The Thermal Decomposition of Carbamates and Carbonates of 2-Arylpropan-2-ols and 1-Aryl-1-phenylethanols: Temperature and Solvent Effects on the Reaction Constant and Kinetic Isotope Effects

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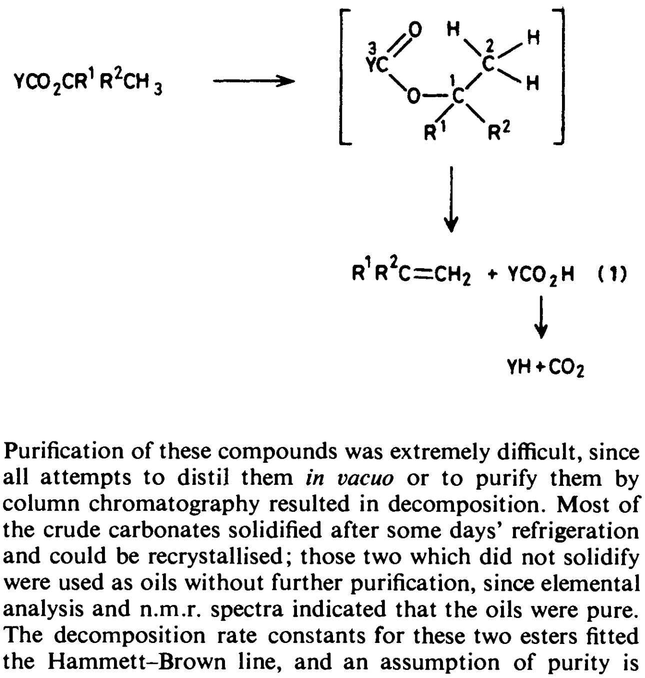
1-Aryl-1-methylethyl *N*-arylcarbamates and phenyl carbonates and 1-aryl-1-phenylethyl *N*-*p*-tolylcarbamates have been prepared and their decomposition kinetics in diphenyl ether, dodecane, and sulpholane studied. Rate constants correlate with σ^+ constants (the value of -0.13 being required for *m*-CH_3 substituents) giving ρ^+ values in the range -1.28 to -2.40 at 400—450 K. Within one reaction series, $\Delta S^\ddagger$ is not constant, so that ρT = constant does not hold. $\Delta H^\ddagger$ varies linearly with σ^+, and ρ^+ values have been corrected for temperature from the slope of $\Delta H^\ddagger$ *versus* σ^+ which equals $2.3R(\rho_1{}^+ - \rho_2{}^+)T_1T_2/(T_1 - T_2)$. The magnitude of ρ^+, which depends on solvent, and which is greatest in the carbonate series, indicates a high degree of carbocation formation. Application of Charton's extended Hammett equation shows good correlations with $\sigma_R{}^+$ (although the data sets are limited) and lends support to this view. $^2H_6$ and $^2H_3$ substitution in $(CH_3)_2C(O_2CNHPh)C_6H_4X$ (X = *m*-CH_3, H, or *p*-CF_3) results in rate retardation arising from both primary and secondary kinetic isotope effects and confirms a polar, but not ionic, reaction mechanism.

Recent work by one of us[1] on the kinetic isotope effects (k.i.e.) in the thermal elimination of olefins from diphenyl ether solutions of *N*-*p*-tolylcarbamates of tertiary alcohols [equation (1; Y = $CH_3C_6H_4NH$)] has demonstrated that, when R^1 and R^2 are saturated alkyl groups, the rate retardation produced on substitution of deuterium atoms at C-2 arises largely from a primary isotope effect on the C–H bond-breaking, although there is some contribution from a secondary effect on the heterolysis of the C–O bond. The magnitude of the primary isotope effect is virtually independent of the nature of the alkyl groups, despite the considerable decomposition rate increases observed in carbamates in which R^1 and R^2 are very large, bulky groups, *e.g.* t-butyl. However, our data[1,2] on k.i.e. for carbamates in which R^1 = phenyl and R^2 = CH_3 indicated that a mechanistic change occurs in this case and C–O bond heterolysis was very well advanced in the transition state. While replacement of a methyl group by a phenyl at C-1 is known to cause an increase in transition-state polarity in gas-phase pyrolysis of secondary and tertiary acetates and carbonates[3] (Y = CH_3, R^1 = Ph, R^2 = H; Y = CH_3, R^1 = Ph, R^2 = CH_3; Y = PhO, R^1 = Ph, R^2 = H), the dramatic mechanistic change apparently indicated by our data was somewhat surprising. As a further probe of the transition state in these reactions, therefore, we have studied the effect of aryl substituents at C-1 on the decomposition kinetics in diphenyl ether and also in dodecane and sulpholane of the 1-aryl-1-methylethyl esters of *N*-phenylcarbamic, *N*-*p*-tolylcarbamic, and phenyl carbonic acids and of the 1-aryl-1-phenylethyl *N*-*p*-tolylcarbamates, together with the deuterium isotope effects in three *N*-phenylcarbamates.



Results

N-*Phenyl*- and N-p-*tolyl-carbamates*, having a total of 13 different substituents, were prepared from the corresponding isocyanates and the alcohols $XC_6H_4C(OH)(CH_3)_2$ and $XC_6H_4C(OH)(CH_3)Ph$. Attempts to prepare 1-(*p*-methoxyphenyl)-1-phenylethyl *N*-*p*-tolylcarbamate were unsuccessful; the reaction of the alcohol (which itself requires very careful preparation) with the isocyanate always resulted in formation of the dehydration product, α-*p*-methoxyphenylstyrene.

