The Gas-phase Pyrolysis of Dithioacetates: a Remarkable Constancy of Substituent Effects

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The gas-phase pyrolysis of dithioacetates is a concerted unimolecular process. The measured rates of these reactions agree well with rates calculated simply from the corresponding thiol- and thion-acetates.

THE mechanism of the gas-phase pyrolysis of alkanoic esters is now well understood, and involves attack of the carbonyl oxygen atom on the β-hydrogen atom of the alcohol grouping.[1] Organic carbonates have been much less studied;[2-5] the reaction involves removal of the same β-hydrogen atom of the alcohol function, but it has not yet been shown whether attack is by the carbonyl or the ethereal oxygen atom.

Our approach to the elucidation of this problem is to substitute the three oxygen atoms of carbonates either successively or simultaneously with sulphur atoms and to observe the new rate of pyrolysis. Unfortunately the basic data for such substitution in esters has not been available, and in previous papers we have reported the replacement by sulphur of the ethereal oxygen atom [6] and the carbonyl oxygen atom [7] of acetates. There is a large difference in rates produced by such substitution. In comparison with esters thiolacetates pyrolyse up to 50 times more slowly, while thionesters undergo reaction up to 400 times more rapidly. If these trends in rate are to be reliably transferred to the correspondingly substituted carbonates, it must be shown that they are constant in different environments. The simplest way of doing this appeared to be to incorporate both sulphur atoms in a single ester group, and we describe below the results we have obtained in this way.

EXPERIMENTAL

n-Butyl dithioacetate was prepared by addition of carbon disulphide to methylmagnesium iodide, followed directly by addition of n-butyl bromide.[8] The other dithioacetates were made *via* the thioimidate.[9] They had the following properties: ethyl dithioacetate, b.p. 130—131° (lit.,[9] 128—132°); *n-butyl dithioacetate*, b.p. 32—33° at 0.05 mmHg, n_D^{25} 1.5041 (Found: M^+, 148.0371. $C_6H_{12}S_2$ requires M, 148.0380); 1-*methylpropyldithioacetate*, b.p. 77° at 16 mmHg, n_D^{20} 1.5380 (Found: M^+, 148.03954); *t-butyl dithioacetate*, b.p. 70—71° at 16 mmHg, n_D^{20} 1.5350 (Found: M^+, 148.03879). All had i.r. and n.m.r. spectra in accord with expectation.

Kinetics.—The primary and secondary dithioacetates were pyrolysed in the flow apparatus previously described.[2] The primary esters were run over the temperature range 651—716 K, while 1-methylpropyl dithioacetate was examined in the range 584—639 K. t-Butyl dithioacetate was too thermally sensitive for use with the flow machine; it was completely decomposed at a temperature sufficient for its passage through the system. It was therefore examined in evacuated sealed tubes which were heated in a molten salt-bath (±0.05 °C) in the region 448—502 K.

Both techniques yielded excellent Arrhenius plots, with very little scatter of the points. Tests for surface or radical reactions were negative and are listed in Table 1. The activation parameters and rate data are listed in Table 2.

TABLE 1

Tests for heterogeneity in the gas phase pyrolysis of alkyl dithioacetates CH_3CS_2R

R	k/s^{-1}	k/s^{-1} (packed tube) *	k/s^{-1} (inhibited) †	T/K
Bu^n	4.2×10^{-2}	4.4×10^{-2}	4.1×10^{-2}	677.4
EtCHMe	7.4×10^{-2}		7.3×10^{-2}	629.0
Bu^t	1.1×10^{-4}	1.1×10^{-4}	1.1×10^{-4}	472.0

* Surface : volume ratio increased by *ca.* 9 fold. † Runs in the presence of 200 mole % cyclohexene.

TABLE 2

Arrhenius parameters and rate data for the gas phase pyrolysis of dithioacetates CH_3CS_2R

R	$\Delta H^‡/$ kJ mol^{-1}	$\Delta S^‡/$J K^{-1} mol^{-1}	$k_{629K}/$ s^{-1}	$k_{rel.}$	k_{629} (calc.)/ s^{-1}
Et	183.7	−11.3	1.8×10^{-3}	1	2.5×10^{-3}
Bu^n	181.6	−9.2	3.3×10^{-3}	1.8	3.4×10^{-3}
EtCHMe	162.8	−13.8	7.4×10^{-2}	41	8.4×10^{-2}
Bu^t	157.7	−10.0	3.1×10^{-1}	172	

Since the main interest of this paper is the reactivity of the dithioesters, we did not examine quantitatively the pyrolysis products. However the reactions appeared particularly clean and gave methane, carbon disulphide, and olefin as the only detectable products (g.l.c.). All esters gave a single olefin bar 1-methylpropyl dithioacetate which gave but-1-ene (51.7%), *cis*-but-2-ene (19.1%), and *trans*-but-2-ene (29.2%). Where the dithioesters were pyrolysed in the flow machine, the products were identified by g.l.c. In addition the olefins were trapped and their identity confirmed by i.r. spectroscopy. With t-butyl dithioacetate the products from a large sealed tube run were analysed by g.l.c. In addition to methane, CS_2, and isobutene, 1—2% H_2S was obtained.

DISCUSSION

The pyrolysis of dithioacetates has the following features. (i) The reaction is of the first order. As rates are not affected by an increase in the surface : volume ratio nor by the addition of a radical chain inhibitor, it is concluded that the reaction is homogeneous and

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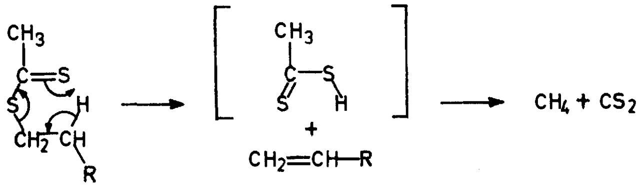
unimolecular. (ii) The reaction products are simple, and are consistent with the mechanism in Scheme 1. (iii) The uniformly negative entropy of activation for all the dithioesters is indicative of an acetate-like transition state for pyrolysis.

