Gas-phase Pyrolysis of the *S*-Butyl Thioacetates

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The activation parameters for the pyrolysis of the four *S*-butyl thioacetates suggest that the mechanism of the reaction is similar to that of the acetates. Evidence is presented showing that there is less charge development in the transition states for the reactions of the sulphur compounds.

WE earlier reported on the gas-phase pyrolysis of some dialkyl carbonates,[1-3] and showed that variation of the alkyl group led to changes of rate that are very similar to those produced by the same variation in the pyrolysis of acetates. Although this is suggestive of a similar mechanism for the pyrolysis of the two types of compound, there are no unambiguous data which distinguish between the two possible transition states with the carbonates involving either carbonyl oxygen or ether oxygen attack on the β-hydrogen atom. In principle, measurement of the ${}^{16}O/{}^{18}O$ kinetic isotope effect could afford such information, in the same way that was successfully used by Bourns and Bader for xanthates.[4] An alternative approach appeared possible in chemical labelling of the reactive atoms, in particular in the substitution by sulphur of the various oxygen atoms of the carbonate.

At the outset of this work literature data were not available on the effect of replacing oxygen by sulphur in esters or carbonates and we therefore undertook such an investigation. Towards its end a preliminary communication on the pyrolysis of thiolacetates appeared,[5] but since only one compound was common to our series, we felt it useful to report our work to date.

EXPERIMENTAL

The *S*-butyl thioacetates were prepared by the slow addition of acetyl chloride to a cooled (0°) solution of the appropriate thiol in pyridine. After distillation they had the following properties: *S*-n-butyl thioacetate, b.p. 161°, n_D^{25} 1·4587 (lit.,[6] b.p. 163·4°, n_D^{25} 1·4570); *S*-isobutyl thioacetate, b.p. 26° at 5 mmHg, n_D^{20} 1·4599 (lit.,[7] b.p. 151—152°, $n_D^{23 \cdot 5}$ 1·4555); *S*-1-methylpropyl thioacetate, b.p. 74° at 90mmHg, n_D^{25} 1·4574 (lit.,[8] b.p. 148—151·5°, n_D^{30} 1·4528); and *S*-t-butyl thioacetate, b.p. 31—32° at 15 mmHg, $n_D^{21 \cdot 5}$ 1·4538 (lit.,[8] b.p. 130—131°, n_D^{30} 1·4435).

Stoicheiometry.—After pyrolysis the major products obtained from all the thiolacetates were butenes, carbonyl sulphide, and methane. Thioacetic acid was found to give the last two products under the same conditions. By heating at 400° for 10 half lives in sealed tubes *S*-n-butyl thioacetate gave the same major reaction products, identified by gas i.r. spectroscopy, in addition to some carbon dioxide plus a trace of carbon monoxide. Separation of these products by distillation on a vacuum line proved impossible, and a quantitative estimate of the products was not obtained. Carbon dioxide and a trace of carbon monoxide were however obtained in the pyrolysis of thio acetic acid, under the same conditions.

Kinetics.—Kinetic runs were performed using a flow apparatus essentially the same as that reported previously,[1] except that the reaction tube was placed in an electrically heated aluminium block. Runs were performed between *ca*. 80 and 20% reaction, using the following temperature ranges: n-butyl, 780—810 K; isobutyl, 790—825 K; 1-methylpropyl, 714—743 K; and t-butyl thioacetate, 650—680 K. The Arrhenius parameters were obtained by plotting log (—log a/a_0) *versus* $1/T$, after Kooyman.[9]

The fact that the data gave good straight lines indicates that the reaction is of the first order. This was confirmed by demonstrating that the extent of pyrolysis at pressures between 210 and 790 mmHg in sealed tubes was independent of pressure.

Runs were also performed in a flow tube packed with glass helices which gave an approximately nine-fold increase in surface to volume ratio and in the presence of 500—800 mol % of cyclohexene. The results of this are discussed later. The activation parameters were obtained by the method of least squares from the first-order plots. Values quoted are the average for the runs performed on each compound. Individual rates were obtained after plotting confidence ellipses of the activation parameters and were calculated at the temperature given by the slope of this line.[9] The results are given in Table 1.

DISCUSSION

The thiolacetates described in this paper all showed first-order kinetics. The results for the 1-methylpropyl, isobutyl, and t-butyl esters were particularly clear cut. None showed evidence of heterogeneity and the effect of added cyclohexene was negligible. The last two compounds gave a single olefinic product, and the isomeric butenes obtained from the 1-methylpropyl

TABLE 1

Arrhenius data and best [9] rate constants for the pyrolysis of thiolacetates

Thiol-acetate	E_a kcal mol^{-1}	$\Delta S^{\ddagger}/$ cal mol^{-1} K^{-1}	$10^2k/$s^{-1}	$\log_{10}(A/$s$^{-1})$
n-Butyl	46·5 ± 0·9	−10·5 ± 1·2	3·0 (790 K)	11·6
Isobutyl	49·0 ± 1·5	−8·4 ± 1·8	3·3 (804 K)	11·8
1-Methyl-propyl	44·0 ± 1·2	−8·8 ± 1·7	3·2 (730 K)	11·7
t-Butyl	41·6 ± 0·4	−6·2 ± 0·6	1·8 (652 K)	12·2

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[1] D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 926.

