The Gas-phase Pyrolysis of Some Primary and Secondary Thionacetates

By **David B. Bigley** * and **Rosemary E. Gabbott**, University Chemical Laboratory, Canterbury, Kent

Alkyl thionacetates undergo thermal elimination by a homogeneous unimolecular mechanism to give alkenes and thioacetic acid as first products. With the primary esters there is an accompanying rearrangement to thiolacetate. A transition state similar to that for acetate pyrolysis is proposed for the elimination reaction, but it is argued that it is more product-like in the thionester case.

IN a previous paper[1] we reported our findings on the pyrolysis of some alkyl thiolacetates, and compared the rates with literature values for acetate pyrolyses. We have now extended our study to thionacetates, examining the effect of replacing the carbonyl group of the acetate by C=S. There has been considerable interest in the thermal behaviour of aromatic thionesters, in connection with the Schönberg rearrangement.[2] More

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[1] D. B. Bigley and R. E. Gabbott, *J.C.S. Perkin II*, 1973, 1239.

[2] E. J. Hedgley and N. H. Leon, *J. Chem. Soc.* (*C*), 1970, 467 and references cited therein.

recently oxime[3] and hydroxamic acid thionesters[4] have been shown to rearrange by a free radical mechanism in solution.

At the inception of our work there were no kinetic data available on simple alkyl thionesters. During its course, a preliminary report on n-butyl thionacetate appeared.[5] We compare this report with our own more extensive study described below.

EXPERIMENTAL

The thionacetates were prepared[6] by bubbling hydrogen sulphide through a stirred suspension of the appropriate imidate hydrochloride in pyridine for 9 h. After distillation they had the following physical constants: n-butyl thionacetate, b.p. 148—152°, $n_D^{22\cdot5}$ 1·4604 (lit.,[7] b.p. 146—149°, n_D^{28} 1·4196); isobutyl thionacetate, b.p. 146—149°, n_D^{18} 1·4619 (lit.,[7] b.p. 135—140°, n_D^{26} 1·4316); 1-methylpropyl thionacetate, b.p. 142—143°, $n_D^{19\cdot5}$ 1·4593; isopropyl thionacetate, b.p. 119·5°, n_D^{24} 1·4548 (lit.,[7] 119·1°, n_D^{22} 1·4501); ethyl thionacetate, b.p. 106—107°, $n_D^{18\cdot5}$ 1·4658 (lit.,[7,8] 105—107°, n_D^{19} 1·4639); methyl thionacetate, b.p. 88·5—89·5°, n_D^{24} 1·4668 (lit.,[7,9] 88—91°, n_D^{23} 1·4606). Some of these refractive indices show large discrepancies from the literature values. The identity of each compound was therefore checked by i.r. and n.m.r. spectroscopy and by mass spectrometry and its purity was shown to be $>98\%$ by g.l.c.

Stoicheiometry.—After pyrolysis the major products obtained from all except methyl thionacetate were the corresponding olefins and thioacetic acid, which further decomposed to carbonyl sulphide and methane to an extent dependent on temperature. By heating for *ca.* 6 half-lives at 300°, ethyl thionacetate gave the same major products identified by gas i.r. spectroscopy. In addition there was up to 10% of the corresponding alkyl thiolacetate in the pyrolysate of the primary alkyl thionacetates, and methyl thionacetate gave exclusively the thiolacetate under the pyrolysis conditions used.

Kinetics.—Kinetic runs were performed using the flow apparatus as previously reported.[1] Runs were performed between *ca.* 20—80% reaction in the following temperature ranges: n-butyl thionacetate, 613—641 K; isopropyl thionacetate 563—583 K; isobutyl thionacetate 623—657 K; ethyl thionacetate 625—653 K; 1-methylpropyl thionacetate 545—575 K; methyl thionacetate 678—704 K.

The first-order nature of the reaction, indicated by good straight line plots, was confirmed for the case of isopropyl thionacetate where the extent of pyrolysis between 200 and 700 mmHg was independent of pressure.

To show that the reaction is unimolecular several runs were performed on each compound in the presence of not less than 600 mole % of cyclohexene (or toluene in the case of methyl thionacetate) and in a flow tube packed with helices giving a *ca.* 9-fold increase in surface : volume ratio.

The activation parameters were obtained by the method of least squares from plots of log ($-$log a/a_0) *versus* $1/T$ after Kooyman.[10] Values quoted are the average of 8—10 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. To allow for the contribution to pyrolysis rates caused by the rearrangement of thion- to thiol-ester in the primary compounds the rate constants were proportioned according to product ratios at a series of temperatures. Hence, individual activation parameters and rates were obtained for the pyrolysis and rearrangement reactions separately.