1-*Aryl*-1-*methylethyl phenyl carbonates* were obtained by reaction of phenyl chloroformate and 2-arylpropan-2-ols. Purification of these compounds was extremely difficult, since all attempts to distil them *in vacuo* or to purify them by column chromatography resulted in decomposition. Most of the crude carbonates solidified after some days' refrigeration and could be recrystallised; those two which did not solidify were used as oils without further purification, since elemental analysis and n.m.r. spectra indicated that the oils were pure. The decomposition rate constants for these two esters fitted the Hammett-Brown line, and an assumption of purity is therefore justified. Attempts to prepare the *p*-OMe substituted carbonate resulted in dehydration of the alcohol and formation of diphenyl carbonate. All the carbonates decomposed gradually on standing and were used within two or three weeks of preparation.

Carbamate decompositions in three different solvents were followed to at least three half-lives from the rate of CO_2 production by the technique described in our earlier publications.[4] Excellent first-order kinetic plots were obtained. Using the same technique for the carbonate decompositions, the first-order plots showed curvature after *ca.* 20—25% reaction, indicating either autocatalysis or a concurrent reaction between one of the products (phenol) and the reactant. The latter was shown to be the case, since a solid, identified as diphenyl carbonate, could be isolated from the decomposition reaction mixtures. The same solid was also obtained by reaction of phenol with 1-phenyl-1-methylethyl

Table 1. M.p.s (°C) of carbamates and carbonates of 2-arylpropan-2-ol and 1-aryl-1-phenylethanol

X =	*p*-OCH$_3$	*m*-OCH$_3$	*p*-CH$_3$	*m*-CH$_3$	*p*-F	*p*-Cl	*m*-Cl	*p*-Br	*m*-Br	*p*-CF$_3$	*m*-CF$_3$	*p*-NO$_2$
$PhNHCO_2C(CH_3)_2C_6H_4X$	87.88	116.5	118.5	131—132	117.5	145.0	151.5	149.5	135—154	133.5	173—174	175.0
p-$CH_3C_6H_4NHCO_2C$-$(CH_3)_2C_6H_4X$	102.0	109.5	109—110	119.0	102—103	121.0	139.0	139.0	145.5			
p-$CH_3C_6H_4NHCO_2C$-$(CH_3)PhC_6H_4X$			124.0	140.5		148.5			188.0			
$PhOCO_2C(CH_3)_2C_6H_4X$			Oil	25—26	Oil	33—35		58—59	60—61			

phenyl carbonate under the reaction conditions of the kinetic experiments.

The decomposition rate constant of the 1-aryl-1-methylethyl phenyl carbonates was therefore obtained from initial rate studies by following the change with time in the carbonyl absorbance at 1 765 cm^{-1} over the first 15% reaction, since our other analytical technique is unsuitable for initial rate studies. For the slower reactions the rate constants thus obtained were the same, within experimental error, as those determined from the first (linear) portion of the kinetic plots obtained from rate of CO$_2$ production, the onset of curvature in which coincided with the first appearance in the i.r. spectra of the decomposition solutions of a peak at 1 784 cm^{-1} attributable to $\nu_{C=O}$ of diphenyl carbonate, thus verifying that the deviation from first-order kinetics is due to occurrence of the reaction of product phenol with reactant, which becomes kinetically significant after *ca.* 15—20% reaction.

Rate constants and activation parameters for the decompositions in diphenyl ether of 13 1-aryl-1-methylethyl *N*-phenylcarbamates are given in Table 2, and in Table 3 is shown the effect of variation of substituents at Y and R^1 and of solvent on decomposition rates. The logarithms of these rate constants correlate well with Brown's σ^+ constants [5] (and less well with σ constants), except for the *m*-CF$_3$ and *m*-CH$_3$ substituents (Figure 1, Table 4). For *m*-CF$_3$, $\sigma^+ = 0.565$, the value determined by Taylor, was required and for *m*-CH$_3$ a σ^+ considerably more negative than -0.066 was indicated. The value of -0.13 determined by Taylor [3d] for gas-phase pyrolysis of 1-aryl-1-methylethyl acetates and 1-arylethyl phenyl carbonates puts the *m*-CH$_3$ points below our Hammett-Brown lines, but it gives a closer fit than -0.066 and has been used throughout this work.

The rate spread was too large to permit rate constants for all 13 members of the *N*-phenylcarbamate series to be determined at the same temperature. Rate constants at 437.5 K were obtained by extrapolation of the Arrhenius plots for the *p*-OMe, *m*- and *p*-CF$_3$, and *p*-NO$_2$ substituted compounds, for use in the Hammett-Brown plot. Inclusion of the latter three points reduces the ρ^+ value a little, but inclusion of the *k* value for the *p*-OMe compound gives a large increase in ρ^+. The same holds for the other carbamate series. In no case was the correlation coefficient altered significantly. Taylor [3c] has remarked that the linear free energy relationship plots for carbonate pyrolysis are slightly curved and ρ^+ represents the average for the range of substituents. Since the experimentally determined rates for the *p*-OMe substituted esters were at the limits of the accuracy of our system, we have excluded these points from our Hammett-Brown plots. The ρ^+ values in Table 4 were found by linear-least squares analysis of log *k* *versus* σ^+ plots and range from -1.28 to -2.40 depending on the ester, solvent, and temperature.

