The Kinetic Isotope Effect in the Pyrolysis of Esters and the Nature of the Transition State

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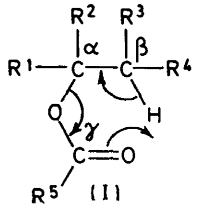
The rates of gas-phase pyrolysis of 1-phenylethyl acetate and its 2,2,2-trideuterio-isomer have been measured by a very accurate static method at 656·1 K and a value for $k_H:k_D$ of 2·15 has been obtained. The same value is obtained from pyrolysis of 1,2-diphenylethyl acetate and its 2,2-dideuterio-isomer at 632·0 K, consequently contributions of secondary isotope effects to the primary value are insignificant; confirmation was provided by kinetic studies of the pyrolysis of *erythro*- and *threo*-2-deuterio-1,2-diphenylethyl acetates. The first detailed portrayal of the transition state for ester pyrolysis is given which is consistent with *all* of the known features, particularly the previously irreconcilable magnitudes of the isotope effects and Hammett ρ-factors.

The pyrolysis of 1-phenylethyl acetate and its 1-deuterio-isomer at 656·1 K proceeds with a kinetic isotope effect $k_H:k_D$ of 1·025, attributed to hybridisation changes at the 1-carbon atom in the transition state.

THE pyrolysis of esters is a reaction which has been studied fairly intensively during the last ten years or so,[1,2] but a complete picture of the reaction transition state has not hitherto emerged. The original portrayal[3,4] of the transition state as a fully concerted process, *i.e.* one in which all the electrons move together as shown in (I) was disproved by the effect of substituents at the α- and β-carbon atoms and it appeared, in general,[5] that electron supply at the α-carbon atom speeded up the reaction, whereas at the β-carbon electron supply speeded the reaction (for secondary and tertiary esters) and slowed it (for primary esters). Studies of this kind were, however, complicated by the need to correct for statistical factors and, more importantly, for the effect of the differing stabilities of the alkene products which is an unknown factor. Consequently we believe that the study[6] of the pyrolysis of 1,2-diarylethyl acetates (II) (either X or Y = H) which removed these objections gave results which were the most relevant. Thus pyrolysis of (II; Y = H) and also of 1-arylethyl acetates (III),[7] gave rates which correlated with σ^+-values in a Hammett plot, a negative ρ-factor (*ca.* —0·65) being obtained. This showed conclusively that the α-carbon possessed carbonium-ion character in the transition state. These latter conclusions were subsequently confirmed by Scheer *et al.*[2] and by Emovon and Maccoll[1] who suggested an ionic transition state (V) for the reaction. The drawback with this portrayal was that the dotted lines gave no indication of the relative extents of bond-making and bond-breaking, and furthermore failed to account for the Hammett correlation with σ-values (ρ = *ca.* +0·15) for reactions of esters (II; X = H) and (IV; X = H).[6,7]



(I)

A further complication is that the ρ-factor for the Hammett correlation of substituents at the α-carbon is approximately four times larger than for the correlation at the β-carbon which implies that the charge developed at the former site in the transition state is four times larger than that developed at the latter. This in itself is no problem, but could not previously be reconciled with the kinetic isotope effects for the β-hydrogen (Table 1) which have been taken[4] to indicate almost complete C–H bond-breaking in the rate-determining step. However, the kinetic isotope effects are in considerable disagreement with each other, none were obtained by accurate static kinetic methods, and in no case is the result unambiguously free of the possibility of hyperconjugative effects. (It is peculiar to eliminations that the hydrogens most readily eliminated are also those ideally situated for hyperconjugative stabilisation of the transition state carbonium ion, or the forming double bond.) The purpose of

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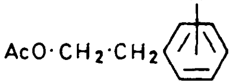

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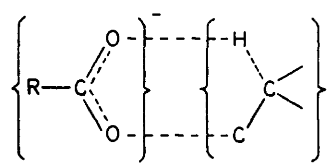

(V)

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[1] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 622; G. G. Smith, K. K. Lum, J. A. Kirby, and J. Pospsil, *J. Org. Chem.*, 1969, **34**, 1095; E. V. Emovon and A. Maccoll, *J. Chem. Soc.*, 1964, 227; and earlier papers in these series.

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

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

[4] C. H. De Puy and R. W. King, *Chem. Rev.*, 1960, 431.

