Pyrolysis of t-Butyl *N*-Arylcarbamates in the Gas Phase, and Correlation of the Elimination Rates with those obtained in Solution

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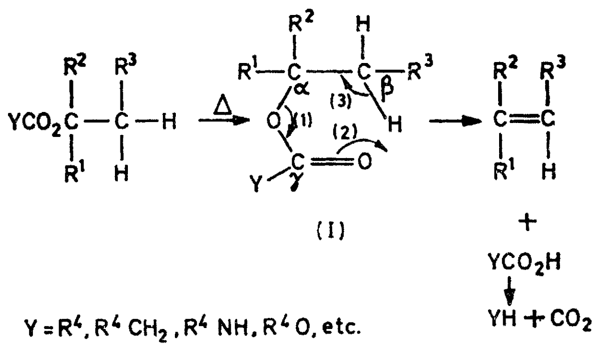
Rates of pyrolysis of t-butyl *N*-arylcarbamates in the gas phase at 548.8 K correlate linearly with their rates of pyrolysis in diphenyl ether at 450.7 K and with σ^0 values (ρ + 0.55). The ρ factor for the gas-phase reaction is almost identical (after correcting for the temperature difference) to that obtained in solution. Both the substituent effects and the ρ factor are therefore largely independent of solvation. Solvation does however increase the reaction rate as expected, and by factors ranging from 4 (dodecane) to 25 (decanol). Comparison of the gas-phase data with those for carbonates show that NH is more effective at transmitting conjugative effects than is O, which confirms similar observations deduced from the pK_a values of substituted acetic acids (measured in solution); these results confirm that the Hammett ρ factor depends not only upon the charge developing at a reaction site but also upon the ability of the system to transmit electronic effects. The magnitudes of the ρ factors for pyrolysis of t-butyl benzoates and carbamates confirms that the transition states for the latter are more polar. The kinetic isotope effect for the reaction, is 1.78 at 569.2 (gas phase) and 2.56 at 468.7 K (diphenyl ether); this is less than for the pyrolysis of secondary acetates and provides further evidence that the breaking of the C–H bond is less kinetically important, the more polar the transition state.

Of the classes of compounds that thermally decompose *via* a six-centre cyclic transition state (I), carbamates are one of the most reactive,[1] and the reactivity of t-alkyl *N*-arylcarbamates is such that their decomposition may be studied in solution.[2,3] Both these studies and those of Daly *et al.*[4,5] have shown that the reaction proceeds *via* the transition state (I) *i.e.* by the same mechanism in the gas phase and in solution. Since there have been very few reactions which it has been possible to study in both gas and solution phases,[6] and none as far as we are aware which permit a direct determination of the absolute effect of various solvents upon the reaction rate and the Hammett ρ factor, we now complement the study by one of us of the effects of solvents upon the rate of decomposition,[3] by a study of the rates of decomposition in the gas phase.



(I)

Y = R⁴, R⁴CH₂, R⁴NH, R⁴O, etc.

Studies of the effects of aryl groups R^2—R^4 on the rates of elimination of various ester types (through determination of the Hammett ρ factors) and of the rate spread between primary, secondary, and tertiary esters (R^3 = H, R^1 = R^2 = H or Me), have identified the following factors as relevant to the mechanism of the elimination.[1,7-12] (i) In the transition state a positive charge develops at the α-carbon, a slightly smaller negative charge develops at the γ-carbon, and a considerably smaller negative charge develops at the β-carbon. Thus at the energy maximum, the electron pairs (1) have moved further than the pair (2) which in turn have moved further than the pair (3).[13] (ii) The magnitude of the former two charges increases along the series acetates < phenylacetates < benzoates < carbamates < carbonates. (iii) The magnitude of these two charges increases along the series primary < secondary < tertiary. (iv) The extent of C–H bond breakage in the transition state decreases along the series primary > secondary > tertiary, *i.e.* the elimination becomes less concerted and tends more (albeit slightly) towards a two-step mechanism as the ester type changes from primary to tertiary.

A further reason for undertaking this work therefore was to see how the decomposition of tertiary carbamates fitted into this general pattern.

RESULTS AND DISCUSSION

First-order coefficients obtained at 548.8 K are given in Table 1, and the logarithms of the relative rates are plotted against those obtained for decomposition (of some of the compounds) in diphenyl ether at 450.7 K (Figure 1) and against σ^0 values (Figure 2).

The following features are noteworthy. (i) Electron-withdrawing substituents enhance the rate and *vice versa* (*i.e.* ρ is positive) so that as with the other esters studied, a negative charge develops on the γ-carbon atom.

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

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

[3] S. J. Ashcroft and M. P. Thorne, *Canad. J. Chem.*, 1972, **50**, 3478.