Although other tests of mechanism are possible, we conclude that the above criteria are sufficient to establish the mechanism of the pyrolysis as the concerted one shown in Scheme 1. It is therefore valid to compare the rates of pyrolysis of the dithioesters with those of the simpler thioesters.



SCHEME 1

Conceptually the dithioesters may be derived from esters by two successive substitutions by sulphur atoms. Replacement of the ethereal oxygen atom of the acetate by a sulphur atom results in thiolacetates; we have already measured the kinetic effect of this substitution,[6] which we call $f(\mathrm{O{-}C{=}O}) \longrightarrow (\mathrm{S{-}C{=}O})$. Conversion to the dithioacetate is completed by substituting the carbonyl oxygen atom by sulphur, $f(\mathrm{S{-}C{=}O}) \longrightarrow (\mathrm{S{-}C{=}S})$. Alternatively the carbonyl oxygen of the acetate may be replaced by a sulphur atom, giving $f(\mathrm{O{-}C{=}O}) \longrightarrow (\mathrm{O{-}C{=}S})$; we have also measured this factor.[7] To complete the conversion to the dithioacetate the factor $f(\mathrm{O{-}C{=}S}) \longrightarrow (\mathrm{S{-}C{=}S})$ is required.

There are thus four factors, two already known and two unknown, which are related by equation (1). This

$$f(\mathrm{O{-}C{=}O}) \longrightarrow (\mathrm{S{-}C{=}O}) \times f(\mathrm{S{-}C{=}O}) \longrightarrow (\mathrm{S{-}C{=}S}) = f(\mathrm{O{-}C{=}O}) \longrightarrow (\mathrm{O{-}C{=}S}) \times f(\mathrm{O{-}C{=}S}) \longrightarrow (\mathrm{S{-}C{=}S}) \quad (1)$$

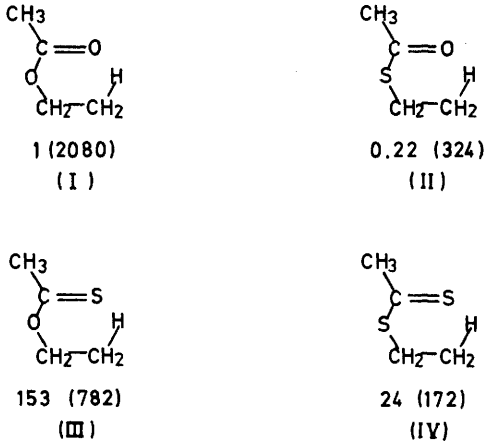
relationship may be used with the data of Table 2 to estimate the values of the two unknown functions. Alternatively, we may assume that the kinetic effect of substituting by sulphur atoms is independent of the other atoms already present, *i.e.* to put $f(\mathrm{O{-}C{=}O}) \longrightarrow (\mathrm{O{-}C{=}S}) = f(\mathrm{S{-}C{=}O}) \longrightarrow (\mathrm{S{-}C{=}S})$ and $f(\mathrm{O{-}C{=}O}) \longrightarrow (\mathrm{S{-}C{=}O}) = f(\mathrm{O{-}C{=}S}) \longrightarrow (\mathrm{S{-}C{=}S})$.

If such an assumption is valid the rates of pyrolysis of dithioacetates may be calculated from the earlier data and comparison be made with experiment. This is what has been done to produce the 'calculated' values of Table 2, and it is seen that the agreement is extraordinarily good. Without doubt some part of this precision derives from fortuitous cancellation of errors, but even if the errors in rates had operated less favourably, the variation would almost have disappeared on conversion to activation energies.

We conclude that, within the limited variation examined in this paper, the energetic change resulting from replacing oxygen by a sulphur atom in a concerted transition state is independent of the nature of those atoms already present. While this conclusion is unlikely to be widely valid, it augurs well for our proposed examination of carbonates described in the Introduction.

This conclusion may be used to calculate the notional rate of pyrolysis of the unknown t-butyl thionacetate. At 629 K the necessary rate constants are:[1,6] t-butyl acetate, 1.56×10^{-1}; t-butyl thiolacetate 5.38×10^{-3}; and t-butyl dithioacetate $3.1 \times 10^{-1}\ \mathrm{s}^{-1}$, giving $9.0\ \mathrm{s}^{-1}$ for t-butyl thionacetate at the same temperature.

The relative rates for the variously substituted acetates at 629 K are shown in Scheme 2, where the first number refers to the ethyl ester compared with ethyl acetate. The numbers in parentheses are the relative rates of the t-butyl esters compared with their own ethyl esters. In terms of the criterion of methylation of the α-carbon atom, esters (I) and (III) with their C_α–O fission have a more polar transition state than esters (II) and (IV). This probably results from the difference in electronegativity between oxygen and sulphur. The ethyl esters of (III) and (IV) are the most reactive, probably as a result of the greater nucleophilic properties of sulphur compared with oxygen. With the t-butyl esters, the distinction is blurred by the differing polarity of the transition states.



SCHEME 2

The correlation that has been observed in simple esters between the rates of pyrolysis and acid strength of the leaving groups [10-12] does not occur here. The strengths of the appropriate acids increase in the order carboxylic < monothio < dithio.[13] This failure is not unexpected since in one case an oxygen atom is leaving, while in another a sulphur atom. General correlations, *e.g.* nucleophilicity with base strength in nucleophilic substitution, only apply for the same attacking atom.

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