The Nature of the Transition State in Ester Pyrolysis. Part II.[1] The Relative Rates of Pyrolysis of Ethyl, Isopropyl, and t-Butyl Acetates, Phenylacetates, Benzoates, Phenyl Carbonates, and *N*-Phenylcarbamates

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Rates of pyrolysis of the title compounds have been measured over not less than a 50° range for each, at temperatures between 522 and 606 K, and the relative rates at 600 K determined. The relative reactivities follow the order: acetates < phenylacetates < benzoates < carbamates < carbonates and the change in the ratios $k_{\mathrm{Bu^t}}/k_{\mathrm{Pr^i}}$ and $k_{\mathrm{Pr^i}}/k_{\mathrm{Et}}$ for each series of compounds increases in the same sequence, so that along this series the extent of polarisation in the transition state increases. The increase in this rate spread with increasing reactivity of the ester type arises mainly from the difference in rates of the ethyl and isopropyl compounds and this trend is maintained through to halide pyrolysis. The difference in the transition state polarities for primary and secondary ester pyrolysis is therefore less than that between the secondary and tertiary ester transition states and these differences diminish with increasing reactivity of the ester type. These generalisations do not apply to pyrolysis of ethyl and isopropyl *N*-phenylcarbamates which are confirmed by the Arrhenius data as decomposing by more than one mechanism.

STUDIES of the correlation of rates of gas-phase elimination of esters in terms of the Hammett equation have shown that the transition state may be represented by (I) wherein the movement of electrons follows the order $1 > 2 > 3$.[1] So well documented is the Hammett equation and so unambiguous its interpretation, that arguments implying that the elimination process is *completely* concerted [2] may be discounted.†

Certain questions remain to be resolved however. (i) How does the charge separation vary between

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† We understand a completely concerted process to be that in which movement of all the electron pairs in the reaction pathway occurs such that no atom involved in this pathway suffers at any moment a nett gain or loss of electrons.

[1] Part I, R. Taylor, *J.C.S. Perkin II*, 1972, 165.

[2] H. Kwart and D. P. Hoster, *Chem. Comm.*, 1967, 1155; H. Kwart and J. Slutsky, *J.C.S. Chem. Comm.*, 1972, 552, 1182.

TABLE 1

Pyrolysis of compounds $R^1CO_2R^2$

R^1	R^2	Correlation coefficient	T/°C	10^3k/s^{-1}	E_a/kcal mol^{-1} [a]	log (A/s^{-1}) [a]
Me	Et	0.999 78	377.3	0.278	47.8 [b] (1.0)	12.5 [b] (0.3)
			395.2	0.725		
			409.8	1.55		
			427.2	3.90		
$PhCH_2$	Et	0.999 93	377.3	0.364	47.8 (0.6)	12.6 (0.2)
			395.2	0.95		
			409.8	2.09		
			427.2	5.05		
Ph	Et	0.999 94	377.3	0.455	47.7 (0.5)	12.7 (0.2)
			395.2	1.19		
			409.8	2.60		
			427.2	6.30		
PhNH	Et	0.990 46	361.4	3.8	(34.7) [c] (3.0)	(9.6) [c] (1.0)
			376.8	9.98		
			393.2	16.3		
			410.0	26.8		
			420.9	40.0		
			426.7	51.0		
			432.6	83.0		
PhO	Et	0.999 96	336.0	0.274	45.3 (0.4)	12.7 (0.1)
			354.7	0.815		
			385.0	4.46		
			394.9	7.29		
Me	Pr^i	0.999 91	336.0	0.65	45.7 [d] (0.6)	13.2 [d] (0.2)
			356.0	2.17		
			376.8	7.18		
			394.9	17.9		
$PhCH_2$	Pr^i	0.999 89	327.6	0.548	45.5 (0.7)	13.3 (0.2)
			339.0	1.165		
			354.7	2.88		
			377.3	10.25		
Ph	Pr^i	0.999 99	319.1	0.443	44.8 (0.15)	13.2 (0.05)
			341.5	1.79		
			354.7	3.86		
			377.3	13.35		
PhNH	Pr^i	0.998 95	293.6	0.648	(39.7) [c] (1.2)	(12.1) [c] (0.4)
			312.1	1.50		
			331.4	4.91		
			345.6	11.6		
			361.4	25.7		
			376.9	51.7		
			394.9	122		
PhO	Pr^i	0.999 99	284.3	0.386	43.1 (0.2)	13.5 (0.05)
			298.2	0.989		
			327.6	6.31		
			339.0	12.55		
Me	Bu^t	0.999 96	284.3	3.11	40.3 [e] (0.35)	13.3 [e] (0.1)
			312.3	17.75		
			326.7	41.4		
			336.0	67.4		
$PhCH_2$	Bu^t	0.999 91	271.2	2.19	39.4 (0.5)	13.2 (0.2)
			284.3	5.15		
			298.2	12.7		
			327.6	66.6		
Ph	Bu^t	0.999 75	271.2	3.03	39.3 (0.7)	13.3 (0.3)
			284.3	7.12		
			298.0	17.8		
			312.3	38.7		
			326.7	87.4		
PhNH	Bu^t	0.999 34	248.0	1.89	39.9 (0.6)	13.8 (0.2)
			262.6	5.50		
			275.6	12.9		
			284.3	22.6		
			298.0	56.7		
PhO	Bu^t	0.999 93	249.4	7.65	36.6 (0.35)	13.2 (0.1)
			271.2	32.1		
			284.3	71.8		
			298.0	152		
			312.3	343		

