Carbonate Pyrolysis. Part 5.[1] The Gas-phase Pyrolysis of Some Unsymmetrical Monothiolcarbonates and a Rationalisation of the Rates of Some Related Reactions

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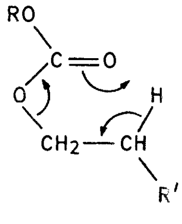
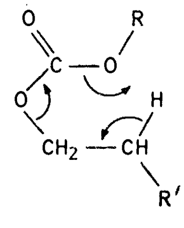
Thiolcarbonates pyrolyse more slowly than carbonates. Where the sulphur atom is attached to the group which will form the olefin, this difference amounts to three orders of magnitude; when the sulphur atom is in the other ether position it is only ten-fold. These rate changes are discussed in terms of similar substitutions in thioacetates.

EARLIER Parts were concerned with the effect on the rate of pyrolysis of organic carbonates of variation of one or both alkyl groups,[2-4] and the stereochemistry of the reaction.[1] The reaction was shown to be unimolecular and consistently to exhibit a negative entropy of activation. Together with the *cis*-stereochemistry of the elimination,[1] this was taken to indicate a cyclic concerted mechanism involving either transition states (I) or (II). To date there is no firm evidence to implicate either of these. Smith *et al.*[5,6] have favoured (I) on the basis of linear free energy arguments but, by their own admission, definitive evidence is required. More recently Stimson *et al.*[7] have speculated that (II) is involved.



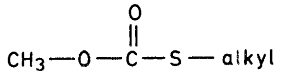
(I)



(II)

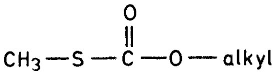
We have attempted to make the choice between (I) and (II) in two ways. The most direct and elegant approach is to label isotopically the various oxygen atoms of the carbonate, and to measure the kinetic isotope effects. We have done this for methyl n-hexyl carbonate, but so far find our results vitiated by isotopic scrambling.[8] We hope to report on this approach at a later date.

The second approach to the problem is to measure the kinetic effect of the introduction of chemical labels. We have chosen sulphur as a suitable chemical label and have measured its kinetic effect in thiol-,[9] thion-,[10] and dithio-acetates.[11] We report below our investigations into some unsymmetrical dialkyl monothiolcarbonates. The six carbonates all contain a methyl group as one of the alkyl groups, the others being ethyl, isopropyl, and t-butyl. The compounds thus fall into two isomeric sets (III) (*O*-methyl *S*-alkyl thiolcarbonates) and (IV) (*S*-methyl *O*-alkyl thiolcarbonates) which belong to the same chemical class, but to different classes according to their pyrolytic behaviour. This difference derives simply from the fact that the methyl group has no β-hydrogen atoms and therefore cannot undergo elimination. It is nevertheless extremely useful in that it gives rise to predictably different transition states and therefore products.



$$CH_3-O-\overset{\overset{O}{\|}}{C}-S-\text{alkyl}$$

(III)



$$CH_3-S-\overset{\overset{O}{\|}}{C}-O-\text{alkyl}$$

(IV)

EXPERIMENTAL

Thiolcarbonates were made by the addition of alkyl chloroformate to the corresponding thiol in pyridine.[12] They had the following properties: *O*-methyl *S*-ethyl thiolcarbonate, b.p. 35° at 29 mmHg, n_D^{23} 1.453 0 (lit.,[13] 66—67° at 81 mmHg); *O*-methyl-*S*-isopropyl thiolcarbonate, b.p. 116—118°, n_D^{23} 1.4524 (lit.,[13] 50.5° at 20 mmHg); *O*-methyl *S*-t-butyl thiolcarbonate, b.p. 49° at 15 mmHg, n_D^{23} 1.451 2 (lit.,[13] 86—87° at 72 mmHg); *S*-methyl *O*-ethyl thiolcarbonate, b.p. 139°, $n_D^{13.5}$ 1.453 0 (lit.,[14] 40° at 12 mmHg); *S*-methyl *O*-isopropyl thiolcarbonate, b.p. 58° at 18 mmHg, $n_D^{13.5}$ 1.458 3; *S*-methyl *O*-t-butyl thiolcarbonate, b.p. 63° at 24 mmHg, $n_D^{13.5}$ 1.457 0 (lit.,[15] 60—62° at 20 mmHg).