We have also measured the rate constants of the *N*-phenylcarbamates of $XC_6H_4C(OH)(CD_3)_2$ (X = *m*-CH$_3$, H, or *p*-CF$_3$) and of $PhC(OH)CH_3CD_3$. These results, together with the kinetic isotope effects, which are of the same order of magnitude as found previously for *p*-tolylcarbamates,[2] are given in Table 5.

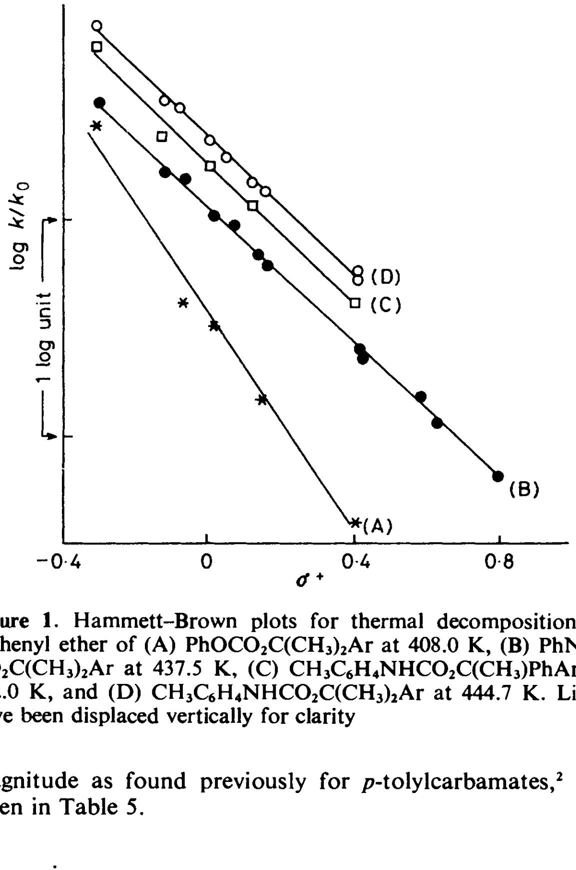


Figure 1. Hammett-Brown plots for thermal decomposition in diphenyl ether of (A) $PhOCO_2C(CH_3)_2Ar$ at 408.0 K, (B) $PhNHCO_2C(CH_3)_2Ar$ at 437.5 K, (C) $CH_3C_6H_4NHCO_2C(CH_3)PhAr$ at 422.0 K, and (D) $CH_3C_6H_4NHCO_2C(CH_3)_2Ar$ at 444.7 K. Lines have been displaced vertically for clarity

Discussion

The excellent correlations of the logarithms of the rate constants with substituent constants for each of our reaction series confirms that the transition states in these reactions involve an election-deficient carbon atom for which stabilisation is provided by the aryl substituents, in the same way as that found for gas-phase pyrolyses of aryl-substituted acetates and carbonates.[3] The magnitudes of the reaction constants provide an indication of the extent of the stabilisation energy requirements and thus of the relative extent of carbocation formation in the different series of compounds. However, values are temperature dependent and for meaningful comparisons it is necessary to extrapolate the experimental data to a common temperature.

Temperature Dependence of ρ^+.—This is often calculated from the approximate relationship ρT = constant, derived from equation (2) on the assumption that $\delta\Delta H^\ddagger$ is temperature

$$\log k_{rel} = \rho^+\sigma^+ = -\delta\Delta G^\ddagger/2.3RT \qquad (2)$$

independent and $\delta\Delta S^\ddagger$ is zero (where δ represents the difference in the activation parameters between the substituted and un-

Table 2. First-order rate data for thermal decomposition of 1-aryl-1-methylethyl *N*-phenylcarbamates, $PhNHCO_2C(CH_3)_2C_6H_4X$, in diphenyl ether

X	T/K	$10^4\ k/s^{-1}$	E_a/kJ mol^{-1}	log A/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} k^{-1}	σ^+
p-OCH$_3$	350.5	3.84					−0.780
	398.0	7.80					
p-CH$_3$	426.0	1.94					
	437.5	4.03	110.2 ± 4.8 [a]	9.8 ± 0.5	106.6 ± 3.9	−69.1 ± 8.9	−0.311
	448.0	8.96					
m-CH$_3$	413.5	0.294					
	426.2	0.752	117.9 ± 2.5	10.3 ± 0.3	114.3 ± 2.7	−58.3 ± 6.3	−0.130
	437.5	1.91					
	448.2	4.08					
p-F	414.5	0.193					
	437.5	1.79	107.1 ± 1.8	9.0 ± 0.2	103.5 ± 1.7	−83.6 ± 3.8	−0.073
	448.2	3.44					
	454.2	5.17					
H	414.2	0.193					
	437.5	1.25					
	448.2	2.81	121.9 ± 0.8	10.7 ± 0.1	118.6 ± 0.8	−51.8 ± 1.7	0.0
	449.7	3.13					
	454.1	4.34					
m-OCH$_3$	426.2	0.502					
	437.5	1.09					
	448.2	2.57	117.5 ± 4.1	10.1 ± 0.5	113.9 ± 4.1	−63.4 ± 9.2	0.047
	458.7	4.99					
p-Cl	437.5	0.788					
	448.2	2.08	128.5 ± 4.1	11.3 ± 0.5	124.7 ± 4.4	−41.3 ± 8.9	0.114
	458.7	4.10					
	469.2	8.97					
p-Br	437.5	0.708					
	448.2	1.51					
	454.2	2.56	127.3 ± 2.1	11.0 ± 0.2	123.5 ± 2.0	−45.5 ± 4.4	0.150
	468.8	7.18					
	469.2	7.35					
m-Cl	437.5	0.281					
	448.2	0.679					
	458.7	1.49	138.7 ± 2.5	12.0 ± 6.3	134.9 ± 2.2	−27.6 ± 4.9	0.399
	469.2	3.44					
m-Br	437.5	0.258					
	448.2	0.673	136.0 ± 2.4	11.7 ± 1.0	132.2 ± 4.5	−33.2 ± 4.5	0.405
	458.7	1.47					
	469.2	3.52					
m-CF$_3$ [b]	454.2	0.812					
	460.0	1.27	148.5 ± 1.0	13.0 ± 0.1	144.6 ± 2.0	−8.7 ± 4.3	0.565
	470.2	2.99					
	479.5	6.38					
p-CF$_3$ [b]	454.2	0.569					
	460.0	0.977					
	470.2	2.26	146.0 ± 2.1	12.6 ± 0.2	142.2 ± 1.4	−16.5 ± 3.0	0.612
	479.5	4.37					
p-NO$_2$ [b]	464.5	0.752					
	470.2	1.26	146.9 ± 3.2	10.9 ± 0.4	142.7 ± 3.4	−20.2 ± 7.2	0.790
	484.2	3.58					
	487.2	4.60					