[4] N. J. Daly and F. Ziolkowski, *Austral. J. Chem.*, 1971, **24**, 2541; *J.C.S. Chem. Comm.*, 1972, 911.

[5] N. J. Daly, G. M. Heweston, and F. Ziolkowski, *Austral. J. Chem.*, 1973, **26**, 1259.

[6] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, pp. 128—129.

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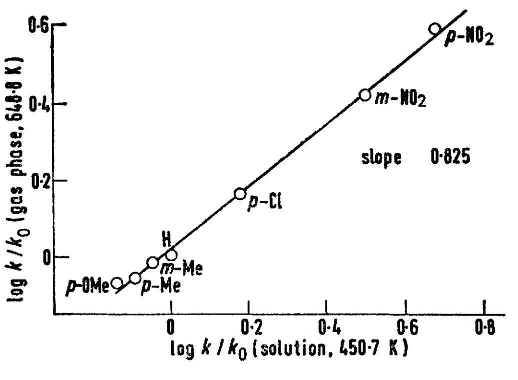


FIGURE 1 Correlation of rates of elimination of t-butyl *N*-arylcarbamates in the gas phase at 548.8 K with those obtained in diphenyl ether at 450.7 K

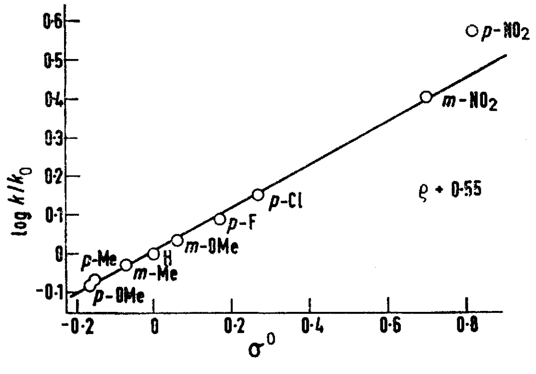


FIGURE 2 Hammett correlation for gas-phase pyrolysis of t-butyl *N*-arylcarbamates

TABLE 1

First-order rate coefficients ($10^3k/\mathrm{s}^{-1}$) for decomposition of $XC_6H_4NHCO_2Bu^t$ at 548.8 K

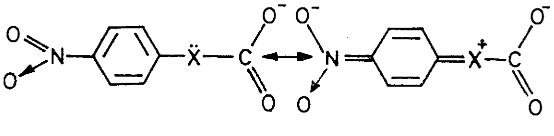
X	*p*-OMe	*p*-Me	*m*-Me	H	*m*-OMe
	10.7	11.05 [a]	12.1	12.9 [b]	13.95
log k_{rel}	−0.081	−0.067	−0.028	0	0.034
X	*p*-F	*p*-Cl	*m*-NO_2	*p*-NO_2	
	15.7	18.2	32.8	48.2	
log k_{rel}	0.085	0.149	0.405	0.572	

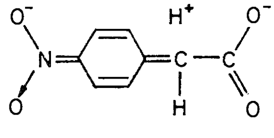
[a] At 569.2 K rates for this compound and its [$^2H_9$]-isomer were 45.7 and 25.75 respectively, giving $k_H : k_D = 1.78$. [b] Rates determined [12] between 521 and 571 K give E_a 39.9 kcal mol^{-1} and log (A/s^{-1}) 13.8.

(ii) The plot of log $k_{rel.}$ against σ^0 gives (with the exception of the point for the *p*-NO_2 substituent, for reasons given below) an excellent correlation with ρ +0.55 (= 0.505 at 600 K). The correlation with σ^0 values parallels the previous observations in pyrolysis of ethyl, isopropyl, and t-butyl benzoates, and ethyl carbonates and two points arise here. First, since the charge in the transition state has been shown to increase on going from acetates through to carbonates we could expect that the ρ factor for substituents at the γ carbon would also increase along this series. Now the ρ factor for the benzoates is 0.58 (corrected to 600 K) and since this is bigger than for the carbamates it appears to contradict our proposal. However the aryl ring in the carbamates is separated from the γ carbon by an NH group and the interposition of heteroatoms or CH_2 groups have been shown to decrease ρ values by a factor of 0.4—0.5.[14] If we correct the carbamate ρ value by this factor we see then that the charge in the carbamate transition state is considerably greater than for benzoates as predicted.

