The Mechanism of the Gas-phase Pyrolysis of Esters. Part 6.[1] Pyrolysis of 1-Arylethyl Benzoates and t-Butyl Phenylacetates

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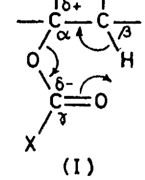
Rate coefficients for pyrolysis of 1-arylethyl benzoates have been measured between 617.9 and 668.4 K and the log k_{rel} values give an excellent correlation with σ^+ values with ρ −0.72 at 600 K; this confirms that the polarity of the transition state for benzoate pyrolysis is greater than for acetates and less than for carbonates. Rate coefficients for pyrolysis of t-butyl phenylacetates, measured between 543.3 and 600.8 K give log k_{rel} values which correlate with σ° values with ρ 0.39 at 600 K, confirming that the polarity of the transition state for phenylacetate pyrolysis is less than that for benzoates and *N*-phenylcarbamates. The phenylacetate data correlate better with σ^n values confirming that these are more accurate resonance-free substituent constants than are σ° values.

In Part 2 one of us showed that the spread of rates for pyrolysis of primary, secondary, and tertiary esters at 600 K (Table 1) increased from acetates to carbonates, and also with reactivity of the class of ester;[2] all the data in Table 1 were obtained under the same conditions. We reasoned that the polarity of the transition state for the pyrolytic elimination increased for the esters down Table 1, and noted that this polarity increase was paralleled by an increase in the rate for the tertiary esters. Confirmation of this belief would be provided by the Hammett ρ factors for pyrolysis of the corresponding 1-arylethyl esters, and the values for the acetates (−0.66)[3] and phenyl carbonates (−0.84)[1] are in the order expected. Data exist in the literature for 1-arylethyl benzoates, but the ρ factor was reported as −0.795 at 647 K ($\equiv$ −0.86 at 600 K).[4] It seemed to us that this value was too high and moreover, the reaction was partly surface-catalysed [as evidenced both by the lack of constancy in the log (A/s^{-1}) values and hence $\Delta S^\ddagger$ values (rate coefficients were determined over a $\not>$30° range), and by the abnormally high reactivity of the *p*-methoxy ester]. Furthermore the ρ factor was determined from a Hammett plot which used the literature values of σ^+ for *m*-Me and *m*-NO$_2$, both of which are now known to be in error.[1,5] We have therefore made a careful re-examination of this reaction, using rate coefficients determined over a temperature range $\not<$50°.

TABLE 1

Pyrolysis rates relative to those of ethyl esters

Ester	Ethyl	Isopropyl	t-Butyl	$k(\mathrm{Bu^tOOCR})/k(\mathrm{Bu^tOAc})$
Acetate	1	28.8	3 315	1
Phenylacetate	1	32.3	3 910	1.55
Benzoate	1	36.3	4 540	2.22
N-Phenylcarbamate				7.00
Phenyl carbonate	1	39.8	5 025	17.8



(I)

It follows also from our analysis that γ-aryl groups [in (I)] should give an increasing (and positive) ρ factor

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[1] Part 5, H. B. Amin and R. Taylor, preceding paper.

[2] R. Taylor, *J.C.S. Perkin II*, 1975, 1025.

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

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

[5] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, 1463.

on going from phenylacetates through to phenyl carbonates. (No analysis of this kind is of course possible for acetates.) Data are so far available for t-butyl benzoates[6] and t-butyl *N*-arylcarbamates.[7] In this paper we report data for t-butyl phenylacetates.

RESULTS AND DISCUSSION

Rate data for pyrolysis of 1-arylethyl benzoates are given in Table 2. These data are more meaningful than those reported in the literature,[4] not only because of the very much superior correlation coefficients, but also because of the constancy of the activation entropies which are 3.1 ± 1.2 cal mol^{-1} K^{-1}, the error being no greater than that which is produced by a ±1% reproducibility in rate coefficients determined over a 50° range. The data give an excellent correlation with σ^+ values (Figure 1) with ρ −0.675 at 641 K [≡ −0.72 at 600 K, calculated *via* the $\rho_1T_1 = \rho_2T_2$ relationship which must hold because of the constancy of the log (A/s^{-1}) values]. Thus the ρ factor lies between those for acetates and phenyl carbonates and is nearer to the value for the former. Likewise the spread of rates between primary and tertiary phenylacetates (and their overall reactivity) lies closer to that for acetates than to that for phenyl carbonates. The relative polarities of the transition states for these three classes of esters is therefore now quite clearly defined.