[a] Errors are statistical standard mean errors. [b] At 437.5 K, $10^4\ k/s^{-1}$ = 0.176 (X = m-CF$_3$), 0.134 (X = p-CF$_3$), 0.074 (X = p-NO$_2$) from Arrhenius parameters.

Table 3. First-order rate constants for decomposition in solvent of $YCO_2R^1(CH_3)C_6H_4X$

				$10^4\ k/s^{-1}$ for X =									
Solvent	T/K	Y	R^1	p-CH$_3$	m-CH$_3$	p-F	H	m-OMe	p-Cl	p-Br	m-Cl	m-Br	p-OMe
DPE [a]	444.7	MeC$_6$H$_4$NH	CH$_3$	5.10	2.29	2.07	1.51	1.28	0.970	0.868	0.341	0.368	
	422.0	MeC$_6$H$_4$NH	CH$_3$	0.95	0.33		0.26						8.56
	422.0	MeC$_6$H$_4$NH	C$_6$H$_5$	5.17	1.97		1.46		0.952			0.335	
Dodecane	453.8	MeC$_6$H$_4$NH	CH$_3$	3.03	1.72	1.32	1.08	1.04	0.774	0.659			
	451.5	C$_6$H$_5$NH	CH$_3$	3.51	1.54	1.69	1.18	0.993			0.279		
Sulpholane	428.9	C$_6$H$_5$NH	CH$_3$	7.64		3.57	3.22	2.45				0.920	
DPE	408.0	C$_6$H$_5$O	CH$_3$	25.6		3.83		3.13		1.36		0.375	

[a] DPE = diphenyl ether.

Table 4. ρ^+ Values for thermal decomposition in solvent of *N*-arylcarbamates and phenyl carbonates

Compounds	Solvent	T/K	ρ^+	No. of points
$PhNHCO_2C(CH_3)_2Ar$	DPE [a]	437.5	−1.58	12
		448.2	−1.47	11
	Dodecane	451.5	−1.56	6
	Sulpholane	428.9	−1.28	5
p-$MeC_6H_4NHCO_2C$-$(CH_3)_2Ar$	DPE	444.7	−1.61	9
		422.0	−1.84	4
	Dodecane	453.8	−1.52	8
p-$MeC_6H_4NHCO_2C$-$(CH_3)Ph{\cdot}Ar$	DPE	422.0	−1.66	5
$PhOCO_2C(CH_3)_2Ar$	DPE	408.0	−2.40	5

[a] DPE = diphenyl ether.

Table 5. Rate constants and kinetic isotope effects for decomposition in diphenyl ether of *N*-phenylcarbamates of deuteriated 2-arylpropan-2-ols

	434.7 K	437.5 K	449.7 K	454.1 K	464.4 K	467.5 K	470.2 K
$PhC(O_2CNHC_6H_5)(CD_3)_2$							
$10^4\ k/s^{-1}$		0.585	1.57	2.04	4.52	5.33 [a]	
$k_{H_6} : k_{D_6}$		2.14 [b]	1.99 [b]				
$PhC(O_2CNHC_6H_5)(CD_3)CH_3$							
$10^4\ k/s^{-1}$		0.912	2.56	3.36			
$k_{H_6} : k_{D_3}$		1.37					
m-$CH_3C_6H_4C(O_2CNHC_6H_5)(CD_3)_2$							
$10^4\ k/s^{-1}$	0.694						
$k_{H_6} : k_{D_6}$	2.10						
p-$CF_3C_6H_4C(O_2CNHC_6H_5)(CD_3)_2$							
$10^4\ k/s^{-1}$							1.12
$k_{H_6} : k_{D_6}$							2.06

[a] E_a 126.6 kJ mol^{-1}, log (A/s^{-1}) = 10.65. [b] Determined from Arrhenius parameters in Table 2 and footnote *a*.

substituted members of the reaction series), but this equation is not valid for systems in which $\delta\Delta S^\ddagger$ differs significantly from zero.[6,7] Our results (Table 4) show that for the two series of compounds for which ρ^+ has been determined at two temperatures, the ρT = constant relationship is not valid, and indeed this is to be expected, since the activation entropies (Table 2) of the 1-aryl-1-methylethyl *N*-phenylcarbamates (and, therefore, presumably of the *N*-*p*-tolylcarbamates) show considerable variations.