[5] A. Maccoll, *Adv. Phys. Org. Chem.*, 1965, **3**, 91.

[6] G. G. Smith, F. D. Bagley, and R. Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 3647.

[7] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

the present work therefore was to determine the kinetic isotope effect by the very accurate static kinetic method,

TABLE 1

Previously observed isotope effects in ester pyrolysis

Ester	T/°C	$k_H : k_D$	Ref.
1,2-Diarylethyl acetates	400	2·8	8
1-Cyclohexylethyl acetate	500	1·7	9
	400	1·9	9
Ethyl acetate	500	2·0, 2·1	10
2-Methylcyclohexyl acetate	400	1·39—1·49	11

and in systems where hyperconjugative effects could be separated from primary isotope effects.

RESULTS AND DISCUSSION

Rate coefficients and kinetic isotope effects obtained in the pyrolysis of various esters are given in Table 2. Main features of these results are as follows.

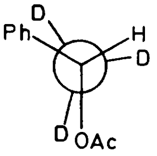
(i) The isotope effect for pyrolysis of 1,2-diphenylethyl acetate and its [2,2-$^2H_2$]-isomer is 2·14, hence the value of 2·8 given in Table 1 (and which was higher than the theoretical maximum *ca.* 2·45 [a]) is confirmed as erroneous; this stems from the method of Curtin and Kellom [8] which was capable of giving an approximate value only.

TABLE 2

Compound	T/°C	10^3k/s^{-1}	Av.	$k_H : k_D$
1-Phenyl[1-$^2H_1$]ethyl acetate	382·9	16·3, 16·4, 16·7, 16·3	16·4	1·025
1-Phenylethyl acetate	382·9	16·7, 16·8, 17·0, 16·8	16·8	
1-Phenyl[2,2,2-$^2H_3$]ethyl acetate	382·9	7·80, 7·79, 7·81, 7·75	7·79	2·15
1,2-Diphenyl[2,2-$^2H_2$]ethyl acetate	358·8	5·22, 5·40, 5·36, 5·21	5·32	2·14
1,2-Diphenylethyl acetate	358·8	11·3, 11·3, 11·5, 11·4	11·4	
threo-1,2-Diphenyl[2-$^2H_1$]ethyl acetate	358·8	5·91, 5·94, 5·94, 5·97	5·94	1·92
1,2-Diphenylethyl acetate	354·4	9·36, 9·39	9·375	1·1175 [a]
erythro-1,2-Diphenyl[2-$^2H_1$]ethyl acetate	354·4	8·40, 8·36	8·38	
1,2-Diphenylethyl acetate	354·2	9·27		1·115 [a]
erythro-1,2-Diphenyl[2-$^2H_1$]ethyl acetate	354·2	8·32		
1,2-Diphenylethyl acetate	354·0	9·12, 9·09	9·12	1·103 [a]
erythro-1,2-Diphenyl[2-$^2H_1$]ethyl acetate	354·0	8·33, 8·21	8·24	

[a] Average = 1·110 ± 0·01.

(ii) The pyrolysis of [2,2,2-$^2H_3$]-1-phenylethyl acetate (VI) proceeds 2·15 times slower than does the pyrolysis of the protium-containing compound. However, this value could be composed of a primary isotope effect arising from the cleavage of the C–H bond, together with secondary isotope effects arising from hyperconjugation involving the two C–H bonds that are not broken. If these secondary effects are real, then reduction in the number of β-deuterium atoms which are not eliminated should produce a diminution in the observed isotope effect. However, comparison of the rate of pyrolysis of 1,2-diphenylethyl acetate and its [2,2-$^2H_2$]-isomer (VII) produces the *same* isotope effect (within experimental error). Consequently the contribution to the observed isotope effects from hyperconjugation is negligible and this presumably arises from the 45° angle between the C–D bonds and the forming *p*-orbitals in the incipient carbonium ion.