TABLE 2

Pyrolysis of 1-arylethyl benzoates $RC_6H_4CH(OAc)CH_3$

R	10^3k/s^{-1}				log(A/s^{-1})	E kcal mol^{-1}	$\Delta S^{\ddagger}$ [a] cal mol^{-1} K^{-1}	Corr. coeff.	log k/k_0 [b]
T/K =	668.4	654.7	633.9	617.9					
p-Me	112	56.4	22.6	9.20	12.15	40.06	−4.3	0.999 36	0.235
m-Me	83.3	43.1	14.6	6.39	12.64	41.94	−2.1	0.999 89	0.084
H	66.0	35.5	12.7	5.15	12.38	41.46	−3.3	0.999 71	0
p-Cl	59.4	30.4	10.6	4.47	12.53	42.06	−2.6	1.000 00	−0.064
m-Cl	37.7	19.6	6.60	2.66	12.70	43.19	−1.8	0.999 89	−0.270
p-CF_3	30.5	14.6	5.14	2.09	12.63	43.29	−2.1	0.999 86	−0.388
m-NO_2	22.8	11.3	3.90	1.95 [c]	12.11	42.10	−4.5	0.999 80	−0.488
p-NO_2	21.1	10.0	3.62	1.72 [c]	12.21	42.50	−4.1	0.999 67	−0.532

[a] At 600 K. [b] At 641 K. [c] At 620.2 K.

TABLE 3

Pyrolysis of t-butyl phenylacetates, $RC_6H_4CH_2COOBu^t$

R	10^3k/s^{-1}											log (A/s^{-1})	E kcal mol^{-1}	$\Delta S^{\ddagger}$ [a] cal mol^{-1} K^{-1}	Corr. coeff.	log k/k_0 [a]
T/K =	600.8	600.2	587.9	587.2	571.4	570.8	557.5	553.3	551.1	544.4	543.3					
p-OMe		55.2		28.2	11.0				3.07			12.90	38.85	−0.9	0.999 85	−0.059
p-Me		55.9		26.3	10.3				2.86			13.22	39.75	0.6	0.999 98	−0.080
m-Me		57.6		28.8	10.8	11.0			3.06			13.12	39.42	0.1	0.999 77	−0.050
H	66.6	64.3	33.2	32.2	12.7		5.15			2.19		13.17	39.42	0.3	0.999 89	0
p-F		71.5		35.5	14.4	14.1			3.89			13.02	38.87	−0.4	0.999 71	0.057
p-Cl		80.5		39.1	15.7	15.5		5.42	4.66			12.73	38.00	−1.7	0.999 95	0.095
m-Cl		87.4		44.4	17.0	16.8			5.01			12.96	38.48	−0.6	0.999 86	0.149
p-NO_2				67.3 [b]	26.7 [c]						4.47	13.42	39.21	1.5	0.999 94	0.343

[a] At 600 K. [b] At 587.3 K. [c] At 571.3 K.

It is noteworthy that the excellent correlation with σ^+ values is obtained using the redefined value[1] of $\sigma^+_{m\text{-}NO_2}$, and also that the value of $\sigma^+_{m\text{-}Me}$ is indicated to be even more negative than that (−0.098) which one of us recently redetermined.[5] This was true also for pyrolysis of 1-arylethyl phenyl carbonates and discussion of this point is deferred to a later paper.

