

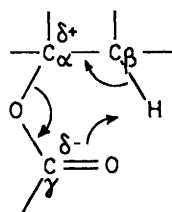
The Nature of the Transition State in Ester Pyrolysis. Part III.¹ The Hammett Correlation for Pyrolysis of *t*-Butyl Benzoates

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Rates of pyrolysis of *t*-butyl benzoates have been measured at 584.9 and 570.8 K. The data give a good correlation with σ^* values with $\rho +0.58$ (corrected to 600 K). The magnitude of this value compared to previously determined values (corrected to 600 K) for ethyl and isopropyl benzoates of 0.26 and 0.335 respectively confirms that the transition state polarity for pyrolysis of esters increases along the series primary < secondary < tertiary with the biggest polarity difference occurring between the secondary and tertiary esters.

In Part II we examined the rates of pyrolysis of the ethyl, isopropyl, and *t*-butyl esters of acetic, phenylacetic, benzoic, carbamic, and carbonic acids and found the rates to increase along the series primary < secondary < tertiary and also along the above sequence of acids. From the spread of rates for elimination from the primary, secondary, and tertiary esters in each series of compounds it was concluded that the polarity of the transition state increases along the series primary < secondary < tertiary with the biggest change in polarity coming between the secondary and tertiary esters.

These experiments evaluate the polarity differences through the charge developed at the α -carbon in the cyclic semi-concerted transition state (I) for the reaction, and we would expect therefore that there would be a commensurate variation in the negative charge which develops at the γ -carbon. A measure of the latter would be given by the Hammett ρ factor for the effect of substituted aryl groups attached to the γ -carbon *e.g.* in ethyl, isopropyl, and *t*-butyl benzoates. Smith and his co-workers² have studied the rates of pyrolysis of



(I)

the former two classes of compounds which gave ρ factors (corrected to 600 K) of 0.26 and 0.335, respectively. These data suggest that the ρ factor does indeed increase along the series primary < secondary < tertiary and it would be valuable therefore to see if the ρ factor for *t*-butyl benzoate pyrolysis would be (a) larger than the above values and (b) larger than that for isopropyl benzoate pyrolysis by a bigger factor than the difference in the factors for ethyl and isopropyl benzoate pyrolysis. A report however by Smith and Yates indicated that pyrolysis of *t*-butyl benzoates was very sensitive to surface effects such that non-reproducible rates were ob-

* The lowest rate for pyrolysis of *t*-butyl benzoate reported by Smith and Yates³ agrees within 2% of the rate which may be interpolated from our Arrhenius plot.

tained. However in our kinetic studies on *t*-butyl benzoate described in Part II we did not experience this difficulty and completely normal Arrhenius data were obtained; this suggested that a kinetic study of a range of *t*-butyl benzoates should be feasible.

RESULTS AND DISCUSSION

The rate coefficients reported in the Table for 584.9 K are the average values for triplicate runs whose rate coefficients agreed within $\pm 2\%$. The relative rates were confirmed by a second series of measurements at 570.8 K and at both temperatures the rates for *t*-butyl benzoate

Pyrolysis of compounds $RC_6H_4CO_2Bu^t$

R	$10^5 k/s^{-1}$ ^a (584.9 K)	$10^5 k/s^{-1}$ (570.8 K)	$\log k_{rel.}$ (584.9 K)
<i>p</i> -OMe	32.3	14.4	-0.075
<i>p</i> -Me	34.2	14.8	-0.054
<i>m</i> -Me	35.8	15.7	-0.020
H	38.3	16.6	0
<i>m</i> -OMe	43.7	18.8	0.056
<i>p</i> -F	48.6	22.3	0.104
<i>p</i> -Cl	59.4	26.2	0.190
<i>m</i> -Cl	66.0	30.2	0.236
<i>m</i> -NO ₂	111.7	50.0	0.465
<i>p</i> -NO ₂	118.0	50.6	0.488

^a Average of triplicate runs whose rates agreed within $\pm 2\%$.

agreed within $\pm 1\%$ of the value which we previously obtained.* Because of the difficulty associated with the removal of the benzoic acid reaction products from the reactor (especially with the nitro- and methoxy-compounds, see Experimental section) which was exacerbated at lower temperatures, kinetic studies were not carried out at the latter so that we did not obtain kinetic data over the 50° range which we have established as our norm in this type of work; consequently no Arrhenius data are reported for these compounds though it is evident from the agreement of the data for the unsubstituted compound that these compounds behave normally. Although we found in preliminary experiments that the benzoates were more susceptible to surface-catalysed decomposition than other compounds which we have examined, we were able to overcome this problem in the manner described in the Experimental section.

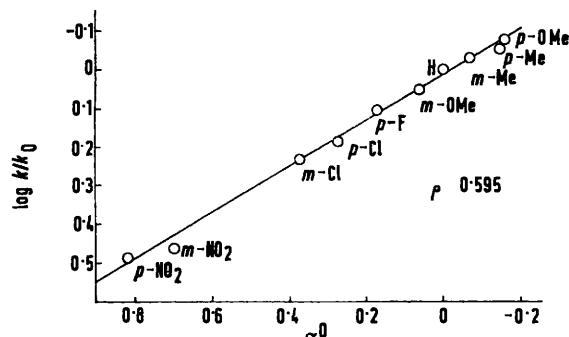
The Figure shows a plot of the $\log k_{rel.}$ values against σ^* values, these having been found in the case of ethyl

¹ Part II, R. Taylor, *J.C.S. Perkin II*, 1975, 1025.