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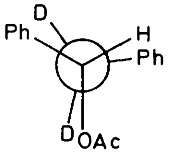
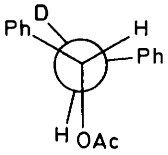


(VII)

(iii) Further support for the above conclusion comes from examination of the kinetic data for *erythro*- and *threo*-1,2-diphenyl[2-$^2H_1$]ethyl acetates. Comparison of the rate of the former compound (VIII) with that for 1,2-diphenylethyl acetate suggests at first that there is a contribution to the observed isotope effect of *ca.* 1·11 per β-deuterium atom. However, Curtin and Kellom showed that in the pyrolysis of (VIII) 97 ± 2·5% of deuterium is retained in the stilbene product, and by a more accurate (n.m.r.) method of determination we find the retention to be 95·5%, *i.e.* the small isotope effect that is kinetically observed arises from the fact that a small percentage of the reaction involves C–D bond-breaking. Indeed we can calculate on the basis of the result in (ii) above, that if 4·5% of C–D bond-breaking occurs, then the observed isotope effect should be 1·00 + (4·5 × 2·14 ÷ 100) = 1·10, in excellent agreement with the value obtained. Similar arguments can be applied to account for the difference in rate of *threo*-1,2-diphenyl[2-$^2H_1$]ethyl acetate (IX) and 1,2-diphenylethyl



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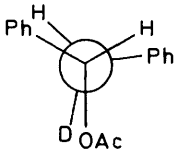

(IX)

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[a] Calculated assuming that non-reacting bonds are unaffected during the reaction, that the carbon–hydrogen bond is completely broken in the transition state, and neglecting tunnelling.

[8] D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, 1953, **75**, 6011.

[9] C. H. De Puy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, 1959, **7**, 123.

[10] A. T. Blades and P. W. Gilderson, *Canad. J. Chem.*, 1960, **38**, 1401, 1407.

[11] E. A. Halevi, 'Progress in Physical Organic Chemistry,' Wiley, London, 1963, p. 109.

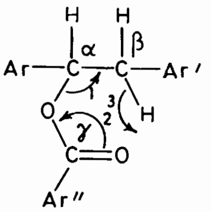
acetate and striking proof of the consistency of all three sets of results is the fact that multiplication of the observed isotope effect of 1·92 in the latter case by the previous value of 1·11, gives a predicted true isotope effect of 2·13 (*cf.* the experimental value of 2·14).

(iv) The substitution of an α-deuterium atom produces a very minor rate retardation ($k_{\mathrm{H}} : k_{\mathrm{D}} = 1{\cdot}025$), and this small effect (which is outside our experimental error) can be reasonably attributed to the hybridisation changes (sp^3 to sp^2) that occur at the α-carbon during the transition state for the reaction; the general principles involved in this proposal have been reviewed by Halevi.[11] (It also shows that where such effects occur in solution reactions they may not be dismissed as arising from solvation differences.)

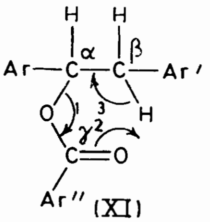
We have established then that there is a real primary isotope effect in this reaction and that it is fairly large since the theoretical maximum at 360 °C is *ca.* 2·70. However it has been argued that the maximum isotope effect is to be expected when the hydrogen is *half transferred.*[12] Furthermore this maximum at half transference applies when transfer occurs between atoms of like basicity and in the present case the greater basicity of oxygen relative to carbon should mean that the isotope maximum will be obtained when the hydrogen is less than half transferred, and probably as little as one third. Since the observed isotope effect is less than 80% of the theoretical maximum we may safely infer that the β-carbon-hydrogen bond is *no more than one third broken in the rate-determining step.* Indeed even this may be a considerable overestimate since calculations indicate that the isotope effect increases rapidly with a small degree of bond breaking and then levels off as the bond tends towards being half broken.[13]

Now the respective ρ-factors for substituents in α- and β-aryl groups are −0·63 and +0·15. However, since an incipient carbonium ion and an incipient carbanion are adjacent to each other, the effect of a substituent in stabilising one of these, will also be to destabilise the other (though less effectively); this is much more important than has hitherto been realised. Suppose the effect of the substituent falls off by the usual inductive factor of 2·3 per atom (if conjugative effects are significant the fall off will be even less than this). Suppose the true ratio of charge at the α- and β-positions in the transition state is 2 : 1. The net effect of a substituent in the α-aryl ring (which is the observable factor) will be to stabilise the carbonium ion of relative charge 2^+ and to destabilise the carbanion of relative charge $1/2{\cdot}3^-$, *i.e.* a net effect of $1{\cdot}56^+$. Likewise a similar β-aryl substituent will be to destabilise a relative charge of 1^- and stabilise a relative charge of $2/2{\cdot}3^+$, *i.e.* a net effect of $0{\cdot}12^-$. Hence the ratio of the observed Hammett correlations will be 13 : 1 so that *the observed ratio of the Hammett ρ-factors is much greater than the ratio of charges developed at the α- and β-carbons.* By similar reasoning it can be shown that the ratio of the Hammett ρ-factors (*ca.* 4·5) obtained in the acetate pyrolysis indicates that the charge at the α-carbon is only 1·65 times larger than that at the β-carbon in the transition state.