Rate data for t-butyl phenylacetates are given in Table 3, and the log $k_{rel.}$ values at 600 K are plotted against σ^0 values in Figure 2 (lower plot). The ρ factor for the reaction (0.39) is shown in Table 4 along with the values for related reactions.[6-8] The value for the phenylacetates is clearly less than that for the *N*-arylcarbamates as predicted. Precise quantitative discussion of the effect of γ-aryl groups in the manner of the effects of β-aryl groups is however not possible because the transmission factor for the group X in (I) has to be taken into account. For benzoates there is no group X and the ρ factors are all enhanced. Insertion of an extra atom in a chain between reaction site and substituent reduces the ρ factor in reactions at ambient temperature by *ca.* 2.5, and between benzoic and phenylacetic acids the factor is 2.2 at 25°.[9] This corresponds to a factor of *ca.* 1.45 at 600 K, so division of the benzoate values by this gives ρ factors of 0.18

TABLE 4

Hammett ρ factors for pyrolysis of esters at 600 K

	Phenyl-acetates	Benzoates	*N*-Aryl-carbamates	Aryl-carbonates
Ethyl		0.26		0.19
Isopropyl		0.335		
t-Butyl	0.39	0.59	0.48	

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[6] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1975, 1802.

[7] R. Taylor and M. P. Thorne, *J.C.S. Perkin II*, 1976, 799.

[8] G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403; G. G. Smith and D. A. K. Jones, *ibid.*, p. 3896; G. G. Smith, D. A. K. Jones, and R. Taylor, *ibid.*, p. 3547.

[9] See, for example, J. Shorter, 'Correlation Analysis in Organic Chemistry,' Oxford University Press, Oxford, 1973, p. 1.

(primary), 0.23(secondary), and 0.40(tertiary) so that the data are all nicely self-consistent.

It is apparent from Figure 2 that the correlation with σ^0 values is not very good and in particular the relative reactivities of the *p*-methyl and *p*-methoxy esters is

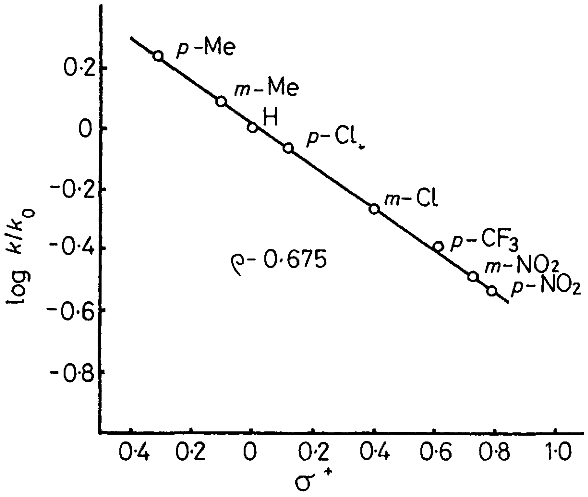


FIGURE 1 Hammett correlation for pyrolysis of 1-arylethyl benzoates at 641 K

wrongly predicted by these parameters. To understand this it is first necessary to understand why the rates of carbonates, carbamates, and benzoates correlate with σ^0 rather than with σ values. The latter are an 'exalted' version of the former due to the fact that interactions such as in (II) retard, in the case of the standard ionisation which defines σ values, the breaking of the O–H bond because of the unfavourable juxtaposition of like charges that results. The analogous effect would not be unfavourable to ester elimination, indeed, as shown in (III) it might favour reaction through increasing the rate of attack upon the β-hydrogen. Consequently a parameter indicative simply of the ability of an aryl group to stabilise an adjacent partially negative charge [as in (I)] is required, *i.e.* σ^0 values.