The second point of note is that whereas the results for *m*- and *p*-nitro-substituents in ethyl and isopropyl benzoate pyrolysis correlated precisely with σ^0 values, in the present reaction an exalted value of σ (1.01) is needed for the *p*-NO_2 substituent; this is consistent both with the higher charge developed on the γ carbon, and with the polarisability of the lone pair on nitrogen. Striking confirmation of these gas-phase results have recently been provided by Wepster and his co-workers [15] who find that in measurements of pK_a values of the acids $ArXCH_2CO_2H$, exalted σ values are needed to correlate the effect of the *p*-NO_2 substituent, the degree of exaltation following the order: NH > O > CH_2. In carbonate pyrolysis the *p*-NO_2 substituent was found to be *less* activating than *m*-NO_2 [9] and we have carefully rechecked this result using freshly prepared compounds, but with the same result. We cannot exclude the possibility that this result may arise from a small contribution to the elimination rate from the competing conversion of the carbonate to the corresponding alkyl aryl ether.[16] On the other hand it does suggest that the O group transmits conjugative effects less readily than the CH_2 group, and evidence that the CH_2 group does indeed transmit conjugative effects is shown by the recent observation that the *p*-NO_2 substituent requires an exalted σ value in correlation of the ionisation of phenylacetic acids.[17]

It is necessary to show how the 'saturated' groups can transmit conjugative effects, and one possibility is that interaction occurs as shown in (II), with subsequent stabilisation of X^+ by the carboxylate anion. This would fit all the observed facts, since the lone pair on oxygen should be held more firmly than the lone pair on nitrogen. As a consequence transmission of conjugative


(II)


(III)

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[17] A. J. Hoefnagel and B. M. Wepster, *J. Amer. Chem. Soc.*, 1973, **95**, 5357.

effects by the methylene group in the phenylacetic acids, requires intervention of the hyperconjugative structure (III).

(iii) The correlation of the rates of elimination in the gas phase with those obtained in solution (Figure 1) is, with the possible exception of the point for the *p*-MeO substituent, an excellent one. The *p*-MeO compound is slightly more deactivated in solution and a slight interaction of the oxygen lone pair with the solvent could account for this. The effect, if real, rather than if due to experimental error is, however, trivial, and in general the effect of solvation upon the substituent effect is insignificant. This confirms the results obtained with the non-polar reactions described in ref. 6, and also results obtained on pyrolysis of 1-arylethyl acetates.[18] Here the effects of ring substituents on the centre of charge (opposite sign to the present case) parallels their effects on electrophilic aromatic substitutions carried out in solution.

The ratios of the ρ factors under the two sets of conditions is 0.85 compared with 0.825 which may be predicted from the $\rho T = \rho' T'$ relationship. The remarkable closeness of these factors show that the ρ factor in diphenyl ether is only slightly affected by solvation and this confirms the previous observation of a relatively small effect of different solvents upon the ρ factors for elimination in various solvents.[3] Table 2 shows the relative rates of elimination of t-butyl and t-pentyl *N*-phenylcarbamate in various solvents at 463 K together with the Hammett ρ factors for decomposition of t-pentyl *N*-arylcarbamates in some of the solvents.[3] Now from the Arrhenius data for the elimination of t-butyl *N*-phenylcarbamate, the rate coefficient for elimination at 450.7 K is predicted to be 0.56×10^{-5} s^{-1} which may be compared with the value 4.45×10^{-5} s^{-1} observed for elimination in diphenyl ether, *i.e.* solvation in diphenyl ether increases the rate eight-fold and from the data in Table 2 we can calculate that the accelerating effects of the solvents range from 3.6-fold in dodecane to 24.7-fold in decanol; the ρ factor in diphenyl ether is almost precisely that which may be predicted from the value obtained in the gas phase.

TABLE 2

Relative rates of pyrolysis of t-alkyl *N*-phenylcarbamates ROCONHPh in various solvents at 463 K, and Hammett ρ factors for elimination

Solvent	R = t-Butyl	t-Pentyl	ρ^a(t-Pentyl)
Dodecane	1.0	0.97	0.60
Diphenyl ether	2.18	2.15	0.65 [b]
Acetophenone	2.55	2.51	0.85
Nitrobenzene	4.22	4.10	0.63
Decanol	6.80	5.85	

[a] For consistency with the gas-phase data these have been calculated using σ^0 values [and $\sigma(p\text{-NO}_2) = 1.01$] instead of the σ values used previously.[3] [b] For the t-butyl compounds the ρ factor in this solvent is 0.66.