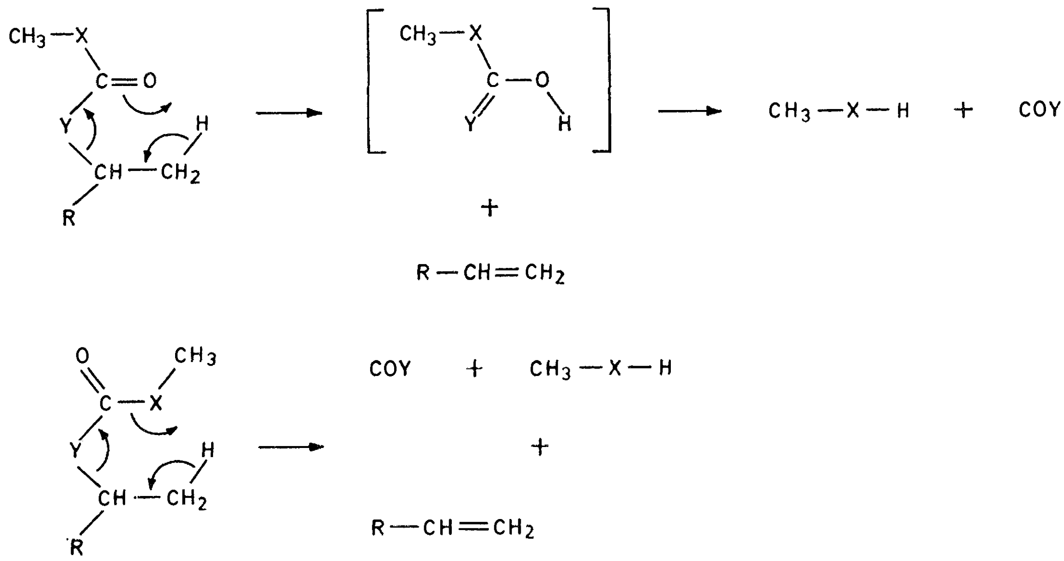
Stoicheiometry.—All the *O*-methyl *S*-alkyl thiolcarbonates decomposed to carbonyl sulphide, methanol, and the expected olefin as the only identifiable products in our flow machine. The olefins and COS were trapped and were identified by their gas i.r. spectra. The *S*-methyl *O*-alkyl thiolcarbonates were pyrolysed in evacuated break-seal tubes and the products handled on a vacuum line. The only products identified were methanethiol, carbon dioxide, and the appropriate olefin.

Kinetics.—The *O*-methyl *S*-alkyl thiolcarbonates were well behaved in our analytical flow apparatus.[2] They were examined in the following temperature ranges: *S*-ethyl, 490—550 °C; *S*-isopropyl, 440—480 °C; *S*-t-butyl, 370—420 °C. The reactions were shown to be of the first order by heating varying pressures of the thiolcarbonate in evacuated sealed tubes and showing that, for a given reaction time, the extent of reaction was independent of pressure. The homogeneity of the reaction was checked by adding 500 mol % cyclohexene to the mixture plus internal standard and by performing the runs in a packed flow tube. In no case was there a significant variation in the rate. The Arrhenius parameters were obtained in the usual way.[2]

S-Methyl *O*-ethyl thiolcarbonate was also well behaved in the analytical flow machine and was handled as described in the preceding paragraph. The *O*-isopropyl and *O*-t-butyl analogues totally decomposed at temperatures sufficient for their passage through the flow machine.

S-Methyl *O*-isopropyl thiolcarbonate showed good first-order behaviour in evacuated sealed tubes in the range 547—584 K. At 570 K the rates in packed tubes and in the presence of cyclohexene were not materially different from that in the normal tubes and the reaction is therefore homogeneous and non-radical chain.