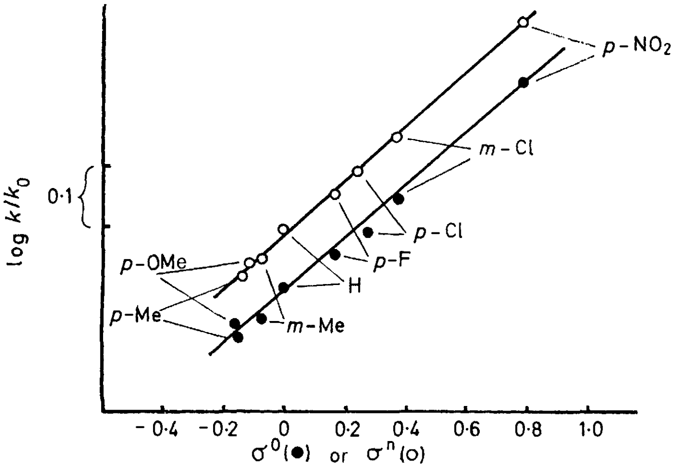
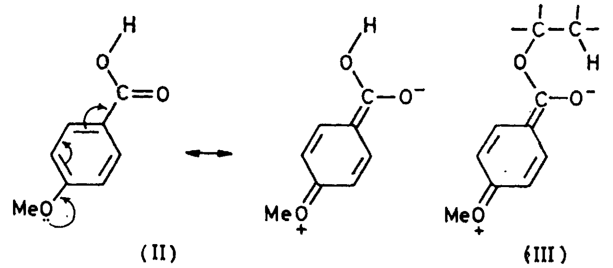


FIGURE 2 Hammett correlation for pyrolysis of t-butyl phenylacetates at 600 K



(II) (III)

In principle, σ^0 values are supposed to represent the resonance free interaction of a substituent with a reaction site, and were defined from reactions in which the substituent and site are 'insulated' from each other by a saturated chain.[10] However it is now appreciated that such saturated chains can transmit conjugative effects so that the σ^0 values are themselves 'exalted'. Nevertheless good correlations are generally obtained with these parameters in reactions where the resonance-transmitting ability of the saturated linkage (*e.g.* the NH group in pyrolysis of *N*-arylcarbamates) [7] is comparable to that in the standard reaction. The recognition that σ^0 values are not truly resonance-free parameters led Wepster and his co-workers to introduce the more fundamental σ^n values,[11] and is noteworthy that the data for pyrolysis of t-butyl phenylacetates give a better correlation with these parameters (Figure 2, upper plot) which is consistent with the lower ability of the CH_2 group to transmit conjugative effects.[7,12] Thus in both the ionisation of phenylacetic acids and in the pyrolysis, the *p*-MeO substituent is less electron supplying than the *p*-Me substituent as predicted by the σ^n values.

EXPERIMENTAL

1-*Arylethyl Benzoates*.—These were obtained in good yields (70% or greater) by the action of benzoyl chloride and pyridine upon the corresponding 1-arylethyl alcohols.[3,13] All the products gave good C and H analyses, and the correct i.r. and n.m.r. spectra. The physical properties (b.p. or m.p. and refractive index at 20°) are as follows and it should be noted that all our refractive indices are substantially higher than those given in the literature; [4] we therefore checked the calibration of our refractometer but found it to be perfectly accurate: (substituent =) H, 110° at 0.3 mmHg, 1.559 4; 4-Me, 120° at 0.3 mmHg, 1.557 2; 3-Me, 116° at 0.3 mmHg, 1.557 6; 4-Cl, 126° at 0.3 mmHg, 1.569 0; 3-Cl, 130° at 0.2 mmHg, 1.571 5; 4-CF_3, 110° at 0.3 mmHg, 1.509 3; 3-NO_2, 160° at 0.3 mmHg (m.p. 66°); 4-NO_2, 94—95°.

t-Butyl Phenylacetate.—The preparation of this has been described.[2]

t-Butyl 4-*Methoxyphenylacetate*.—4-Methoxyphenylacetic acid was heated under reflux with freshly distilled thionyl

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[10] R. W. Taft, *J. Phys. Chem.*, 1960, **84**, 1805.

[11] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[12] A. J. Hoefnagel, J. C. Monshower, E. C. G. Snorn, and B. M. Wepster, *J. Amer. Chem. Soc.*, 1973, **95**, 5350.