[a] Errors shown are for 95% confidence limits. A more meaningful indication of the accuracy of the data is given by the correlation coefficients. [b] Average literature [3,4] values are 47.8 kcal mol^{-1} and 12.5 s^{-1} with 10^5k = 0.263 at 650 K *cf.* 0.268, this work. [c] See text. [d] Average literature [3,5] values are 45.7 kcal mol^{-1} and 13.2 s^{-1} with 10^5k = 7.04 at 650 K *cf.* 6.95, this work. [e] The most reliable literature [6] values are 40.5 kcal mol^{-1} and 13.3 with 10^5k = 521 at 650 K *cf.* 540, this work.

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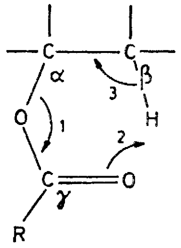
[3] A. T. Blades, *Canad. J. Chem.*, 1954, **32**, 366.

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

[5] E. U. Emovon and A. Maccoll, *J. Chem. Soc.*, 1962, 335.

[6] C. E. Rudy and P. Fugassi, *J. Phys. Chem.*, 1948, **52**, 357.

primary, secondary, and tertiary esters? (ii) What are the relative reactivities of different ester types and how do the reactivity differences arise? (iii) Do the charges formed at the α-, β-, and γ-carbons of (I) differ for different ester types and in a parallel way? (iv) Will the spread of rates between primary, secondary, and tertiary derivatives of different ester types parallel the changes in ρ factors in Hammett correlations of aryl derivatives of these ester types?



(I)

In this paper we answer (i), (ii), and to a certain extent (iv), through pyrolysis of the ethyl, isopropyl, and t-butyl derivatives of acetates (I; R = Me), phenylacetates (I; R = $PhCH_2$), benzoates (I; R = Ph), phenylcarbamates (I; R = NHPh), and carbonates (I; R = OPh). Subsequently we hope to obtain evidence concerning the remaining questions.

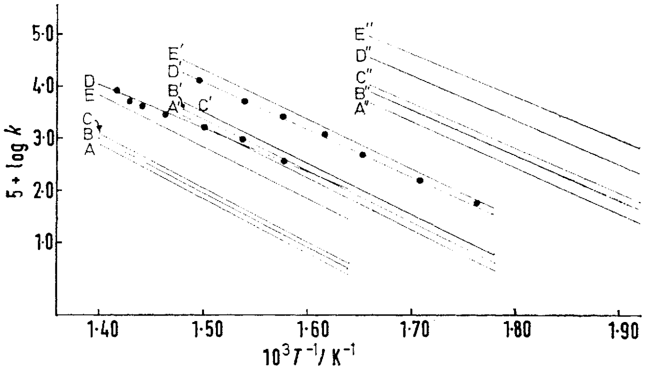


FIGURE 1 Arrhenius diagrams for pyrolysis of alkyl esters: A, A′, A″, ethyl, isopropyl, and t-butyl acetates; B—B″, phenylacetates; C—C″, benzoates; D—D″, *N*-phenylcarbamates; E—E″, phenyl carbonates

RESULTS AND DISCUSSION

The kinetic data are assembled in Table 1 and represent the most extensive study of the pyrolysis of different types of esters carried out under the same set of conditions; consequently the results are likely to be the most valid. Where rates of pyrolysis of some of the compounds have been measured previously (and under different conditions) the results are in impressive agreement as indicated by the footnotes to Table 1. The relative rates of pyrolysis at 600 K are given in Table 2 and this temperature has been chosen as it is that at which ρ values have been calculated in Hammett analyses of pyrolysis data, and also because it requires minimal extrapolation of the Arrhenius plots.