Hepler[8] has shown that for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, both temperature independent, $\rho = \rho_\infty\ (1 - \beta/T)$ where β is the 'isokinetic temperature' defined by Leffler and Grunwald as $\delta\Delta H^\ddagger/\delta\Delta S^\ddagger$.[9] However, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, as found from the transition state theory equation, are not mutually independent, so that a plot of one against the other may give spurious values for β.[10]

An alternative approach to calculating ρ^+ at different temperatures, which eliminates $\delta\Delta S^\ddagger$ from our considerations and assumes $\delta\Delta H^\ddagger$ to be temperature independent, is to substitute ρ_1 at T_1 and ρ_2 at T_2 into equation (2) and to subtract, giving (3). The last term in equation (3) can be taken as

$$\delta\Delta H^\ddagger = 2.3R(\rho_1{}^+ - \rho_2{}^+)T_1T_2/(T_1 - T_2)\sigma^+ - (\delta\Delta S_{T_1}{}^\ddagger - \delta\Delta S_{T_2}{}^\ddagger) \quad (3)$$

zero for small temperature differences, so that ρ_2 can be found from the slope of the plot of $\Delta H^\ddagger$ against σ^+, provided $\rho_1{}^+$ at T_1 is known.

Application of our data from Table 2 to this equation gave a line with correlation coefficient r 0.942 and slope 3.82 × 10^4 J mol^{-1}. The point corresponding to the *p*-F compound lies below the line, outside the 95% confidence limits. Omission of this point gave a line of slope 3.70 × 10^4 J mol^{-1} and r 0.960 (Figure 2.) Using this slope and the experimental value of $\rho^+ = -1.58$ at 437.5 K, ρ^+ values for the 1-aryl-1-methylethyl *N*-phenylcarbamates have been calculated for a number of other temperatures (Table 6). Agreement between experimentally determined and calculated values of ρ^+ at 448.2 K is good, so that we can, with confidence, use the values in Table 5 to compare reaction constants of other systems with that of the 1-aryl-1-methylethyl *N*-phenylcarbamates in diphenyl ether.

The validity of this approach is also confirmed by substituting the value 6.14 × 10^2K for β, obtained from the $\Delta H^\ddagger$ *versus* $\Delta S^\ddagger$ line (r 0.991) and $\rho^+ = -1.58$ at 437.5 K into Hepler's equation.[8] The ρ^+ values obtained in this way are identical to those in Table 6. (In determining β, the point for the *p*-F compound was again omitted from the graph.)

Solvent Effects.—Changes in solvent polarity affect both the rates of decomposition of the carbamates and the reaction constants to a small, but significant, degree. The relative decomposition rates of $PhNHCO_2C(CH_3)_2Ph$ in dodecane, diphenyl ether, and sulpholane are *ca*. 0.32 : 1 : 6, the ratio for the first two solvents being smaller than that found previously (0.45 : 1) for t-butyl and t-pentyl *N*-phenylcarbamate decompositions.[4b] The ρ^+ values decrease as solvent polarity increases, but the solvent effects are not large. For diphenyl ether and dodecane, the relative ρ^+ values are 1 : 1.07 at 451.5 K and for diphenyl ether and sulpholane relative values are 1 : 0.76 at 425.5 K. These results are consistent with a polar transition state in which greater solvent stabilisation of the electron-deficient C-1 in the more polar media reduces both the free energy of activation and the requirement for stabilisation by the aryl substituent. The comparatively small rate changes with solvent indicate that carbocation formation is not complete, but the difference in *relative* rates in dodecane and diphenyl ether in the t-butyl and 1-aryl-1-methylethyl systems shows the larger cationic involvement in the latter series of compounds. The magnitude of the ρ^+ values in Table 4 also indicates that cation formation is enhanced by the presence of solvent. These values are numerically larger than would be expected from a consideration of the ρ^+ values for gas-phase pyrolysis of 1-aryl-1-methylethyl acetates[3d] and 1-arylethyl acetates[11] and carbonates,[3c] even when temperature differences are taken into account, and hence indicate greater carbocation formation in the solvent relative to the gas phase. This is in contrast to the t-butyl *N*-arylcarbamate systems, where we have shown that solvent does not greatly influence the degree of charge separation.[12]

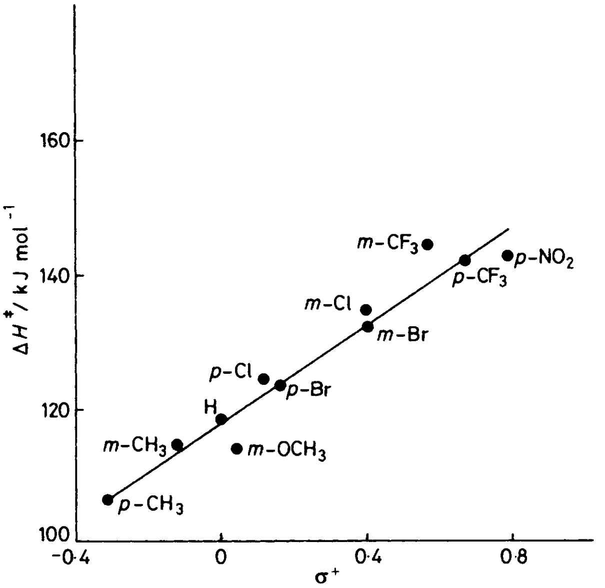


Figure 2. Plot of activation enthalpy against σ^+ constants for decomposition in diphenyl ether of $PhNHCO_2C(CH_3)_2Ar$

