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The Preparation and Thermal Decomposition of Alkyl Acyl Dithiol- and Trithiocarbonates. A Convenient Method for the Synthesis of Thiolesters

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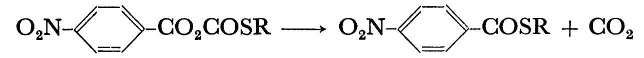
New alkyl acyl dithiol- and trithiocarbonates (**1** and **2**) were prepared from acid chlorides and tetramethylammonium alkyl dithiol- and trithiocarbonates (**3** and **4**). **1** and **2** decomposed at around 100°C to give the corresponding thiolesters in good yields. The kinetic studies of the decomposition of **1** and **2** showed that, in *o*-dichlorobenzene, the decomposition reaction was first order and that it proceeded *via* a four-membered intramolecular cyclic mechanism.

The decomposition of mixed carbonic carboxylic anhydrides (or alkyl acyl carbonates)[1] has been known to lead to two concurrent paths, A and B:

$$\mathrm{ROCO_2COAr} \begin{cases} \rightarrow \mathrm{ROCO_2R} + \mathrm{(ArCO)_2O} & \text{(A)} \\ \rightarrow \mathrm{ROCOAr} + \mathrm{CO_2} & \text{(B)} \end{cases}$$

In contrast to these anhydrides, *p*-nitrobenzoic alkyl thiolcarbonic anhydrides (or *p*-nitrobenzoyl *S*-alkyl monothiocarbonates) (**5**) gave solely the corresponding thiolesters and carbon dioxide.[2]

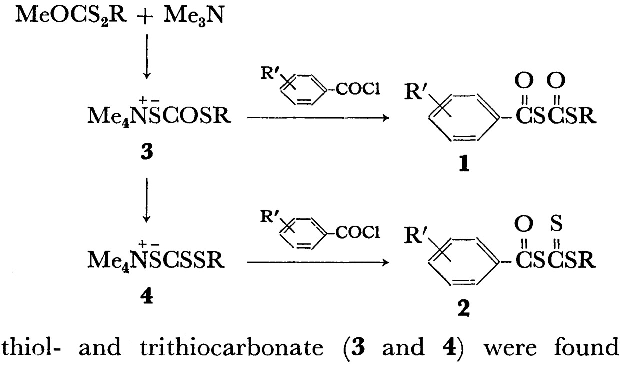


However, no other system of thiolcarbonates has been studied.

The present authors have found a convenient route for the preparation of *S*-alkyl *S*-acyl dithiol- and trithiocarbonates (**1** and **2**). In this report the thermal decompostion of **1** and **2** will be described.

Results and Discussion

In the course of the studies of the reaction of xanthates with tertiary amines, tetramethylammonium alkyl dithiol- and trithiocarbonate (**3** and **4**) were found to be prepared in good yields.[3] The action of acid chlorides on **3** and **4** at −10—0°C gave **1** and **2** (Table 1).



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[1] D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

[2] L. Wei and D. S. Tarbell, *ibid.*, **33**, 1884 (1968).

[3] H. Yoshida, *Nippon Kagaku Zasshi*, **89**, 883 (1968).

Table 1. S-alkyl S-acyl dithiol- and trithiocarbonates

Compound			Mp(°C)	Anal. (%) Found (Calcd)		NMR of S-methyl(δ) in o-$C_6H_4Cl_2$	
	R	R′		C	H	**1** or **2**	Decomposed thiolester
1a	Me	p-NO_2	72—73	42.00(42.02)	2.75(2.74)	2.33	2.38
1b	Me	p-Cl	72—75	44.49(43.81)	2.71(2.86)	2.32	2.37
1c	Me	H	20—23	50.77(50.92)	3.95(3.80)	2.29	2.36
1d	Me	p-Me	59.5—60	53.99(53.07)	4.73(4.45)	2.28	2.35
1e	Me	p-MeO	72—74	49.51(49.57)	4.23(4.16)	2.27	2.38
2a	Me	p-NO_2	130—133	39.81(39.55)	2.59(2.58)	2.58	2.38
2b	Me	m-NO_2	74—76.5	40.15(39.55)	2.69(2.58)	2.59	2.40
2c	Me	p-Cl	132—134	41.43(41.13)	2.61(2.68)	2.56	2.37
2d	Me	m-Cl	82.5—83.5	41.15(41.13)	2.99(2.68)	2.54	2.34
2e	Me	H	76—78	43.01(43.34)	3.59(3.53)	2.56	2.36
2f	Me	p-Me	88—90	49.83(49.55)	4.32(4.16)	2.58	2.38
2g	Me	p-MeO	62—63	46.80(46.49)	3.95(3.90)	2.56	2.35
2h	Et	H	41—43	49.17(49.55)	4.09(4.16)		

Compounds **1** and **2** decomposed gradually at temperatures above their melting points and vigorously at about 160°C, with the evolution of gases. The decomposition products were analyzed by vpc with known samples (Table 2). These results indicate that **1** and **2** decompose solely by sulfur-acyl bond fission to yield the corresponding thiolesters (path B).