² 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.

³ G. G. Smith and B. L. Yates, *Canad. J. Chem.*, 1965, **43**, 702.

and isopropyl benzoate pyrolysis to give a better correlation than σ -values. This is found to be true also in the present case and the slope of the correlation line is 0.595 at 584.9 K. Applying the $\rho T = \rho' T'$ relationship we find that the ρ factor is 0.58 at 600 K. It is evident that there is more negative charge developed at the γ -carbon in the transition state for pyrolysis of *t*-butyl benzoates



Hammett correlation for pyrolysis of *t*-butyl benzoates at 584.9 K

than for pyrolysis of ethyl and isopropyl benzoates and moreover that the increment in charge on going from the transition state for the isopropyl to the *t*-butyl compounds is greater than that between the ethyl and isopropyl compounds, thereby confirming in full the proposals in Part II. Since the spread of rate pattern given in Part II was qualitatively identical for a range of ester types it follows that the above observations can be applied generally rather than to benzoate pyrolysis in particular.

EXPERIMENTAL

The apparatus and general techniques have been described.⁴ The reactor surface was thoroughly deactivated at 410° by repeated pyrolysis of samples of but-3-enoic acid. The temperature was lowered to 311.7°, the ester samples injected into the reactor, and the rates of elimination determined. Preliminary experiments showed that the reactor surface gradually became reactivated and this was aggravated the larger the samples used in a series of runs. Furthermore the first order kinetic runs showed a very slight curvature which was constant with a very slight diminution (*ca.* 2%) of the P_∞ reaction pressure. This suggests that the reactor surface becomes reactivated by association with a small amount of the benzoic acid reaction product (and in so doing produces a diminution in the

infinity pressure). To overcome these problems the following procedure was adopted: each kinetic run was carried out on not more than 100 μ l of compound, which was thoroughly degassed of oxygen by purging with argon under vacuum immediately prior to injection into the reactor. The reactor was exhausted for at least 20 min between individual runs in order to remove, as far as possible all traces of the benzoic acid. After each set of 10 runs (one on each compound) the reactor was purged with chlorobenzene (10 ml), the temperature raised to 410°, and the deactivation procedure repeated. In this way we experienced no difficulty in obtaining good kinetic plots (first order to >90% of reaction) with $\pm 2\%$ reproducibility. The removal of the involatile benzoic acids from the reactor was sufficiently difficult (it tended to block the valve exhaust assembly) that no runs were carried out below 570.8 K. It may be relevant that (a) Smith and Yates attempted to study the rates of elimination at 544.9 K which would have exacerbated the problem of removal of the acids and (b) their success in studying the pyrolysis of isopropyl benzoates may be related to the higher temperature (610 K) needed to obtain measurable rates with these secondary esters.

All of the esters were made by the general procedure of refluxing the acid chloride with excess of *t*-butyl alcohol in the presence of pyridine during 3 h. Normal work-up and fractional distillation yielded the following products: *t*-butyl *p*-nitrobenzoate (45%), m.p. 115–116° (lit.,⁵ 115–116°); *t*-butyl *m*-nitrobenzoate (18%), b.p. 126–128° at 1 mmHg, m.p. 28° (lit.,⁵ 31°); *t*-butyl *p*-chlorobenzoate (56%), b.p. 60–62° at 0.2 mmHg, n_D^{20} 1.5071 (lit.,⁵ 158.5° at 3 mmHg, n_D^{25} 1.5041; lit.,² 94° at 0.33 mmHg, n_D^{20} 1.5070); *t*-butyl *m*-chlorobenzoate (64%), b.p. 58–60° at 0.2 mmHg, n_D^{20} 1.5041; *t*-butyl *p*-fluorobenzoate (55%), b.p. 60° at 1 mmHg, n_D^{20} 1.5755 (Found: C, 67.6; H, 6.8. C₁₁H₁₃O₂F requires C, 67.3; H, 6.7%); *t*-butyl *m*-methoxybenzoate (60%), b.p. 88–90° at 1.5 mmHg, n_D^{20} 1.4994 (Found: C, 69.6; H, 7.75. C₁₂H₁₆O₃ requires C, 69.2; H, 7.75%); *t*-butyl *p*-methoxybenzoate (63%), b.p. 78–80° at 0.2 mmHg, n_D^{20} 1.5083 [lit.,⁵ 162° at 2.5–3 mmHg, n_D^{25} 1.5370 (this must be in error); lit.,² 93–94° at 0.5 mmHg, n_D^{20} 1.5080]; *t*-butyl *p*-methylbenzoate (53%), b.p. 74–76° at 1 mmHg, n_D^{20} 1.4937 (Found: C, 75.1; H, 8.35. C₁₂H₁₆O₂ requires C, 75.0; H, 8.4%); *t*-butyl *m*-methylbenzoate (56%), b.p. 72–74° at 1 mmHg, n_D^{20} 1.4919 (Found: C, 75.1; H, 8.4%). *t*-Butyl benzoate was available from previous studies, and each compound was indicated by g.l.c. analysis to be >99% pure.

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⁴ R. Taylor, *J. Chem. Soc. (B)*, 1968, 1397.

⁵ R. Altschul, *J. Amer. Chem. Soc.*, 1948, **70**, 2569