TABLE 2

Relative rates of pyrolysis of $R^1CO_2R^2$ at 600 K

R′	k^a_{rel} (t-butyl esters)	$k(Pr^i)/k(Et)$	$k(Bu^t)/k(Pr^i)$	$k(Bu^t)/k(Et)$
Me	1.0	28.8	115	3 315
$PhCH_2$	1.55	32.3	121	3 910
Ph	2.22	36.3	125	4 540
PhNH	7.00			
PhO	17.8	39.8	126	5 020

[a] Relative to t-butyl acetate at 600 K.

Noteworthy features of the results are as follows. (i) The reactivity order for the different ester types is carbonate > carbamate > benzoate > phenylacetate > acetate. From studies of the effects of substituents in aryl groups attached to the γ-carbon atom,[7-10] it is evident that electron withdrawal facilitates reaction. Since an electron-withdrawal series should be OPh > NHPh > Ph > CH_2Ph > CH_3, the reactivity order observed is the expected one. Indeed there is an approximate correlation between the logarithms of the relative rates of the t-butyl esters and Taft σ^* values [11] and very recently, Barroeta *et al.* have drawn attention to a correlation between these parameters and activation energies for pyrolysis of ethyl esters.[12]

(ii) The most reactive ester types have the most polar transition states. This is shown by the relative rates between the primary, secondary, and tertiary esters given in Table 2 and which is greatest for the most reactive esters. [It may appear that these results contradict some data of Daly and Ziolkowski which indicated the rate spread between primary, secondary, and tertiary carbamates to be less than for acetates.[13] However their studies relate to *dialkyl* carbamates in which the increase in electron supply at the α-carbon of (I) would be compensated by an increase in electron supply at the γ-carbon of (I).]

From these results one would expect that the presence of highly electron-withdrawing groups attached to the γ-carbon would result in a significantly more polar transition state. This appears to be the case for in pyrolysis of chloroformates the isopropyl ester was 100-fold more reactive than the ethyl ester, the t-butyl ester being so much more reactive as to be unstable at room temperature.[14]

Since the polarity of the transition state (at the γ-carbon) decreases along the series from carbonates to acetates one could expect a parallel charge decrease at the α-carbon. Some indication that this is true comes

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

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

[9] G. G. Smith, D. A. K. Jones, and R. Taylor, *J. Org. Chem.*, 1963, **28**, 3547.

[10] M. P. Thorne, *Canad. J. Chem.*, 1967, **45**, 2537.

[11] V. A. Palm, *Russ. Chem. Rev.*, 1961, **30**, 471.

[12] N. Barroeta, V. de Santis, and M. Rincon, *J.C.S. Perkin II*, 1974, 911.

[13] W. J. Daly and F. Ziolkowski, *J.C.S. Chem. Comm.*, 1972, 911.

[14] E. S. Lewis and W. C. Herndon, *J. Amer. Chem. Soc.*, 1961, **83**, 1955.

from the pyrolysis of 1-arylethyl benzoates and 1-arylethyl acetates for which the ρ-factors (corrected to 600 K) are −0.86 and −0.66, respectively.[15,16]

(iii) The reactivity order in each class of esters is tertiary > secondary > primary as expected on statistical and electronic grounds; this has been previously shown to be the case for acetates. The relative rate coefficients for the acetates at 673 K are ethyl (1.0) : isopropyl (24.4) : t-butyl (1 740). These values are in excellent agreement with those quoted in the literature (1 : 26 : 1 660)[17] considering that the latter were obtained by extrapolation from work of differing origins.

(iv) Since an increased reaction rate is commensurate with a more polar transition state it suggests that the polarity of the transition state increases in the order primary < secondary < tertiary. Three other factors support this notion more firmly. First the relative elimination rates of tertiary and secondary esters is greater than for secondary to primary, whereas on electronic and statistical grounds similar rate ratios could be expected. Secondly, the ρ factor corrected to 600 K for pyrolysis of isopropyl benzoates (0.33) is greater than that for pyrolysis of ethyl benzoates (0.26).[7,8] Thirdly, it can be seen from Table 2 that as the transition state for pyrolysis of the ester types becomes more polar the isopropyl : ethyl rate ratio increases more than the t-butyl : isopropyl ratio; this would follow if the t-butyl ester has the most polar transition state as this will be subject to a smaller relative increase in polarity on going to a more reactive ester type than will a transition state of lower initial polarity.

