITH TRIMETHYLAMINE IN DMF AT 30°C

Time (min)	Abs ($\lambda^{275.5}$)
0	0.783
40	0.724
80	0.670
100	0.633
140	0.569
180	0.502
220	0.437
260	0.382
300	0.329
330	0.280
1740	0.006

$[A_0]=[X_0]=0.0466$N in DMF. Absorbance of 15 *μl* aliquot diluted with 10 m*l* of ethanol in a 1 cm cell.

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