

Thermolysis of ^{18}O Labelled Ethyl Acetate¹

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Summary There was only minor scrambling of the oxygen in the unpyrolysed ^{18}O labelled ethyl acetate when heated to pyrolysis temperatures in a carefully deactivated reactor.

THE thermolysis of alkyl esters has been considered to proceed through (i) a completely concerted process,² (ii) a polarized transition state³ and (iii) an ion pair intermediate.⁴ The marked activation on the rate caused by α -alkyl or α -aryl groups in the alcohol portion of the ester suggests for this unimolecular homogeneous reaction an ion-pair intermediate mechanism⁴ or an ion-pair mechanism based on molecular rearrangements⁵ rather than a concerted process.³ The relative rates for the thermolysis of acetates of ethyl, isopropyl, and t-butyl alcohols at 400 °C are 1 : 24 : 2000 and

their ratios extrapolated to 25 °C give 1 : 410 : 1.8×10^6 .^{4a,4c}

An ion-pair intermediate in rapid equilibrium with the ester would result in scrambling of the oxygens in the ester prior to thermolysis into olefins and acids. Hence, an observation of total scrambling would support the ion-pair intermediate in equilibrium with the ester if thermolysis were carried out under homogeneous reaction conditions.

The partial thermolysis (40%) of ethyl acetate enriched in ^{18}O , $\text{Et}^{18}\text{O}-\text{COMe}$, carried out in a carefully deactivated reactor, revealed that only a minor amount of scrambling of the oxygens could have occurred during heating.

The analysis was based on the distribution of ^{18}O between the MeCO and the OEt measured by mass spectrometry. If total scrambling occurred each position would bear 50% of the ^{18}O independent of the ^{18}O enrichment. As shown in Table 2 the measured distribution of the ^{18}O in the enriched

ethyl acetate (I) is very close to the calculated value of 50% in each fragment. The values obtained by mass spectrometry, 48.2 and 51.8, showed the suitability of this

pair during thermolysis. If an intimate ion pair occurs in course of the reaction, essentially none of it reverts to unpyrolysed ester. This result supports a cyclic concerted

TABLE I

Relative abundance of ions found in the mass spectra of ethyl acetate

		MeCO	MeC ¹⁸ O	¹⁸ OEt	¹⁸ OEt	MeCO ₂ Et		
		43	45	45	47	88	89	90
(I)	Ethyl acetate	1000	2.2	157	0.37	60	3.3	0.53
(II)	Ethyl acetate (enriched with ¹⁸ O at the ether oxygen)	1000	3.5	148	4.5	50	2.7	2.3
(III)	Ethyl acetate (enriched ¹⁸ O heated to pyrolysis temperature)	1000	5.8	162	4.5	50	2.3	2.0

method of measurement. After enrichment of the ether oxygen position of the ester with ¹⁸O (Table 2 II) it was calculated that the MeCO position contained 6.55% of ¹⁸O. However, it was determined to be 10.4%, (indicating that some scrambling occurs during the mass spectral analysis), and when the ester is heated (Table 2, III) this percentage increased to 16.3%. If complete scrambling had occurred, the value would be *ca* 50%.

TABLE 2

Distribution of ¹⁸O in major fragments of labelled ethyl acetate^a

Ester			Percent of Total ¹⁸ O	
			MeCO	OEt
(I) Unenriched	Me-CO ₂ -Et	Theoretical	50.0	50.0
		Experimental	48.2	51.8
(II) Enriched	Me-CO ₂ -Et	Theoretical	6.5	93.5
		Experimental	10.4	89.6
(III) Enriched, heated	Me-CO ₂ -Et	16.3	83.7

^a Calculated as percentage of ¹⁸O detected in either the acyl fragment or ethoxide fragment compared to the total ¹⁸O occurring in both of these fragments as measured by ion abundances.

These data show that rapid equilibration *does not* occur between the ester of primary alcohols and an intimate ion

mechanism^{3a} and places the ion-pair intermediate mechanism in serious question. Had it been established that equilibration occurred, this would have provided the most convincing evidence in favour of the ion-pair mechanism.

The ¹⁸O labelled ethyl acetate was prepared from 82.5 atom % [¹⁸O] ethyl alcohol and ketene and purified by preparative g.l.c.

Mass spectrometry showed the ethyl acetate to be enriched 4–5 times over the naturally occurring amount with ¹⁸O in the ether moiety.

Labelled ethyl acetate (250 μl) was injected into a deactivated stainless steel static reactor⁶ at 346° and thermolysis was continued until 40% of the ester had been pyrolysed (as noted by the increase in pressure). The gaseous mixture was collected in a dry-ice-Pr¹OH trap. Unpyrolysed ester was separated from the acetic acid on a 20' × 1/4" 20% Carbowax 20 M g.l.c. column at 190°.

Mass spectral analysis was performed on an A.E.I. MS-9 instrument (reservoir temperature 85°, inlet temperature 185°, ion source temperature 225°, trap current 100 μA, ionizing voltage 70eV). The MeC¹⁸O, *m/e* 45, ion was easily distinguished from the EtO, *m/e* 45 ion.

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² C. D. Hurd and F. H. Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.

³ (a) K. K. Lum and G. G. Smith, *Internat. J. Chem. Kinetics*, 1969, **1**, 401; (b) R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

⁴ (a) J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123; (b) T. Sato, K. Murata, A. Nishimura, T. Tsuchiya, and N. Wasada, *Tetrahedron*, 1967, **23**, 1791; (c) A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, 1967, **4**, 119.

⁵ (a) E. U. Emovon, *J. Chem. Soc. (B)*, 1966, 588; (b) M. Hanack, J. J. Schneider, and H. Schneider Berlohr, *Tetrahedron*, 1967, **23**, 2195.

⁶ G. G. Smith and J. A. Kirby, *Analyst*, 1969, **94**, 242.