S-Methyl *O*-t-butyl thiolcarbonate gave erratic results in evacuated sealed tubes. It was found, however, that the addition of cyclohexene reduced the rate, but above 20 cmHg of cyclohexene addition of further cyclohexene depressed the rate no further and the results were no longer erratic. Kinetic runs (479—502 K) were therefore done in the presence of 400 mol % cyclohexene, in the region of maximally inhibited rate. Under these conditions, the use of packed tubes did not materially alter the rate.



S—Methyl *O*—alkyl thiolcarbonates X = S, Y = O
O—Methyl *S*—alkyl thiolcarbonates X = O, Y = S

Scheme

The results of the sealed tube pyrolyses were subjected to the usual least squares treatment.

The Arrhenius parameters, rates, and relative rates for all six thiolcarbonates are collected together in Table 1.

DISCUSSION

The two isomeric sets of thiolcarbonates of Table 1 both undergo pyrolysis in a homogeneous and unimolecular fashion. The products of pyrolysis are different in the two series as a result of the change of position of the sulphur atom with respect to the alkyl group which will ultimately become olefin. The consistently negative entropies of activation require a cyclic transition state. By analogy with carbonates one may draw two transition states which satisfy these criteria for each series. These are shown in the Scheme.

Table 1

Arrhenius parameters, rates, and relative rates for the pyrolysis of thiolcarbonates R–O–CO–S–R′ (629 K)

R	R′	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta^{\ddagger}S$/ J K^{-1} mol^{-1}	k_{629}/s^{-1}	k$_{rel}$
Me	Et *	226	−9.2	$7.7_5 \times 10^{-7}$	1
Me	Pr^i *	203	−12	4.6×10^{-5}	59
Me	Bu^t *	176	−27	1.2×10^{-3}	1 550
Et	Me *	190	−25	1.0×10^{-4}	1
Pr^i	Me†	162	−33	9.4×10^{-3}	94
Bu^t	Me ‡	128	−54	4.2×10^{-1}	4 200

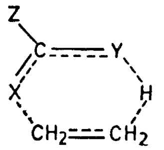
* Flow tube method (±6 kJ mol^{-1}). † Evacuated sealed tube method (±10 kJ mol^{-1}). ‡ Inhibited sealed tubes (see text).

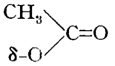
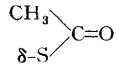
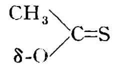
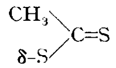
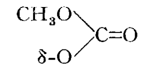
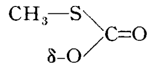
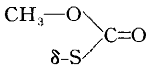
Table 1 shows an increase of rate with α-methylation in both series of thiolcarbonates, which compares with *ca.* 1 : 3 200 for carbonates.[4] The figure for the *O*-methyl *S*-alkyl series is probably accurate, and reflects less polarity in the transition state than found with carbonates. The ratio for the *S*-methyl *O*-alkyl series should be treated with some reserve since the t-butyl derivative was not well behaved kinetically and the calculated rate constant k_{629} is taken at 127° above the highest measured rate constant. However, there is probably a little more charge development in the transition state of the *S*-methyl series than there is in the *O*-methyl series.

Table 2 shows the rates and relative rates of pyrolysis of the ethyl esters of a series of compounds which do or might pyrolyse through an acetate-like transition state. In all cases the reaction is concerted and unimolecular but with a polar contribution. Unfortunately the absolute magnitude of this polar contribution cannot at present be estimated. It is commonly stated that the rate of ester pyrolysis is inversely proportional to the pK_a of the constituent acid (see *e.g.* ref. 16), but the supporting evidence is not entirely straightforward. Emovon found an 18.6-fold increase in the rates of pyrolysis of the t-butyl esters from acids with a pK_a difference of 3.4,[17] but Smith *et al.* found only a three-fold

Table 2

Rates, relative rates, and polar contributions to the transition states for pyrolysis of some ethyl esters