DISCUSSION

The thionacetates investigated were pyrolysed with good first-order kinetics. None gave evidence of rate decrease in the presence of a radical chain inhibitor although the primary compounds showed up to 30% rate increases in the packed tube and the secondary compounds exhibited up to 20% rate increases. These correspond to a heterogeneous component of 2—3% in the normal runs, and it is concluded that data obtained refer to the homogeneous unimolecular decomposition.

As noted in our previous paper,[1] and elsewhere,[5] the quantitative estimation of products was severely hampered by the variable extent of decomposition of the thiolacetic acid. However, the reaction was particularly clean and we could find only one product other than the olefin(s) and thiolacetic acid, together with variable amounts of methane and carbonyl sulphide. This product was the isomeric thiolacetate, and it will be discussed below. The olefins were identified by g.l.c. and gas i.r. spectroscopy; where more than one olefin was formed, the ratio was estimated by g.l.c. Since the kinetic technique used monitored the loss of starting material, we believe that the purely qualitative identification of products, while not desirable, does not detract from the value of the results.

The activation parameters obtained are listed in Table 1. As with acetates,[10] thiolacetates,[1] and carbonates[11] the highest value for E_a is shown in the ethyl ester, and is in good agreement with the value quoted by Oele *et al.* (log $k = 12\cdot5 - 41\cdot2/2\cdot303RT$).[5] Alkylation of the α-carbon atom has a marked effect on E_a, a methyl group reducing the value by 3·6 and an ethyl

TABLE 1

Arrhenius parameters and rates of total reaction of alkyl thionacetates $ROCSCH_3$

R	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\log_{10}(A/\text{s}^{-1})$	10^2k/s^{-1}
Et	41·5	$-4\cdot6$	$12\cdot5_5$	1·78 (634·6 K)
Bu^n	39·4	$-6\cdot8$	12·1	2·97 (632·8 K)
Bu^i	40·2	$-6\cdot4$	12·2	4·38 (649·4 K)
Pr^i	$37\cdot9_5$	$-3\cdot0$	$12\cdot8_5$	1·01 (559 K)
1-Methylpropyl	36·2	$-5\cdot1$	12·4	3·4 (570·5 K)

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[3] R. F. Hudson, A. J. Lawson, and E. A. C. Lucken, *Chem. Comm.*, 1971, 807.

[4] W. B. Ankers, C. Brown, R. F. Hudson, and A. J. Lawson, *Chem. Comm.*, 1972, 935.

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

[6] U. Schmidt, E. Heymann, and K. Kabitzke, *Chem. Ber.*, 1963, **96**, 1478.

[7] Y. Sakurada, *Mem. Coll. Sci. Eng. Kyoto*, 1926, **9**, 237.

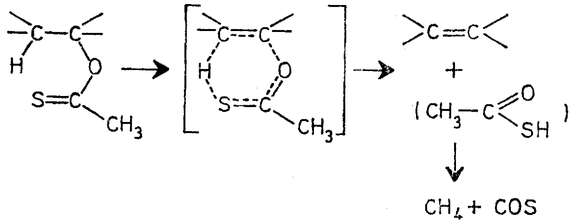
[8] M. Delépine, *Ann. chim. Phys.*, 1912, **25**, 529.

[9] M. Delépine, *Compt. rend.*, 1911, **153**, 279, 726.

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

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

group by 5·4 kcal mol^{-1}. As with acetates β-alkylation is less effective, reducing E_a by only 2·1 kcal mol^{-1}. The consistently negative entropy of activation is in accord with a transition state similar to that accepted for acetates (and to that we have proposed for thiolacetates [1]).



Each compound was pyrolysed several times, and the values for E_a and $\Delta S^\ddagger$ were plotted against each other. The resulting confidence ellipse was in all cases a straight line, and the rate calculated at the temperature of this line is the 'best' rate for each compound.[10] These rates are given in Table 1 with the temperature in parentheses.

In the pyrolysis of the primary thionacetates elimination was accompanied by isomerization to the thiolacetate. Fortunately the thiolacetates were thermally stable at the temperatures used, and the overall rate constant measured by thionacetate disappearance could be simply dissected into k_{isom} and k_{elim}. The rate constants and activation parameters for these processes are given in Tables 2 and 3. We believe the rate data to be of good accuracy (±3%), but that the activation parameters are less reliable. This comes about because partitioning the measured $\Delta G^\ddagger$ into E_a and $\Delta S^\ddagger$ is very sensitive to error, and therefore values derived from partitioning of $\Delta G^\ddagger_{\text{isom}}$ and $\Delta G^\ddagger_{\text{elim}}$ will be less reliable. For this reason we believe the real values of $E_{a\ \text{elim}}$ for ethyl thionacetate should be smaller and that $\Delta S^\ddagger_{\text{elim}}$ should be negative. With this reservation in mind, it can be seen that the average activation parameters for isomerization and elimination are similar, a fact emphasized by the relative rates: $k_{\text{elim}}/k_{\text{isom}}$, Et 6·6; Bu^n 7·55; Bu^i 5·2. The most accurate Arrhenius parameters for isomerization are those for methyl thionacetate, since this compound cannot undergo elimination. These are in reasonable agreement with Louw *et al.*,[5] who quote $\log k \sim 13{\cdot}3 - 46{\cdot}5/2{\cdot}303RT$. At 629 K our data give $k = 9{\cdot}0 \times 10^{-4}$ s^{-1}, while Louw's figures give $k = 1{\cdot}37 \times 10^{-3}$. We agree with these authors' conclusions that the data require a transition state of type (A) used for the Schönberg rearrangement.