We are now in a position to rationalise for the first time the primary isotope effect (which is proportional to the amount of bond-breaking) with the observed Hammett correlation since it follows from the above that the α-carbon–oxygen bond will still be far short of completely broken (little more than half in fact) if the β-carbon–hydrogen bond is approximately one-third broken. Consequently we can now develop a more detailed picture of the transition state for ester pyrolysis than hitherto available. Consider the two semi-concerted processes depicted by (X) and (XI), *i.e.* processes in which the electrons move in a cyclic manner but not at precisely the same time, so that charge develops in the six-membered ring. Examination of the kinetic data shows that we can discount process (X) and confirm (XI). Take the case of (X) first. Not only does this require unfavourable polarisation of the C_α–O bond, but predicts that C_α will be electron-rich which we know not to be the case. Neither can we explain the results by assuming that in (X) the electron pair 3 moves first creating an electron deficiency at C_β which is relayed to C_α for if this were so, a correlation with σ^+-values with a larger negative ρ-value should be obtained for substituents in Ar′ and this again is contrary to observation.



(X)



(XI)

It is clear then that the electrons cannot move in a clockwise direction so that we must concern ourselves with the alternative (XI), and we have established also that C_β is less electron rich than C_α is electron deficient. In addition, pyrolysis rates for ethyl benzoates (XI; Ar = Ar′ = H) correlated with σ-values with ρ = +0·2[14] and likewise isopropyl benzoates (Ar = Me, Ar′ = H) gave a similar correlation (ρ = +0·33),[15] the latter results being the most relevant since the temperature of measurement was closer to that for the

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[12] W. S. Briggs and C. Djerassi, *J. Org. Chem.*, 1968, **33**, 1625.

[13] R. P. Bell, 'The Proton in Chemistry,' Methuen, London, 1959, p. 202; *Trans. Faraday Soc.*, 1961, **57**, 961; *Discuss. Faraday Soc.*, 1965, **39**, 16; C. G. Swain, *J. Amer. Chem. Soc.*, 1961, **83**, 2154; F. W. Westheimer, *Chem. Rev.*, 1961, **61**, 265; L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press Co., New York, 1959; J. Bigeleisen, *Pure Appl. Chem.*, 1964, **8**, 217; C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3214; A. V. Willi and M. Wolfsberg, *Chem. and Ind.*, 1964, 2097; A. M. Katz and W. H. Saunders, *J. Amer. Chem. Soc.*, 1969, **91**, 4469; R. A. More O'Ferrall, G. W. Koepl, and A. J. Kresge, *ibid.*, 1971, **93**, 9.

[14] G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403.

[15] G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, 1963, **28**, 3496.

acetates, and the kinetic data more accurate. Hence C_γ is also electron-rich in the transition state, so it follows that the electron pair 2 cannot have progressed as far away from C_γ as the electron pair 1 has moved towards it. Likewise the substituent effects at C_β show that this is acquiring a net negative charge so clearly the C_β–H bond has stretched in the transition state, but the electrons cannot have moved sufficiently towards forming the double bond since C_α is still clearly electron deficient.

It is very apparent therefore that *the extent of movement of the electrons follows the order* $1 > 2 > 3$ and as far as we are aware this is the first time that it has proved possible to evaluate precisely the timing of electron movements in a cyclic transition state of this type. We suggest that our portrayal of the transition state for ester pyrolysis is more accurate than any previous model and accommodates all the known experimental facts.*

EXPERIMENTAL

All compounds described below are indicated to be at least 99% pure by g.l.c. analysis.