Substituents at C-3.—The effect on the transition state of changes in Y is reflected in the ρ^+ values in Tables 4 and 5. At 408.0 K, the relative ρ^+ for the phenyl carbonates and *N*-phenylcarbamates is 1.24, while the reaction rates of the carbonates are 3—4 times those of the carbamates. This is consistent with the gas-phase behaviour of esters, where pyrolysis rates increase in the order acetate < *N*-phenylcarbamate < phenyl carbonate [13] and where ρ^+ values for (secondary) carbonates and acetates of 1-arylethanols at 600 K are in the ratio 1.27 : 1.[3c] For the tertiary 1-aryl-1-methylethyl esters, in which carbocation formation is more advanced, the carbonate : acetate ρ^+ ratio will not be less than 1.27 : 1 and may be greater. Carbamates are intermediate in reactivity, so that the carbonate : carbamate ρ^+ ratio in the gas phase at 600 K would be less than 1.27 : 1, in fact our value of 1.24 : 1 would not be unreasonable. Thus the diphenyl ether assists carbocation formation to about the same extent in the two series of compounds.

Comparison of the ρ^+ values for the *N*-phenyl and *N-p*-tolylcarbamates of 2-arylpropan-2-ols shows that for the latter, less reactive series the reaction constants in diphenyl ether are marginally greater, by a factor of 1.06, while in dodecane they are about the same, when temperature differences are taken into account. The differences in diphenyl ether are not great and may represent no more than variations in determining ρ^+ by inclusion of more or less points in the Hammett–Brown plot. Recalculation of the data for the *N*-phenyl series, using only the points for those substituents which can be paralleled in the *N-p*-tolyl series, gives ρ^+ −1.64 and −1.53 at 437.5 and 448.2 K, respectively, and a slope of $\Delta H^{\ddagger}$ *versus* σ^+ of 3.44×10^4 J mol^{-1}, from which the calculated value of ρ^+ is −1.53 at 448.2 K (in agreement with experiment) and −1.57 at 444.7 K, which is within experimental error of the −1.60 determined for the *N-p*-tolylcarbamates at 444.7 K.

Table 6. ρ^+ Values for thermal decomposition of 1-aryl-1-methylethyl *N*-phenylcarbamate in diphenyl ether calculated from $\delta\Delta H^{\ddagger}$ *versus* σ^+ plot

T/K	$\rho^{+\,a}$	$\rho^{+\,b}$
453.8	−1.41	−1.50
451.5	−1.44	−1.52
448.2	−1.47	−1.55
444.7	−1.51	−1.58
428.9	−1.67	−1.73
422.0	−1.75	−1.80
408.0	−1.91	−1.95

[a] Using slope $(3.70 \times 10^4) = 2.3RT_1T_2/(T_1 - T_2)(\rho_1 - \rho_2)$ and ρ_1 at 437.5 K = −1.58. [b] Using slope 3.44×10^4 and ρ_1 at 437.5 K = −1.64.

Kinetic Isotope Effects.—The k.i.e. for the [$^2H_6$]- and [$^2H_3$]-1-phenyl-1-methylethyl *N*-phenylcarbamates do not appear to be cumulative, as was the case for the *N-p*-tolyl carbamates. The $^2H_3$ compound is only 93% deuteriated, but the true $k_{H_6} : k_{D_6}$ would therefore be only *ca.* 1.40, whereas for a cumulative effect its value should be 1.46. We can estimate the extent of the primary and secondary contributions to the k.i.e. from the equations used previously,[1] making an allowance for the incomplete deuteriation. Thus we obtain $0.467 = 1/ac^2$ and $0.730 = 1.07/2c + 0.93/ac$ where a is the primary isotope effect and c the secondary effect, which solve to give c 1.1 per CD_3 and a 1.76. Thus the secondary effect, although significant, is calculated to be considerably less than found in the earlier study by one of us on the comparable *N-p*-tolylcarbamates.[1,2]

As was stated earlier,[1] the above type of calculations is very sensitive to the k.i.e. values and a small adjustment, within the experimental error limits, can lead to very different values for c; in the same way small errors in k.i.e. determinations due to incomplete deuteriation can give spurious results. We have now re-determined the isotopic purity of our samples of deuteriated *N-p*-tolylcarbamates, using a much more accurate n.m.r. spectrometer, and we find that one of the samples of [$^2H_6$]-1-phenyl-1-methylethyl *N-p*-tolylcarbamate was indeed incompletely deuteriated, probably by as much as 10% [a result which is surprising in view of the fact that the deuterium source was $(CD_3)_2C{=}O$ which is sold as >99% pure and acid conditions which promote deuterium exchange were scrupulously avoided]. We must therefore assume the previous calculations for the secondary isotope contribution in the 1-phenyl-1-methylethyl *N-p*-tolylcarbamates to be in error. Using the Arrhenius parameters to extrapolate to 437.5 K, and taking into account the incomplete deuteriation, we obtain values of *ca.* 1.08 and 1.75 for the secondary and primary isotope effects in these compounds, values which are not inconsistent with the other results reported herein. The *N-p*-tolyl compounds, having somewhat less carbocation character than the *N*-phenyl, require less hyperconjugation from the methyls and this is shown in a smaller secondary isotope effect. A secondary effect of *ca.* 1.1 per CD_3 at 437.5 is also much more consistent with the 1.22 per CD_3 reported by Shiner *et al.*[14] for solvolysis of 1-phenylethyl chloride in 50% aqueous ethanol at 25 °C. This compound solvolyses by a limiting S_N1 mechanism, with virtually no elimination, and the reduced β isotope effect, relative to t-butyl chloride (1.33 per CD_3), is attributed to less hyperconjugative β-C–H bond weakening, because of the charge stabilisation provided by the phenyl ring. Now, kinetic isotope effects in solvolysis reactions are both temperature and solvent dependent, so that a value of 1.1 at 437 K in a polar solvent would indicate a high degree of charge separation, but in a less polar solvent, which is less able to stabilise the transition state charge, hyperconjunction becomes of greater significance and the secondary isotope effect could be expected to increase accordingly, so that the maximum (*i.e.* for complete charge formation) may be considerably in excess of 1.1.