TABLE 2

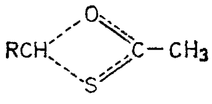
Arrhenius parameters and rates of isomerization of alkyl thionacetates $ROCSCH_3$

R	E_a/kcal mol^{-1}	$\Delta S^\ddagger$/cal mol^{-1} K^{-1}	$\log_{10}(A/$s$^{-1})$	$10^4k/$s^{-1} (629 K)	$k_{\text{rel.}}$ (629 K)
Me	45·8	$-3{\cdot}1_5$	12·9	8·97	0·52
Et	45·3	−2·7	—	17·3	1·00
Bu^n	41·5	−7·6	11·9	28·6	1·65
Bu^i	40·9	−8·9	—	24·9	1·44

TABLE 3

Arrhenius parameters and rates of elimination in alkyl thionacetates $ROCSCH_3$

R	E_a/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal mol^{-1} K^{-1}	$\log_{10}(A/$s$^{-1})$	$10^2k/$ s^{-1} (629 K)	k_{rel}	$k_{\text{thionacetate}}/k_{\text{acetate}}$
Et	47·7	+4·7		1·15	1·00	156
Bu^n	40·5	−5·2	12·4	2·16	1·88	314
Bu^i	41·6	−4·6	$12{\cdot}5_5$	1·30	1·13	471
Pr^i	$37{\cdot}9_5$	−3·0	12·9	51·2	44·5	324
1-Methylpropyl	36·2	−5·1	12·4	73·3	63·7	402



(A)

Dissociation into radicals as in the oxime thionesters[3] would require a positive entropy of activation, and the rate of reaction should have been lowered by the addition of cyclohexene. Finally the six-centre transition state invoked for allylic thionacetates[12] is not structurally possible.

The secondary thionacetates were pyrolysed at lower temperatures than their primary counterparts, the activation energies being lower. This reduction of E_a with alkylation of the α-carbon atom evidently does not extend to the isomerization reaction, as the latter was not evident under the conditions of our flow system.

It is now possible to turn attention to the elimination reactions. The absolute and relative rates of these at 629 K are given in Table 3. The two most striking features of the data are evident in the final column of Table 3, where the rates for thionacetates are compared with those for acetates, both at 629 K. First the thionacetates undergo elimination at some 150—450 times the rate shown by the corresponding acetates. This behaviour is not unexpected. In the transition state drawn earlier the relatively weak C=S is breaking to form C–S while the stronger C=O is forming from C–O. Thermochemically this is a favourable process [D(C=O) − D(C=S) *ca.* 40 kcal mol^{-1}], which is not available to the acetate. Further, sulphur is more nucleophilic than oxygen and might be expected to attack the β-hydrogen atom the more readily.

The second notable feature of Table 3 is the greater variation of rate with structure exhibited by thionacetates when compared with acetates. Comparison of n-butyl and isopropyl thionacetates with the corresponding acetates shows that both α- and β-alkyl groups have a greater effect on rate in the former compounds.

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[12] S. G. Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 4285.

We interpret this as indicating that the transition state for thionacetate elimination is more product-like than in the acetates, *i.e.* the double bond of the incipient olefin is more developed in the transition state of the thionacetates. We find this conclusion supported by the ratios of products. Thus 1-methylpropyl acetate gives almost a statistical ratio of but-1- to -2-enes on pyrolysis; on the basis of this type of evidence several authors have concluded that the stability of the developing double bond has no effect in determining the ratio of products.[13] While we cannot in detail support this conclusion, it is broadly true. In the thionacetates inclusion of a factor for stability of the forming double bond should move the product ratio from statistical towards thermodynamic. The data in Table 4 on 1-methylpropyl esters show this to be so.

TABLE 4

Pyrolysis of 1-methylpropyl esters

	But-1-ene	But-2-enes	
Statistical ratio	60	40	(*cis* 20; *trans* 20)
Acetate [10]	57	43	(*cis* 15; *trans* 28)
Thionacetate	38	62	(*cis* 21; *trans* 41)
Thermodynamic ratio at 500° [13]	28	72	(*cis* 31; *trans* 41) [14]

[4/1313 *Received*, 1*st July*, 1974]

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[13] 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.

[14] H. H. Voge and N. C. May, *J. Amer. Chem. Soc.*, 1946, **68**, 550.