[2] D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 1744.

[3] D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 2359.

[4] R. F. W. Bader and A. N. Bourns, *Canad. J. Chem.*, 1961, **39**, 348.

[5] P. C. Oele, A. Tinkelenberg, and R. Louw, *Tetrahedron Letters*, 1972, 2373.

[6] F. W. Wenzel, jun., and E. E. Reid, *J. Amer. Chem. Soc.*, 1937, **59**, 1089.

[7] P. N. Rylander and D. S. Tarbel, *J. Amer. Chem. Soc.*, 1950, **72**, 3021.

[8] R. E. Dunbar and A. N. Bolstad, *J. Amer. Chem. Soc.*, 1955, **77**, 4672.

[9] J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.

ester were stable at the temperature of the reaction. The reaction is therefore a homogeneous unimolecular process.

S-n-Butyl thioacetate decomposed in a higher temperature range than the secondary and tertiary esters.

TABLE 2

Rates of pyrolysis for acetates [9] and thiolacetates at 629 K

	Thiolacetates		Acetates		
Alkyl group	$10^5k/s^{-1}$	$k_{rel.}$	$10^5k/s^{-1}$	$k_{rel.}$	R [a]
n-Butyl	1·08	1	6·87	1	6·4
Isobutyl	0·51	0·47	2·76	0·40	5·4
1-Methylpropyl	21·5	20	182	26·5	8·5
t-Butyl	538	498	25,100	3554	55

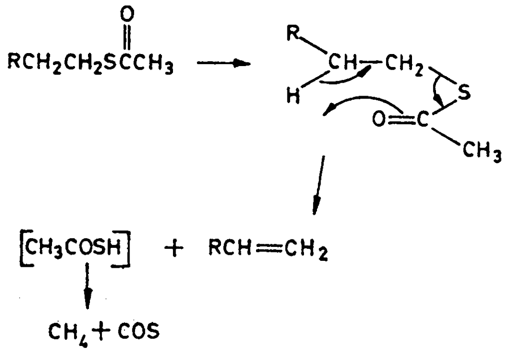
[a] $R = k_{acetate}/k_{thiolacetate}$.

There was a rate increase of 40% in runs using a packed pyrolysis tube. This suggests that 4·5% of the rate constant for normal runs is due to a heterogeneous reaction. Further, a 14% decrease in rate was observed with runs performed in the presence of 800 mole % cyclohexene, showing a radical component of this order of magnitude in the normal runs. In addition to but-1-ene, 6—14% of but-2-enes was detected in the pyrolysate. The amount depended on temperature and was presumably due to the radical component as authentic but-1-ene showed no isomerisation when run as a control.

S-Alkyl thioacetates have previously been shown to decompose to olefin and thioacetic acid.[5] Thioacetic acid was unstable at the temperature of the present reactions, decomposing to an extent dependent on temperature, giving methane and carbonyl sulphide. We were therefore satisfied to demonstrate by chromatography and gas i.r. spectroscopy that the same major products were obtained.

The Arrhenius parameters in Table 1 are indicative of the concerted unimolecular process shown in the Scheme. The most accurate rate constants are those calculated at the temperature given by the confidence plot of the Arrhenius parameters, and are shown in Table 1. Table 2 lists the rate constants calculated at 629 K, a convenient temperature for comparison with acetates and carbonates, and inside the range used for the present compounds. The rate constants for the acetates are calculated from the data of Kooyman *et al.*[9] and are some 6—55-fold greater than those for thiolacetates. The thermochemistry of the acetate pyrolysis is more favourable than that of thiolacetates by *ca.* 20 kcal mol^{-1}, but this large difference has very little effect on the rate constants.

The most interesting feature of the comparison of rate constants is the smaller sensitivity in the rate of thiolester pyrolysis to methylation of the α-carbon atom. This clearly indicates that charge development on the α-carbon atom is less marked than in the acetates. Presumably the more electronegative ether oxygen atom of the acetates is better able to bear a partial negative charge than the sulphur atom of the thiolacetates.



SCHEME

In this connection the ratios of olefins produced from the 1-methylpropyl compounds are of some interest (Table 3). Richardson and O'Neal [10] have concluded that the stability of the incipient double bond has no effect on the direction of elimination in acetate pyrolysis. In thiolacetates, smaller charge development should imply greater double bond formation in the transition state. The direction of elimination may therefore be more influenced by the stability of the incipient double bond, and the figures above show that the yield of but-1-ene is decreased to the advantage of that of but-2-ene.

TABLE 3

Olefin ratios for hydrolysis of 1-methylpropyl esters

	But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene
1-Methylpropyl acetate [9]	57	15	28
1-Methylpropyl carbonate [2]	53	18	29
S-1-Methylpropyl thioacetate	45	19	36

S-Isobutyl thioacetate decomposes at about one half of the rate for *S*-n-butyl thioacetate. This is consistent with no influence of double bond stability, and a reduction in the number of β-hydrogen atoms from two to one. However, as with the carbonates and acetates, the activation parameters change in the wrong sense; all are on the bounds of experimental error, but for all three series $\Delta S^{\ddagger}$ is less negative for the isobutyl than for the n-butyl compound.

[2/2861 *Received, 20th December,* 1972]

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[10] W. H. Richardson and H. E. O'Neal, 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 5, p. 381.