Decomposition of Carbamates of Tertiary Alcohols. Part 3.[1] Influence of Phenyl and Vinyl Substituents at the α-Carbon Atom

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Rates of thermal decomposition of *N*-(*p*-tolyl)carbamates of the alcohols $Me_2C(OH)R$ (R = Me. Ph. or $HC{:}CH_2$) and $MeC(OH)Ph_2$ in diphenyl ether have been measured. The results show that the activating effect of the single phenyl and vinyl groups is about the same (*i.e.* 10-fold at 463 K): two phenyl groups on the α-carbon atom increase the rate constant a further 7-fold and provide the first evidence of the effect of αα-diphenylation in ester decompositions. The rate increases are reflected in progressively lower $\Delta H^\ddagger$, but in more highly negative $\Delta S^\ddagger$. values. These data indicate that unsaturated substituents assist incipient carbocation formation by resonance stabilisation. Increased solvation, as charge separation becomes more important, accounts for deviations from the equation $\log k_{rel} = \rho\sigma^*$ and for the changes in $\Delta S^\ddagger$.

N-SUBSTITUTED carbamates have been shown[2-9] to decompose by a six-centre cyclic mechanism in a similar way to other ester types. On heating, these esters decompose to yield an olefin and an acid (or its decarboxylation products) (Scheme). Factors which increase the reaction rate are electron-withdrawing groups

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

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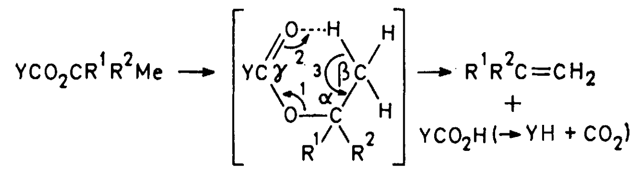
[7] H. Kwart and J. Slutsky, *J.C.S. Chem. Comm.*, 1972, 552.

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

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

at Y (*e.g.* *N*-phenylcarbamates decompose faster than the corresponding acetates) and electron-releasing groups at R^1 and R^2 (*e.g.* decomposition rates are in the order t-butyl > isopropyl > ethyl).[8] These effects are attributed to an increase of charge separation in the transition states of the faster reacting esters.

In acetates, the effects of substituents at the α-carbon atom are fairly well documented. Besides α-methyl substitution, aryl,[10,11] vinyl,[11] and cyclopropyl[11] substitution have also been shown to increase the reaction rates in both secondary and tertiary acetates. For 1-arylethyl acetates, the rate constants correlate well with σ^+ values[12] to give a negative Hammett ρ value. The magnitude of these effects is small (relative to similar substitutions in solvolysis reactions) indicating that in the rate-determining step the α-carbon atom has developed little carbocation character.



SCHEME

Less is known about the influence of α-carbon substituents in carbamates. Daly and his co-workers[5] have shown that decomposition rates of *NN*-dimethylcarbamates increase with increasing α-methylation, but that the relative effect of α-methylation is not as great in the dimethylcarbamates as in acetates. Taylor[8] has found that gas-phase decomposition rates of t-butyl, isopropyl, and ethyl *N*-phenylcarbamates increase in the expected order, but that the Arrhenius plots indicate that the secondary and primary compounds decompose by another mechanism in addition to the cyclic mechanism, making comparison of pyrolysis rates unmeaningful. Dyer and Wright[2] have also reported that decomposition of primary and secondary *N*-phenylcarbamates can yield products other than those obtainable from the reaction shown in the Scheme.

A detailed study of the effects of unsaturated substituents in tertiary *N*-arylcarbamates should therefore provide further useful evidence about the nature of the transition state in this particular type of ester; it is already known that the heterolytic character of the transient six-membered ring is more fully developed than in corresponding acetates. Accordingly, we report here the results of a kinetic study of the rates of decomposition in diphenyl ether of *N*-(*p*-tolyl)carbamates of tertiary alcohols 2-methylpropan-2-ol, 2-phenylpropan-2-ol, and 2-methylbut-3-en-2-ol, of the general formula $(CH_3)_2C(OH)R$ (R = Me, Ph, or $CH{:}CH_2$, respectively) and of the disubstituted alcohol 1,1-diphenylethanol.

N-Tolylcarbamates were chosen in preference to *N*-phenylcarbamates because they gave measurable kinetic data over a more convenient range of temperatures. Earlier studies[3] had shown that the methyl substituent on the benzene ring decreased the reaction rate, but that the decomposition mechanism was essentially the same as in the *N*-phenyl compounds.

EXPERIMENTAL

Carbamates.—The carbamates were prepared by treating a solution of *p*-tolyl isocyanate (0.1 mol) in toluene with the appropriate alcohol (0.11 mol) in the presence of the catalyst tin(II) 2-ethylhexanoate as described fully in ref. 13. For 1,1-*diphenylethyl* N-(p-*tolyl*)*carbamate* the reaction mixture was stirred for 48 h at room temperature. Evaporation left a white solid (80%), m.p. 162 °C (from benzene) (Found: C, 80.0; H, 6.45; N, 4.3. $C_{22}H_{20}NO_2$ requires C, 79.75; H, 6.35; N, 4.25%).