Table 2. Thermal decomposition products of **1** and **2** without solvent

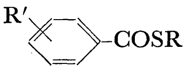
Material	Decomposition temp.(C°)	Product (Yield in %)		
			RSCOSR	Gas
1b	80—90	92	8	COS
1c	80—90	94	5	COS
1d	95—100	88	6	COS
2e	110—120	91	3	CS_2
2h	110—120	87	4	CS_2

Table 3. First-order rate constants for the thermal decomposition of **1** and **2** in o-dichlorobenzene

Compound	Temp.(°C)	$k\times 10^4$ sec^{-1}
1a	100.0	1.85
	96.0	1.25
	90.1	0.74
1b	100.0	1.35
1c	100.0	1.38
1d	100.0	1.06
1e	100.0	0.76
2a	105.8	2.38
	100.0	1.45
	96.0	1.02
2b	100.0	1.30
2c	100.0	1.05
2d	100.0	1.14
2e	105.8	2.23
	100.0	1.36
	94.7	0.83
2f	100.0	1.09
2g	100.0	0.887

The decomposition of the carbonates **1** and **2** in o-dichlorobenzene gave good first-order constants (k) up to 75% completion, as followed by NMR spectroscopy, and the constants were independent of the concentration of **1** and **2** at 0.5—3 weight% (Table 3). At these concentrations the crossed dialkyl dithiol- and trithiocarbonate were found to be produced in yields of less than 1%. Thus the decomposition of **1** and **2** seems to proceed practically *via* an intramolecular mechanism.

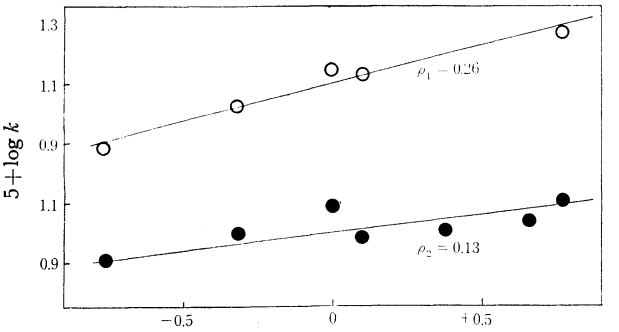
Compound **5** (R=i-Pr and t-Bu) has been suggested[2] to decompose *via* an intramolecular cyclic mechanism judging from activation parameters and the small solvent effect on the reaction. However the effect of the substituents of the acyl group has not yet been made clear.

Table 4. Activation parameters for the decomposition of **1** and **2** in o-dichlorobenzene

Compound	ΔE(kcal/mol)	ΔS(e. u.)
1a	24.0	−9.9
2a	23.8	−12.6
2e	24.5	−10.8
5(R=t-Bu)[a]	30.3	−5.1
5(R=i-Pr)[a]	30.6	−3.7

a) Taken from Ref. 2.

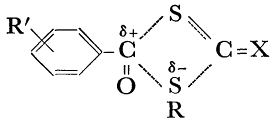
There are no marked difference in the activation parameters between **1** and **2**, as Table 4 shows, but the values considerably deviate from those of **5**.[2] This observation may be attributed to the nature of the bridge atoms, sulfur (**1** and **2**) and oxygen (**5**). The difference in the activation energies may come from the fact that, in bond energies, C–O>C–S. In going from the ground state to the transition state, a relatively larger loss in degree of freedom would occur in the **1** and **2** system than in the **5** system due to desolvation (bond length, C–S>C–O). This is consistent with the larger loss of entropy in the **1** and **2** system than in the **5** system. The samll negative values of the activation entropy seem to indicate that **1** and **2** decompose *via* a four-membered cyclic mechanism similarly to **5**.



Brown-Okamoto's σ^+

Fig. 1. Hamett relationship for the decomposition of **1** and **2** in *o*-dichlorobenzene at 100°C.
○ for **1**. ● for **2**.

Although an ordinary Hammett's plot of log*k* *vs* σ did not give a linear relationship, plots of log*k* *vs*. Brown-Okamoto's σ^+ gave relatively good straingh lines (Fig. 1). The small positive ρ values seem to indicate that, in the transition states of the decomposition of **1** and **2**, a partial charge on the reacting sites is not highly developed, and that the *S*-alkyl group, as a nucleophile, attacks the carbonyl carbon of the acyl group. The difference in ρ values, ρ_1 and ρ_2, may then, be attributed to the difference in nucleophilicity of *S*-alkyl groups of **1** and **2**, resulting from the difference in mesomeric effects of the carbonyl and the thiocarbonyl groups. Thus the transition state may be pictured as in **6** with a partial negative charge on the sulfur, and a partial positive charge on the carbonyl carbon.



6 (X=O or S)

Experimental

Materials. Tetramethylammonium alkyl dithiol- and trithiocarbonate (**3** and **4**) were prepared according to the previously-described method.[3] To a dry ether suspension of **3** or **4**, we added, drop by drop at −10—0°C, an ether solution of acid chloride. After the removal of the tetramethyl ammonium chloride, the solution was concentrated *in vacuo*. The residual **1** or **2** was recrystalized from ligroin for **1** or from carbon tetrachloride for **2**. The physical constants of the products are collected in Table 1.

Thermal Decomposition of 1 and 2 without a Solvent. (*Table* 2). This reaction was carried out in a test tube at 100—160°C. At higher temperatures, a vigorous evolution of gas was observed. The decomposition products were analysed by vpc using known samples.

Kinetic Studies of the Decomposition of 1 and 2. Kinetic runs were carried out at a constant temperature in an oil bath. A solution of **1** or **2** in *o*-dichlorobenzene was sealed in an NMR sample tube. The rate was followed at suitable time intervals by analyzing the NMR spectra of *S*-methyl groups using a Hitachi Parkin-Elmer R-20 60 MHz spectrometer.

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