1-*Phenylethyl acetate*.—This was available from previous studies and give $n_D^{20} = 1{\cdot}4978$ (lit.,[7] n_D^{25} 1·4998).

1-*Phenyl*[1-$^2H_1$]*ethyl Acetate*.—Reduction of acetophenone by lithium aluminium deuteride followed by acetylation with acetic anhydride and pyridine gave 1-phenyl[1-$^2H_1$]-ethyl acetate (83% based on starting material), b.p. 41°/0·4 mmHg, n_D^{20} 1·4936.

1-*Phenyl*[2-$^2H_1$]*ethyl Acetate*.—Reduction of [$^2H_3$]acetophenone (99% minimum isotopic purity, supplied by Prochem Ltd.) with sodium borohydride followed by acetylation as above gave 1-*phenyl*[2-$^2H_1$]*ethyl acetate* (76% based on starting material), b.p. 40°/0·4 mmHg, n_D^{20} 1·4933.

1,2-*Diphenylethyl Acetate*.—This compound was prepared in 60% overall yield by the method of Curtin and Kellom[8] and had b.p. 103—108°/0·5 mmHg, n_D^{20} 1·5481 (lit.,[8] 121—123°/0·8 mmHg 1·5478; lit.,[6] 153·5—154°/10 mmHg 1·5480).

1,2-*Diphenyl*[2,2-$^2H_2$]*ethyl Acetate*.—Ethyl benzoate (30 g. 0·2 mol) was reduced with lithium aluminium deuteride (4·0 g > 99% deuterium content) in ether. Work-up yielded [αα-$^2H_2$]benzyl alcohol (8 g, 32·5%). Conversion of this into the chloride by thionyl chloride and treatment of the Grignard reagent from this with excess of benzaldehyde gave the crude alcohol which was acetylated as above to give 1,2-diphenyl[2,2-$^2H_2$]ethyl acetate (3 g, 16·5% based on benzyl alcohol), b.p. 104—106°/0·5 mmHg, n_D^{20} 1·5492.

erythro-1,2-*Diphenyl*[2-$^2H_1$]*ethyl Acetate*.—This compound was prepared by the method of Curtin and Kellom[8] and had b.p. 96—100°/0·4 mmHg, n_D^{20} 1·5487. The peak areas due to the two CH groups in the n.m.r. spectrum indicated at least 98% deuterium incorporation. The *trans*-stilbene oxide intermediate, m.p. 67·5°, was shown by n.m.r. spectroscopy to be completely free of *cis*-stilbene oxide.

threo-1,2-*Diphenyl*[2-$^2H_1$]*ethyl Acetate*.—This compound was prepared *via cis*-stilbene oxide by the method of Curtin and Kellom[8] and had b.p. 96°/0·2 mmHg, n_D^{20} 1·5475. The deuterium incorporation was shown as above to be at least 98%. The *cis*-stilbene oxide intermediate, m.p. 37·5—39·0° (lit.,[8] 37·0—37·5°; lit.,[16] 40°; lit.,[17] 42°) appeared from g.l.c. analysis to contain *ca.* 10% of the *trans*-isomer whereas n.m.r. spectroscopy showed this to be entirely absent. Consequently the *cis*-oxide readily isomerises under g.l.c. conditions.

The general kinetic method has been described.[18]

Determination of the retention of deuterium in the product from pyrolysis of *erythro*-1,2-diphenyl[2-$^2H_1$]ethyl acetate was carried out by n.m.r. spectroscopy. The peak from the aliphatic hydrogen should be split into a triplet of equal heights due to the deuterium on the adjacent carbon. The height of the central peak was slightly enhanced however and by comparison with the corresponding peak from pure *trans*-stilbene the amount of the latter impurity in the *trans*-[1-$^2H_1$]stilbene was shown by a number of determinations to be 4·5 ± 0·2%; analysis on A-60 and HA-100 instruments gave identical results.

[1/1284 *Received, July 26th,* 1971]

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* The model involving formation of an intimate ion pair (V) has now been firmly disproved by experiments with ^{18}O-labelled ethyl acetate (G. G. Smith, K. J. Vorhees, and F. M. Kelly, *Chem. Comm.*, 1971, 789).

[16] J. Boeseken and G. C. C. C. Schneider, *J. prakt. Chem.*, 1931, **131**, 285.

[17] J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 1930, 2378.

[18] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 2382.