Carbonate Pyrolysis. Part 6.[1] The Kinetics and Mechanism of the Pyrolysis of Thion- and Dithio-carbonates. Implications for the Transition State in Carbonate Pyrolysis

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The kinetic effect of substituting sulphur for carbonyl oxygen in carbonates and thiolcarbonates is consistent only with a transition state like that for ester pyrolysis.

In earlier Parts we showed that carbonate pyrolysis is a *cis*-concerted elimination [2] which takes place more rapidly than the reaction of the corresponding acetates.[3,4] Judged by the effect on rate of α-methylation of the alcohol moiety, the two reactions have transition states of similar polarity.[5] However, the evidence collected to date does not firmly distinguish between transition state modes (1) and (2). We proposed to make the distinction by the use of sulphur as a kinetic label. The ground was prepared by the determination of this kinetic effect in thiol-,[6] thion-,[7] and dithio-acetates;[8] it was possible to calculate the rate of dithioacetate pyrolysis from a knowledge of the rates for acetate, thiol-, and thion-acetate. Within this series, therefore, the kinetic effect of replacing an oxygen atom by a sulphur atom is independent of the nature of the neighbouring atoms.

Part 5 examined the kinetic effect of sulphur atoms in the ether positions of carbonates. In the present paper we present our results for thioncarbonates and xanthates, and we draw mechanistic conclusions from comparisons with the parent carbonates.

RESULTS

Thioncarbonates.—The thioncarbonates in Table 1 were examined in our flow machine;[9] the results were not significantly affected by the use of a packed flow tube or by the addition of excess of cyclohexene. The reaction was therefore homogeneous. Further, in sealed tubes, the extent of decomposition (*ca.* 70%) was not affected by reactant pressure (2—800 mmHg) and the decomposition was therefore of the first order. The reaction products, alkene, carbonyl sulphide, and methanol were identified by i.r. spectroscopy. No thiolcarbonate was detected at any stage of the reaction.

TABLE 1

Arrhenius parameters for the pyrolysis of alkyl methyl thioncarbonates

Alkyl	T/K	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	k_{629}/s^{-1}
Et	570—660	144	−59	1.3×10^{-2}
Pr^i	500—560	126	−48	1.5

Xanthates.—Kinetically, the xanthates fell into two groups; those where the oxygen atom was involved in the bonding changes of the transition state, and those where it was not. These are the *O*-alkyl *S*-methyl and *S*-alkyl *O*-methyl carbonates, respectively. All were well behaved kinetically and survived the tests for homogeneity described in the last section. The products of reaction were identified (but not estimated) by i.r. spectroscopy of single compounds and authentic mixtures. They were, from *O*-alkyl *S*-methyl dithiocarbonates, methanethiol, carbonyl sulphide, and alkene and, from *S*-alkyl *O*-methyl dithiocarbonates, methanol, carbon disulphide, and alkene. Data are in Tables 2 and 3.

TABLE 2

Arrhenius parameters for the pyrolysis of *O*-alkyl *S*-methyl dithiocarbonates

Alkyl	T/K	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	k_{629}/s^{-1}
Et	590—620	161	−28	1.4×10^{-2}
Pr^i	500—550	144	−26	5.6×10^{-1}

S-Ethyl *O*-methyl dithiocarbonate was not well behaved kinetically, giving a curved Arrhenius plot. Being a primary dithiocarbonate it required a higher temperature for pyrolysis, and the thion–thiol rearrangement became apparent. After 70% reaction the bulk of the undecomposed material was methyl ethyl dithiolcarbonate, which is more thermally stable.

TABLE 3

Arrhenius parameters for the pyrolysis of *S*-alkyl *O*-methyl dithiocarbonates

Alkyl	T/K	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	k_{629}/s^{-1}
Pr^i	580—630	163	−32	7.9×10^{-3}
Bu^t	540—570	135	−44	4.3×10^{-1}

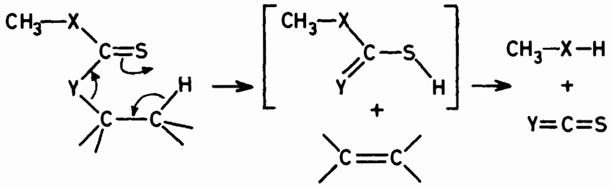
Dithiolcarbonates.—A single representative of this class was examined, diethyl dithiolcarbonate. It was much more stable than the previous compounds and, examined in the region 745—785 K, had $\Delta H^‡$ 228 kJ mol^{-1}, $\Delta S^‡$ −6 J K^{-1} mol^{-1}, and k_{629} 7.8×10^{-7} s^{-1}. The products of pyrolysis were ethylene, ethanethiol, and carbonyl sulphide.

Errors in $\Delta H^‡$ are ±6 kJ mol^{-1} and in $\Delta S^‡$ ±10 J K^{-1} mol^{-1}.

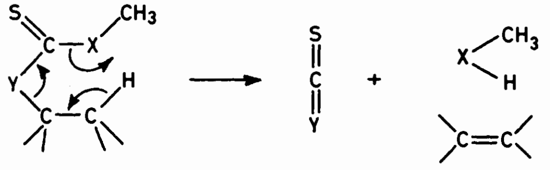
DISCUSSION

All the reactions described in the Results section are of the first order, and their rates are largely unaffected by an increase of surface : volume ratio or by the addition of radical inhibitor. They are therefore homogeneous unimolecular reactions. The entropies of activation are all negative, indicating a restriction of freedom in going to the transition state but, as with carbonate pyrolysis, the products do not distinguish between the two possible modes of decomposition shown in (1) and (2). Mode (1), involving attack of C=S on the β-hydrogen atom, will be referred to as 'ester-like' and mode (2) as 'ether attack.'