(iv) The kinetic isotope effect for elimination from t-butyl *N*-*p*-tolylcarbamate and its fully deuteriated isomer was 1.78 at 569.2 K (gas phase). This is considerably less than the theoretical maximum of 2.56 (calculated from the values of $h\nu_H$ 2 980 and $h\nu_D$ 2 235 cm^{-1}).[19] It is also considerably less than the value (2.6) reported by Kwart and Slutsky for t-butyl *NN*-dimethylcarbamate (gas phase) and its fully deuteriated isomer at 550 K. Kwart and Slutsky also claim, but appear to provide no evidence to support the view, that ethyl and t-butyl esters give the same kinetic isotope effect[20] (and therefore that the transition state polarity for pyrolysis of t-butyl and ethyl esters is the same). However, it has been shown unambiguously that this latter is not the case, the polarity decreasing from tertiary to primary esters,[1,7-10] and the present result is certainly in accord with this. Of a range of carboxylate esters, tertiary carbamates have the most polar transition state which should have the least kinetic importance of the breaking of the β-C–H bond. The isotope effect which we observe is considerably lower than that (2.15 at 656 K, *ca.* 2.45 at 570 K) found for secondary acetates[13] which have a less polar transition state with greater kinetic importance of C–H bond breakage, so that there are no inconsistencies in our results. We hope in due course to report kinetic isotope effects for other classes of esters to try to evaluate the picture even more clearly.

One possible explanation of the results of Kwart and Slutsky (assuming no experimental error) lies in the fact that they studied an *NN*-dialkylcarbamate. One of us has shown that increased electron supply at the γ carbon in the transition state (I) makes the transition state less polar. The dialkyl group would be much more electron supplying than our single aryl group and if this is the source of the discrepancy it shows the extent to which transition state polarity can alter with ester structure.

We have also determined the kinetic isotope effect as 2.56 for elimination in diphenyl ether at 469.7 K. This is 82% of the theoretical maximum at this temperature whereas the gas-phase value is 70% of the maximum at 569.2 K. To what extent this result reflects a fundamental dependence of isotope effects upon the environment cannot be evaluated without the acquisition of further data.

EXPERIMENTAL

The preparation and properties of most of the t-butyl *N*-arylcarbamates have been described.[2] Additional compounds used in this study and prepared by the same route were as follows: *t-butyl* N-(3-*methoxyphenyl*)*carbamate*, m.p. 56° (Found: C, 64.7; H, 7.82; N, 6.4. $C_{12}H_{17}NO_3$ requires C, 64.5; H, 7.62; N, 6.3%); *t-butyl* N-(4-*fluorophenyl*)-*carbamate*, m.p. 125.5° (Found: C, 62.4; H, 6.77; N, 6.63. $C_{11}H_{14}NFO_2$ requires C, 62.5; H, 6.68; N, 6.63%). [$^2H_9$]t-butyl alcohol (Stohler Isotopic Chemicals) containing at least 99% deuterium was used to prepare the deuteriated carbamate.

The general method of pyrolysis has been described.[21] The carbamates were all solids and were therefore injected into the reactor as a *ca.* 1 : 1 solution in chlorobenzene, this

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[18] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, **1783**, and earlier papers in the series.

[19] K. Wiberg, *Chem. Rev.*, 1955, **55**, 713.

[20] H. Kwart and J. Slutsky, *J.C.S. Chem. Comm.*, 1972, 1182.

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solvent having been shown to be quite stable in the gas phase under the reaction conditions. Reactions were followed to 10 half-lives and gave excellent first-order kinetics to beyond 95% reaction (5 half-lives) as shown by a typical kinetic plot (Figure 3). Rate coefficients could be duplicated to within ±2% and the average values are shown in Table 1. No spurious (enhanced) rates were obtained which confirms the indications from the first-order kinetics that no surface reactions were taking place. In addition, the unsubstituted ester gave a normal Arrhenius plot with an activation energy similar to the values obtained from a range of esters of similar structure.[1]

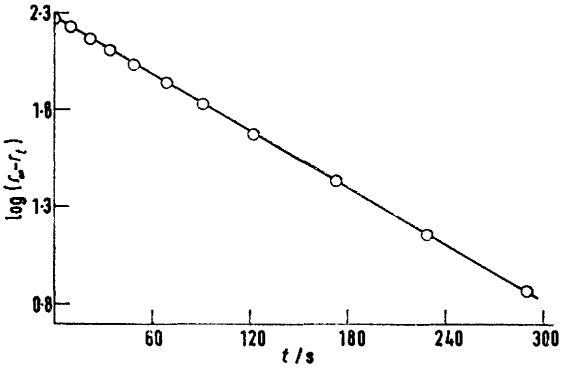

FIGURE 3 Kinetic plot for pyrolysis of t-butyl *N*-phenylcarbamate at 548.8 K

In contrast to previous studies of primary and secondary benzoates and of 1-arylethyl ethyl carbonates [7,9] excellent first-order kinetics were obtained to beyond 95% reaction even for the nitro-compounds. This arises from the lower temperature employed in the present study so that the nitroaniline reaction product does not decompose, in contrast to the nitrophenol or nitrobenzoic acid at higher temperatures.

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