Ethyl compound	Polar contribution	k_{629}/s^{-1}	Relative rate	Ref.
Acetate	 $\overset{CH_3}{\underset{\delta\text{-}O}{>}}C{=}O$	7.7×10^{-5}	1	*a*
Thiolacetate	 $\overset{CH_3}{\underset{\delta\text{-}S}{>}}C{=}O$	1.7×10^{-5}	0.2	9
Thionacetate	 $\overset{CH_3}{\underset{\delta\text{-}O}{>}}C{=}S$	$1.1_5 \times 10^{-2}$	150	10
Dithioacetate	 $\overset{CH_3}{\underset{\delta\text{-}S}{>}}C{=}S$	1.8×10^{-3}	23	11
Methyl carbonate	 $\overset{CH_3O}{\underset{\delta\text{-}O}{>}}C{=}O$	6.9×10^{-4}	9	*b*
S-Methyl thiolcarbonate	 $\overset{CH_3\text{—}S}{\underset{\delta\text{-}O}{>}}C{=}O$	1.0×10^{-4}	1.3	This work
O-Methyl thiolcarbonate	 $\overset{CH_3\text{—}O}{\underset{\delta\text{-}S}{>}}C{=}O$	7.8×10^{-7}	0.01	This work

[a] A. T. Blades, *Canad. J. Chem.*, 1954, **32**, 366. [b] R. E. Gabbolt, Ph.D. Theses, University of Kent at Canterbury, 1975.

difference [18,19] and Stimson none at all [20] over a pK_a range of *ca.* 2. In view of the unpredictability of effect the absence of pK_a data is not too severe a handicap in discussing Table 2. It is argued that the rate changes result from the polar contributions (as implied by pK_a comparisons) and that these can be related in structure–activity terms by resonance and inductive effects.

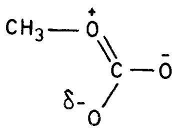
The acetate ion is taken as base for the comparisons of Table 2. The negative charge is delocalised over both oxygen atoms which, being electronegative, are well able to support it. This flow of charge to what had been the carbonyl oxygen atom should also enhance its nucleophilicity if the β-hydrogen atom is abstracted with protonic character.

The thiolacetate is at a triple disadvantage compared with acetate. Sulphur is less electronegative than oxygen and therefore less well able to support the negative charge. Since sulphur belongs to the second period it is larger than carbon, resulting in inefficient π-bonding between the two; there is therefore less delocalization of the negative charge than with acetates, resulting in less stabilization. A consequent effect is that the nucleophilicity of the carbonyl group is also less enhanced. As a result of these three effects the thiolacetate is expected to have a less polar transition state than the acetate, and therefore to react more slowly. This conclusion is supported by the rate ratios of n-butyl : t-butyl for the two series, this being 1 : 498 for the thiolacetates but 1 : 3 554 for acetates.[8]

The reactivity of the thionacetate is dominated by the dipolar component of the thiocarbonyl group.[21] The oxygen atom is able to delocalize its negative charge into the partial carbonium ion of the thiocarbonyl group, but this will not greatly enhance the high nucleophilicity of the sulphur atom since the latter was already partly uncoupled from its adjacent carbon atom. The combination of high nucleophilicity and charge delocalization should therefore give rise to a polar transition state and the fast rate observed. In support of this analysis, we have earlier shown the transition state for thionacetate pyrolysis to be more polar than that for acetates.[9]

For dithioacetates, the small carbon atom acts as an insulator between the two large sulphur atoms. Accordingly these compounds should have properties intermediate between the two preceding classes. As with the thiolacetates the negative charge on the leaving sulphur atom is less extensively delocalized and the already high nucleophilicity of the thion sulphur will not be enhanced. In fact we have shown that the reactivity is close to the product of that of the other two types.[11]

Turning now to the various carbonates of Table 2, it will first be assumed that pyrolysis proceeds through the ester-like transition state (I). Methyl ethyl carbonate is nearly ten times more reactive than ethyl acetate. The negative charge of the leaving oxygen atom will be delocalized as in acetates, but the nucleophilicity of the carbonyl oxygen atom will be enhanced by donation from the ether oxygen atom in (V). This argument apparently implies cross-conjugation. However both processes involve incomplete, and possibly very small, charges and can therefore coexist.