The kinetic isotope effects are temperature dependent and the effect of substituents on them must be compared at the same temperature. The data in Table 5 indicate that less reactive compounds show larger kinetic isotope effects, and this must imply that the secondary rather than the primary effect is greater in the less reactive members of the series. A larger primary effect in a less reactive compound can only be interpreted if the hydrogen is more than half-way transferred in the transition state, but this cannot be the case in these systems, as the ρ^+ values indicate considerable C–O bond heterolysis. The greater secondary effect in the less reactive compounds indicates that the methyl groups at C-1 assist incipient carbocation stabilisation by hyperconjugation to a greater extent in the *p*-CF_3 than in the *m*-CH_3 substituted compounds and thus off-set to some extent the loss of electron supply from the aryl group.

The m-CH_3 *Substituent.*—*m*-CH_3 has been reported by Taylor[3d] to require a number of different substituent constants, depending on the reaction series being investigated. It appears that this substituent is more activating in many other systems than in the solvolysis of 1-aryl-1-methylethyl chlorides, for which its σ^+ constant was defined as -0.066. For gas-phase ester pyrolysis, Taylor has suggested *m*-CH_3 substituent constants ranging from -0.098 to -0.13, depending on the ester. He suggested that in the absence of solvent this substituent was somehow more activating than in solvent. In our systems, we require a value of -0.116 for the *m*-CH_3 points to fall exactly on the line, so that it is not only in the gas phase that enhanced activating effects are shown. Interestingly, Brown,[15] in defining a new set of substituent constants, $\Delta\delta_C{}^+$ to relate ^{13}C chemical shift changes to aryl substituents on a tertiary carbocation, has shown that the *m*-CH_3 [and *m*-$CH(CH_3)_2$] substituents are relatively more activating than in his original σ^+ scale. A value of -0.13 for $\Delta\delta_C{}^+$ is assigned for *m*-CH_3 (the other $\Delta\delta_C{}^+$ constants for *meta*-substituent in this scale being set equivalent to σ^+ constants), from ^{13}C chemical shifts of $XC_6H_4\overset{+}{C}(CH_3)_2$ in FSO_3H–SbF_5–SO_2. Thus it is not only in the gas phase or non-polar solvents that *m*-CH_3 is more activating than in $XC_6H_4C(CH_3)_2$ solvolysis, and this must arise from field effects rather than through-bond inductive effects. In our calculations we have used the value -0.13, since a proliferation of substituent constants is self-defeating.

Substituents at C-1.—Substitution of an additional phenyl group at C-1 increases the reaction rates, but the reaction constant for the 1-aryl-1-phenylethyl *N*-*p*-tolylcarbamates is numerically smaller than that for the 1-aryl-1-methylethyl compounds. This is consistent with a transition state having more carbocationic character, where the required additional stabilisation is supplied by the second phenyl substituent. We also attempted to decompose 1-phenyl-1-trifluoromethylethyl *N*-phenylcarbamate, but the rate was negligibly slow at temperatures up to 493 K, the limit of our apparatus, indicating that the highly election-withdrawing CF_3 group hindered the transfer of electrons from C-1 towards the ether oxygen.

Data from earlier work by one of us was fitted to Charton's extended Hammett equation (4).[16] Although there were

$$\log k = L\sigma_I + D\sigma_R{}^+ + h \qquad (4)$$

insufficient data to permit definite conclusions, the rate coefficients for decomposition in diphenyl ether at 463 K[17] of *p*-$MeC_6H_4NHCO_2CMe_2X$, where the substituent X (CH_3, $CH{=}CH_2$, $C{\equiv}CH$, Ph) is directly bonded to C-1, correlated reasonably well with $\sigma_R{}^+$ values ($-L$ 2.17, $-D$ 3.17, h -0.986, r 0.953), and provide further confirmation of partial positive charge at C-1.

Good correlations were also obtained for the rate data given in Tables 2 and 3, using the $\sigma_R{}^+$ substituent constants, although again the data sets were not very well defined. The values for h and D for the *para*-substituted compounds are given in Table 7, from which it is seen that the value of L parallels the σ^+ values and $-D$ is of the order of 2—3 for the carbamates and 4.5 for the carbonates. When compared with systems in which it is known that positive charge is well developed, the magnitude of D might suggest that C–O bond-breaking is not very well advanced. However, our systems are studied at much higher temperatures than any for which D has previously been calculated, and furthermore, since $-D$ is known to decrease with temperature, our values may represent considerable resonance interactions of the aryl substituents with an electron deficient C-1.