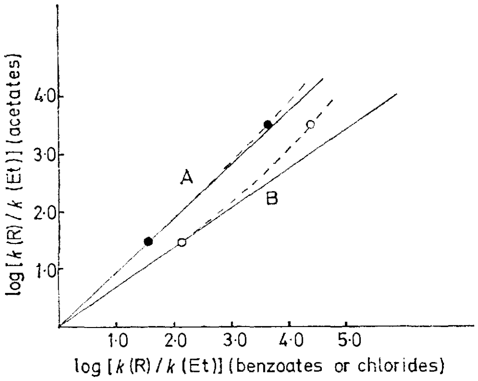
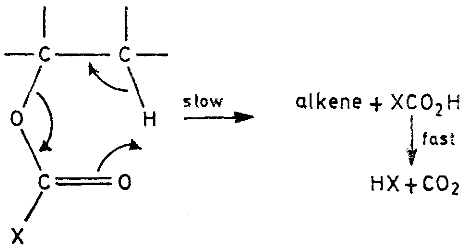


FIGURE 2 Correlation of relative rates of ester and halide pyrolysis: A, acetates *vs.* benzoates; B, acetates *vs.* chlorides

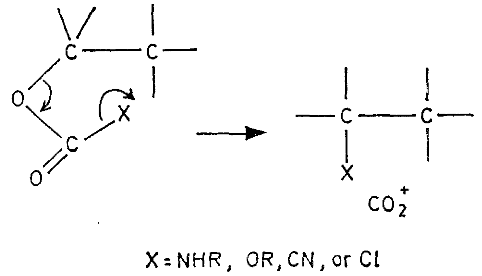
This latter trend is not only confined to esters. Figure 2 shows the log k_{rel} values for the t-butyl and isopropyl esters (relative to the ethyl ester) plotted for acetate data against the carbonate data. The result is a curve for the reasons given above. Figure 2 also shows the acetate data plotted against data for pyrolysis of alkyl chlorides,[17] and again we have a curve in the same direction but more marked because of the greater polarity of the transition state for chloride pyrolysis (similar results are obtained using data for bromide or iodide pyrolysis).

(v) The kinetic data for ethyl and isopropyl *N*-phenylcarbamates is anomalous. Although each gave excellent first-order kinetics, these were not reproducible in the case of the former compound (indicating surface catalysis) and the Arrhenius plots (Figure 1) are inconsistent with those for the other esters. Dyer and Wright[18] found that in addition to the normal mode of pyrolysis of the carbamates[10,19] (Scheme 1; X = NHR) decomposition to a tertiary amine and carbon dioxide or into isocyanate and alcohol can occur if the carbamate is primary or secondary. Our Arrhenius plots also indicate that an additional reaction is occurring, that it has a lower activation energy than the primary elimination, and is most serious for the primary ester.



SCHEME 1

We believe that this alternative reaction producing amine proceeds *via* an S_Ni reaction (Scheme 2) thereby demonstrating the parallel between elimination in the gas phase and in solution in that both are accompanied by nucleophilic substitution. Such a reaction would also account for the thermal formation of alkyl halides from chloroformates,[20] alkyl cyanides from cyanoformates,[12] and alkyl ethers from carbonates.[21] These reactions are also surface-catalysed and have a lower activation energy than the accompanying eliminations given by Scheme 1.[14,20,21] This nucleophilic substitution



SCHEME 2

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[15] G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, 1969, **34**, 2090.

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

[17] A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, 1967, **4**, 199.

[18] E. Dyer and G. C. Wright, *J. Amer. Chem. Soc.*, 1959, **81**, 2138.

[19] N. J. Daly and F. Ziolkowski, *Austral. J. Chem.*, 1971, **24**, 2541; N. J. Daly, G. M. Heweston, and F. Ziolkowski, *ibid.*, 1973, **26**, 1259.

[20] E. S. Lewis and E. R. Newman, *J. Amer. Chem. Soc.*, 1969, **91**, 7455; E. S. Lewis and J. T. Hill, *ibid.*, p. 7458.

[21] R. Taylor, *Tetrahedron Letters*, 1975, 593.