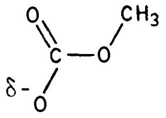


(V)

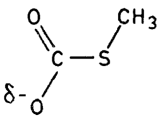
The delocalization of the negative charge on the leaving oxygen atom should be the same in *S*-methyl carbonates as in the all oxygen counterpart above. The sulphur atom does not strongly conjugate with the carbonyl group, however, so there is no enhanced nucleophilicity of its oxygen atom. Sulphur has nearly the same electronegativity as carbon and inductively two are similar; accordingly the rates for ethyl acetate and *S*-methyl *O*-ethyl thiolcarbonate are almost the same. The rate ratio of ethyl : t-butyl esters of *S*-methyl thiolcarbonates at 1 : 4 000 is also very similar to that of acetates.

Finally, the analysis for thiolacetates may be applied to *O*-methyl *S*-ethyl thiolcarbonate. The negative charge on the sulphur atom is not extensively delocalized and any enhancement of the nucleophilicity of the carbonyl group will come from the ether oxygen atom. Accordingly relative rates of acetate to thiolacetate (1 : 0.2) should compare with carbonate : *O*-methyl thiolcarbonate. In fact the latter ratio is *ca.* 1 : 0.001, about two orders of magnitude smaller than expected. This analysis therefore puts the three types of carbonate in the correct *sequence* of rates, but predicts the actual rate for the *O*-methyl thiolcarbonate rather badly. Possibly the analysis used is too simplistic, but equally it could have been applied to the wrong transition states.

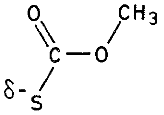
The alternative leaving groups [corresponding to pyrolysis (II)] are shown idealized in polar form in (VI)—(VIII). For carbonates the leaving group is (VI). The electronegative oxygen atom easily supports the negative charge which is in any case delocalized into the carbonyl oxygen atom. Elimination is completed by attack of the ether oxygen atom on the β-hydrogen atom of the other alkyl group (not shown). There will be some contribution of the dipolar structure (IX) but it will be less than for normal esters, there being competition for the carbonyl group. The transition state (VI) for carbonate pyrolysis is different from that for acetates and it is therefore neither necessary nor easily possible to relate the rates of the two processes.



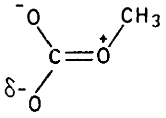
(VI)



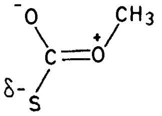
(VII)



(VIII)



(IX)



(X)

S-Methyl thiolcarbonates will pyrolyse through the analogous fragmentation (VII). The negative charge can delocalize in the same way as in (VI), but the sulphur atom (soft) is less nucleophilic towards hydrogen (hard) than is the corresponding oxygen atom (hard) of (VI). The rate of pyrolysis is therefore expected to be less than for carbonates, as found, but it is not possible to predict by how much.

The *O*-methyl thiolcarbonate transition state (VIII) may be analysed in much the same way as the thiol esters. The sulphur atom is not sufficiently electronegative easily to bear its negative charge (in comparison with oxygen) but is too large for efficient overlap with the carbonyl group. The pyrolysis of the *O*-methyl thiolcarbonates should be slowed down on this basis by the same factor as was observed for thiolacetates. In addition they will be slowed further as a result of contribution from structure (X), where the competition for the carbonyl group noted in (IX) is absent. This reduced nucleophilicity of the ether oxygen atom now provides a basis for the low reactivity of these compounds.

In conclusion, use of an ester-like transition state permits an ordering of the rates of pyrolysis of the three types of carbonate, but fails by two orders of magnitude to account for the rate of pyrolysis of the *O*-methyl thiolcarbonates. Use of the other transition state type (II) gives a good account of the rate ratio carbonate : *O*-methyl thiolcarbonate. It also correctly predicts that *S*-methyl thiolcarbonates will react more slowly than carbonates themselves, but leaves the relative rates of the two types of thiolcarbonate an open question. On present evidence, therefore, the latter transition state must be given slight preference.

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