[13] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 622.

chloride during 2 h. The excess of thionyl chloride was removed under reduced pressure and the crude *p*-methoxyphenylacetyl chloride heated with t-butyl alcohol (excess) in the presence of anhydrous pyridine during 2 h. Normal work up yielded *t-butyl* 4-*methoxyphenylacetate* (23% based on the acid), b.p. 74—76° at 0.2 mmHg, n_D^{20} 1.494 2, $\tau(CCl_4)$ 3.22 (4 H, m, ArH), 6.28 (s, $ArOCH_3$), 6.73 (s, CH_2), and 8.63 (s, CMe_3).

t-Butyl 4-Methylphenylacetate.— 4-Methylphenylacetic acid, treated as above gave 4-methylphenylacetyl chloride, b.p. 52—54° at 1.0 mmHg (lit.,[14] 108—111° at 20 mmHg), n_D^{20} 1.529 2. This was converted as above into *t-butyl* 4-*methylphenylacetate* (33%), b.p. 40—42° at 0.3 mmHg, n_D^{20} 1.484 3, $\tau(CCl_4)$ 3.13 (4 H, m, ArH), 6.66 (s, CH_2), 7.72 (s, $ArCH_3$), and 8.63 (s, CMe_3).

t-Butyl 3-*Methylphenylacetate.*— 3-Methylphenylacetic acid was converted *via* the acid chloride as above to *t-butyl* 3-*methylphenylacetate* (18% based on the acid), b.p. 74—76° at 0.5 mmHg, n_D^{20} 1.485 3, $\tau(CCl_4)$ 3.12 (4 H, m, ArH), 6.69 (s, CH_2), 7.72 (s, $ArCH_3$), and 8.63 (s, CMe_3).

t-Butyl 4-*Fluorophenylacetate.*—4-Fluorophenylacetic acid was converted as above to 4-fluorophenylacetyl chloride, b.p. 58—60° at 3 mmHg (lit.,[15] 202—204°), and thence to *t-butyl* 4-*fluorophenylacetate* (48%), b.p. 40° at 0.2 mmHg, n_D^{20} 1.469 5, $\tau(CCl_4)$ 3.97 (4 H, m, ArH), 6.63 (s, CH_2), and 8.62 (s, CMe_3).

t-Butyl 4-*Chlorophenylacetate.*—4-Chlorophenylacetic acid was converted *via* the acid chloride as above into *t-butyl* 4-*chlorophenylacetate* (22% based on the acid), b.p. 68—70° at 0.2 mmHg, n_D^{20} 1.498 0, $\tau(CCl_4)$ 2.98 (4 H, m, ArH), 6.70 (s, CH_2), and 8.65 (s, CMe_3).

t-Butyl 3-*Chlorophenylacetate.*—3-Chlorophenylacetic acid was converted as above into 3-chlorophenylacetyl chloride, b.p. 42—44° at 0.3 mmHg (lit.,[14] 121° at 17 mmHg), and thence to *t-butyl*-3-*chlorophenylacetate* (43%), b.p. 58° at 0.3 mmHg, n_D^{20} 1.496 0, $\tau(CCl_4)$ 2.98 (4 H, m, ArH), 6.69 (s, CH_2), and 8.63 (s, CMe_3).

t-*Butyl* 4-*Nitrophenylacetate.*—4-Nitrophenylacetic acid was converted as above into 4-nitrophenylacetol chloride, m.p. 45—46° (lit.,[14] 45.8—46.8°), and thence to *t-butyl* 4-*nitrophenylacetate* (41%), b.p. 74—76° at 0.3 mmHg, m.p. 37—39°, $\tau(CCl_4)$ 3.12 (4 H, m, ArH), 6.39 (s, CH_2), and 8.60 (s, CMe_3).

Kinetic Studies.—These were carried out in the manner previously described[16] and good reproducible first-order kinetics to beyond 95% of reaction were obtained with the benzoates. For the least reactive phenylacetates secondary decomposition of the primary reaction product, phenylacetic acid, was discernible. However, this did not seriously interfere with derivation of the first-order kinetic plots which were linear to beyond 80% of reaction for the worst affected runs. As is customary in ester elimination which produces an acid which decomposes significantly during a kinetic run, the problem is most noticeable at the highest temperatures employed because the activation energy of the secondary decomposition is substantially higher than that of the primary elimination.

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[14] P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, 1960, **82**, 1756.

[15] G. A. Olah, A. E. Pavlath, J. A. Olah, and F. Herr, *J. Org. Chem.*, 1957, **22**, 879.

[16] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1397.