Table 7. Decompositions in diphenyl ether of *para*-substituted 1-aryl-1-methylethyl carbamates and carbonates. Correlation of rate constants with substituent constants using Charton's equation, $\log k = L\sigma_I + D\sigma_R{}^+ + h$.[a]

Compounds	T/K	$-L$	$-D$	h	r
$PhNHCO_2C(CH_3)_2Ar$	437.5	1.55	2.56	0.129	0.999
$CH_3C_6H_4NHCO_2C(CH_3)_2Ar$[b]	444.7	1.76	2.94	0.202	0.999
$PhOCO_2C(CH_3)_2Ar$	408.6	2.84	4.48	0.479	0.986
$CH_3C_6H_4NHCO_2C(CH_3)_2Ar$[c]	453.8	1.50	2.47	0.056	0.999

[a] σ_I, $\sigma_R{}^+$ Values taken from ref. 16. Calculations kindly performed by Professor M. Charton. [b] Includes *p*-OMe substituent. [c] Dodecane as solvent.

We must conclude therefore that decompositions in solvents of tertiary carbamates and carbonates having an aryl substituent at C-1 proceed by a mechanism which is more *E*1-like than comparable reactions of alkyl-substituted carbamates or of gas-phase reactions of aryl-substituted acetates and carbonates, but that, contrary to an earlier suggestion, the carbocation is not fully developed.

The Slope of the Linear Free Energy Relationship Plots.—It is a statistical fact that the slope of a line is more influenced by points at the extremities than by those in the middle, and the variation in slopes of our Hammett–Brown plots, depending on the spread of the substituents used, highlights the need for caution in attaching too much significance to absolute values of ρ^+ obtained from any given set of experiments. It is an unfortunate consequence of the rate changes with substituent that the rate constants at the extremities of the Hammett–Brown line are often those which have had to be determined by extrapolation of Arrhenius data, and yet it is precisely these points which need accurate experimental determination, particularly if slight curvature in the lines is to be detected.

In this work we have omitted the rate constants for the *p*-OMe substituted compounds, because of lack of confidence in the accuracy of an Arrhenius extrapolation. This omission does not detract from our argument of a transition state with considerable *E*1 character, and in fact inclusion of the data would further support it.

Experimental

2-Arylpropan-2-ols and 1-aryl-1-phenylethanols were prepared from the appropriate ketones and alkyl- or aryl-magnesium halides (15% excess) by the standard Grignard reaction, except for *m*-chlorophenyl- and *p*-nitrophenyl-propanols, which were obtained from reaction of methyl *m*-chlorobenzoate (2 mol equiv.) with methylmagnesium iodide (1 mol equiv.) and by oxidation of *p*-nitroisopropylbenzene with chromic anhydride,[18] respectively. Care was taken to ensure that the Grignard reaction conditions and all glass-ware were acid-free. Vacuum distillation of the crude products gave alcohols whose b.p.s compared well with reported values.[18,19] B.p.s (not previously reported) of $CF_3C_6H_4C(OH)(CH_3)_2$, 106 °C at 14 mmHg; of p-$CF_3C_6H_4C(OH)(CD_3)_2$, 103 °C at 15 mmHg; and of m-$CH_3C_6H_4C(OH)(CD_3)_2$, 117 °C at 135 mmHg.

Carbamates were prepared by reaction of phenyl or *p*-tolyl isocyanate with alcohol in dry toluene at 60 °C in the presence of tin(II) 2-ethylhexanoate as described previously,[20] and were purified by two recrystallisations from light petroleum (b.p. 60—80 °C). For *p*-OMe substituted alcohols the reactions were done at room temperature. All carbamates gave elemental analyses correct to within 0.3% and satisfactory n.m.r. spectra. M.p.s are given in Table 1.

Carbonates were prepared by dropwise addition of phenyl chloroformate to an ice-cold solution of the alcohol in pyridine–methylene dichloride (1 : 5 v/v) under nitrogen, and worked up in the usual way, after overnight stirring. Crude products were refrigerated until they solidified (sometimes one week) and recrystallised from light petroleum (b.p. 40—60 °C). The p-CH_3 and *p*-F substituted carbonates did not solidify and were used as oils (see text). All carbonates gave elemental analyses correct to within 0.3% and satisfactory n.m.r. spectra.

Solvents for kinetic studies were purified before use. Diphenyl ether and dodecane were distilled *in vacuo*, b.p. 68 °C at 0.25 mmHg and 97—99 °C at 15 mmHg, respectively. Sulpholane was refluxed over NaOH for 24 h and then vacuum distilled. The middle fraction, b.p. 143 °C at 14 mmHg, was redistilled over NaOH twice and again immediately before use to give a fraction, b.p. 92 °C at 0.06 mmHg (lit.,[21] 147 °C at 15 mmHg). G.l.c. analysis of this fraction showed one peak and there was no decolourisation on heating.

Kinetic studies of carbamate decompositions were done by g.l.c. analysis of effluent CO_2 as described previously [1,4] from a *ca.* 0.2 g sample in 10 ml solvent in reaction vessels of *ca.* 25 ml capacity. Rate constants were obtained from the slopes of the linear least squares line through the log (peak height) *versus* time plots. Carbonate decompositions were followed by sampling the solutions under nitrogen pressure, cooling to 30 °C, and analysing aliquot portions by i.r. in the range 1 700—1 800 cm^{-1} using 0.1 mm NaCl cells referenced against diphenyl ether using a Perkin–Bodenseewerk 221 spectrophotometer. Each spectrum was recorded twice and the rate constants obtained from the slope of the linear least squares line through the plot of log (absorbance at 1 760 cm^{-1}) *versus* time, the absorbance having been shown to obey Beer's law.

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