(like the analogue in solution) would be sterically hindered and so decrease along the series primary > secondary > tertiary (as we have shown for carbonates). This would also account for the failure of Daly and Ziolkowski to observe this reaction in the decomposition of the highly hindered but primary ethyl *N*-methyl-*N*-phenylcarbamate.[19]

EXPERIMENTAL

The general method of pyrolysis has been described previously.[22] Excellent first-order kinetic plots were obtained to *ca.* 97% reaction with all the esters studied except ethyl acetate and ethyl phenylacetate. With these two compounds some decomposition of the acid product occurred during the time taken for the primary elimination. This was more marked for ethyl phenylacetate because of the lower thermal stability of phenylacetic acid and was more marked also at higher temperatures because the activation energy for the acid decomposition is higher than for the primary elimination.[23] For these two compounds the P_∞ values were estimated from the P_0 value ($P_\infty = 2P_0$) and in this way linear plots to 85—90% reaction were obtained. Rate coefficients could be duplicated to within ±1% (except for runs on ethyl *N*-phenylcarbamate) and the average values of these rate coefficients are given in Table 1; the kinetic data gave excellent Arrhenius plots (again with the exception of this compound). The Arrhenius plots are shown in Figure 1. Interestingly no difficulty was experienced in studying and reproducing the rates of decomposition of t-butyl benzoate in contrast to the experience of Smith and Yates who reported non-reproducibility with this compound and its ring-substituted derivatives.[24] It seems therefore that some temporary defect in their apparatus or injection technique caused the anomaly. Kinetic studies of ethyl *N*-phenylcarbamate gave both poor reproducibility and a scatter on the Arrhenius plot (Figure 1) and the reason for this is given in the Discussion section.

In this work we were able to study without difficulty reactions with half-lives of only 2 s which is 5-fold faster than the fastest reactions previously studied successfully with this apparatus. The derived rate coefficient (343×10^{-3} s^{-1} for t-butyl phenyl carbonate) showed no deviation from the linear Arrhenius plot obtained over a 63° range.

Ethyl, Isopropyl, and t-Butyl Acetates.—These were good quality commercial samples.

Ethyl, Isopropyl, and t-Butyl Phenylacetates.—These were each prepared by warming during 30 min a mixture of the appropriate alcohol (0.1 mol) with phenylacetyl chloride (0.1 mol) and pyridine (10 ml) followed by work-up and fractional distillation. This gave ethyl phenylacetate, b.p. 142° at 60 mmHg, n_D^{20} 1.4822 (lit.,[25] b.p. 114—117° at 14 mmHg, n_D^{25} 1.4825); isopropyl phenylacetate, b.p. 140° at 60 mmHg, n_D^{20} 1.4881 [lit.,[26] b.p. 157—165° at 12 mmHg (clearly an error), n_D^{25} 1.4845]; and t-butyl phenylacetate, b.p. 140° at 60 mmHg, n_D^{20} 1.4971 (lit.,[27] b.p. 132—138° at 32 mmHg, $n_D^{18.5}$ 1.4992).

Ethyl, Isopropyl, and t-Butyl Benzoate.—The ethyl ester was a good commercial sample. The isopropyl and t-butyl esters were prepared from the corresponding alcohol and benzoyl chloride as above. This gave isopropyl benzoate, b.p. 62° at 1.5 mmHg, n_D^{20} 1.4938 (lit.,[10] 90° at 9 mmHg, n_D^{20} 1.4946) and t-butyl benzoate, b.p. 122° at 60 mmHg, n_D^{20} 1.4911 (lit.,[24] b.p. 116° at 18 mmHg, n_D^{20} 1.4910).

Ethyl, Isopropyl, and t-Butyl N*-Phenylcarbamates.*—These were kindly prepared by Dr. M. P. Thorne.

Ethyl, Isopropyl, and t-Butyl Phenyl Carbonates.—The last compound was a good commercial sample and the first was available from a previous study.[9] Isopropyl phenyl carbonate was prepared by warming during 30 min, isopropyl alcohol (0.1 mol), phenyl chloroformate (0.1 mol), and pyridine (10 ml). Work-up and fractional distillation gave isopropyl phenyl carbonate, b.p. 100° at 60 mmHg, n_D^{20} 1.4815 (lit.,[28] b.p. 141° at 70 mmHg, $n_D^{16.1}$ 1.4843).

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[28] A. Morel, *Bull. Soc. chim. France*, 1899, [3], **21**, 815.