Table 4 compares successive sulphur substitutions in esters with those in carbonates. Ethyl thionacetate (II) is pyrolysed 153 times as fast as ethyl acetate (I),[7] and a similar ratio (110) holds for the thioesters (III)[6] and (IV).[8] It is necessary to compare the isopropyl derivatives for the carbonates since *S*-ethyl *O*-methyl dithiocarbonate (X; R′ = Et) was not kinetically well behaved. However, the same features emerge, comparisons of (VI) with (V),[3] of (IX) with (VII),[1] and of (X) with (VIII)[1] showing consistent rate enhancement with the inclusion of thion sulphur. For the esters, and if carbonates decompose *via* the ester-like transition state, the explanation is fairly simple;[7] exchange of the weak C=S for a strong C=O during reaction is thermochemically favourable, and sulphur is more nucleophilic than oxygen.

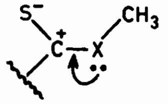


(1)



(2)

Ether attack [mode (2)] can offer no such explanation. Indeed since the C=S is highly polarized as $\overset{+}{C}-\overset{-}{S}$, the nucleophilicity of the atom attacking the β-hydrogen atom will be diminished by contributions such as (A) and the rate of pyrolysis is expected to be the same as, or lower than, that of the carbonyl compound.



(A)

The remarkable additive effect of substitution exhibited by sulphur in the ester series [*i.e.* rates of (I) × (II) × (III) ≃ (IV)] has already been remarked upon.[8] For the isopropyl carbonates there seems to be a similar constancy. Thus, rates of (V) × (VI) × (VIII) = (X). The data for ethyl derivatives may be extracted from the Results section and show that for R′ = Et also, the same equation holds exactly. Where one of the sulphur atoms is not part of the six-membered ring of the transition state, the equation is less exact, but still surprisingly close; thus (V) × (VI) × (VII) ≃ 2.5 × (IX).

Finally we have the dithiolcarbonates represented by a single example, the diethyl ester. Comparison of (VII) with (V) shows that sulphur has a negligible kinetic effect when not actively involved in the bond making–breaking process; it is therefore not surprising to find that diethyl dithiolcarbonate and *O*-methyl thiolcarbonate[1] have identical rates at 629 K.

TABLE 4

Relative rates of gas-phase pyrolysis of some esters and carbonates at 629 K

R = Et	R′ = Pr^i	
(I) $CH_3-\overset{O}{\overset{\|}{C}}-O-R$ 1	(V)[3] $CH_3-O-\overset{O}{\overset{\|}{C}}-O-R'$ 1	
(II)[7] $CH_3-\overset{S}{\overset{\|}{C}}-O-R$ 153	(VI)[a] $CH_3-O-\overset{S}{\overset{\|}{C}}-O-R'$ 150	
(III)[6] $CH_3-\overset{O}{\overset{\|}{C}}-S-R$ 0.22	(VII)[1] $CH_3-S-\overset{O}{\overset{\|}{C}}-O-R'$ 0.9	(VIII)[1] $CH_3-O-\overset{O}{\overset{\|}{C}}-S-R'$ 0.005
(IV)[8] $CH_3-\overset{S}{\overset{\|}{C}}-S-R$ 24	(IX)[a] $CH_3-S-\overset{S}{\overset{\|}{C}}-O-R'$ 55	(X)[a] $CH_3-O-\overset{S}{\overset{\|}{C}}-S-R'$ 0.8

[a] Present work.

EXPERIMENTAL

Thioncarbonates were prepared from the appropriate alcohol and alkyl chlorothioformate.[10] Ethyl methyl thioncarbonate had b.p. 141 °C (lit.,[11] 140 °C); isopropyl methyl thioncarbonate had b.p. 161 °C (Found: *M*, 150.017 403 3. Calc. for $C_5H_{10}OS_2$: 150.017 305 5).

Xanthates were made by the standard route.[12] *S*-Ethyl *O*-methyl dithiocarbonate had b.p. 183 °C, n_D^{21} 1.5520 (lit.,[13] b.p. 184 °C, n_D^{15} 1.5539); *S*-isopropyl *O*-methyl dithiocarbonate had b.p. 109 °C at 54.5 mmHg, n_D^{21} 1.5331; *O*-methyl *S*-t-butyl dithiocarbonate, b.p. 121—122

°C at 55 mmHg, n_D^{24} 1.5239; *O*-ethyl *S*-methyl dithiocarbonate had b.p. 181—182 °C, n_D^{24} 1.5465 (lit.,[13,14] b.p. 182 °C, n_D^{25} 1.5462); *S*-methyl *O*-propyl dithiocarbonate had b.p. 79 °C at 29.3 mmHg, n_D^{21} 1.5360.

Diethyl dithiolcarbonate had b.p. 83 °C at 28.8 mmHg (lit.,[15] 197 °C).

All compounds had simple ^1H n.m.r. spectra in accord with expectation.

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