αα-*Dimethylbenzyl* N-(p-*tolyl*)*carbamate* was prepared by heating the toluene solution at 80 °C for 2 h. The solid product obtained on evaporation was recrystallised from light petroleum (b.p. 60—80 °C); yield 90%; m.p. 121 °C (Found: C, 76.05; H, 7.1; N, 5.35. $C_{17}H_{18}NO_2$ requires C, 75.85; H, 7.05; N, 5.2%).

The preparation of 1,1-dimethylallyl *N*-(*p*-tolyl)carbamate (m.p. 58 °C) is described in ref. 13. The material was purified before use by vacuum sublimation at 50 °C.

Solvent.—Commercially obtained diphenyl ether was distilled once before use; b.p. 70 °C at 0.6 mmHg.

Kinetic Experiments.—The carbamates (0.5 g) in diphenyl ether (20 ml) were heated to within ±0.5 °C of the required temperature in a silicone oil-bath. A stream of helium was used to carry over the effluent gases. The rate was followed by periodic analyses of the carbon dioxide in these gases (g.l.c.). For full details see refs. 1 and 3.

Product analysis. The non-aqueous potentiometric titration of the amine by the method of Siggia *et al.*[14] is described fully in refs. 1 and 3. The volatile products were estimated by sweeping the effluent gases from a decomposition reaction into a standard solution of barium hydroxide in water by using a stream of nitrogen, and then into a solution of bromine in carbon tetrachloride cooled in an ice–salt bath. Back-titration of the barium hydroxide with hydrochloric acid gave the carbon dioxide yield and titration of the residual bromine with potassium iodide and sodium thiosulphate gave a measure of the gaseous olefins. Non-volatile olefins were identified by g.l.c. from comparison of retention times with those of known compounds [5 ft column of 3% silicone OV101 on Supasorb (Phase Separation Ltd.) at 150 °C].

RESULTS

The rates of the decompositions of the carbamates in diphenyl ether were followed to at least three half-lives. Kinetic results have been obtained over a 36 K temperature range.

Product analysis showed that all the carbamates decomposed to give the expected products (Scheme; Y = $p\text{-}MeC_6H_4{\cdot}NH$) in at least 90% yield. The olefins, carbon dioxide, and amine (*p*-toluidine) were identified by g.l.c. and estimated quantitatively as described in the Experimental section.

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[12] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[13] T. Francis and M. P. Thorne, *Canad. J. Chem.*, 1976, **54**, 24.

[14] S. Siggia, J. C. Hanna, and I. Kernenski, *Analyt. Chem.*, 1950, **22**, 1295.

No other products were obtained from the 1,1-diphenylethyl carbamate, but small amounts (up to 10% at lower temperatures) of *NN'*-ditolylurea (identified by m.p.) were obtained from the other carbamates. The total yield of amine and urea, where formed, accounted for 95—100% of the available –NH–. It has been postulated previously [3] that the urea arises from a side reaction in which the carbamate decomposes to yield isocyanate, which then reacts with amine formed in the main reaction.

The kinetic data fitted a first-order equation in all cases. The rate constant, *k*, was calculated from the slope of the line of best fit determined by the least-squares method; duplicate values agreed to within ±5%. The average values of *k* are given in Table 1. Activation energies, log *A* values, and enthalpies and entropies of activation (Table 2) were calculated from the Arrhenius and Absolute Rate Theory equations, for which the transmission coefficient was taken as unity. The $\Delta S^{\ddagger}$ values are averages for the temperature range.

TABLE 1

Rate constants for the decomposition of tertiary carbamates, $p\text{-MeC}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CMeR}^1\text{R}^2$, in diphenyl ether

R^1	R^2	T/K	$10^5k/s^{-1}$	10^5 (k per CH_3)/s^{-1}
Ph	Ph	418.5	9.92	9.92
		427.2	20.34	20.34
		433.3	33.52	33.52
		438.8	44.84	44.84
		444.3	67.48	67.48
		447.5	81.41	81.41
		450.5	104.6	104.6
Ph	Me	427.2	3.75	1.87
		433.3	6.48	3.24
		438.8	9.80	4.90
		444.3	14.60	7.30
		447.5	20.69	10.35
		450.5	24.19	12.10
		457.0	40.60	20.30
		463.0	62.18	31.09
$CH{:}CH_2$	Me	444.3	16.42	8.21
		447.5	19.86	9.93
		450.5	28.18	14.09
		457.0	42.82	21.41
		463.0	66.25	33.13
Me	Me	444.3	1.67	0.56
		447.5	2.32	0.77
		450.5	2.76	0.92
		457.0	4.93	1.64
		463.0	8.85	2.95
		463.5	9.22	3.70
		468.5	13.66	4.55

DISCUSSION

The kinetic results and activation parameters (Tables 1 and 2) show that the activating influence of the substituents on the rates of decomposition of the carbamates increases in the order t-butyl > phenyl ~ vinyl > αα-diphenyl. The rate increases are accompanied by decreasing energies and entropies of activation. The results are in qualitative agreement with published data for acetate pyrolysis, but the rate-enhancing effect of the unsaturated substituents is greater in the carbamates and thus confirms the hypothesis that carbocation formation is further advanced in the cyclic transition state than in the acetates.

Values of k_{rel} (*i.e.* *k* relative to *k* for the Bu^t compound) for the carbamates and for gas-phase acetate decompositions are given in Table 3. To eliminate statistical errors associated with the experimental determination of *k* at any one temperature, the k_{rel} values for the carbamates have been obtained from the values of *k* at 463 and 450 K calculated by using the Arrhenius parameters (Table 2). For the secondary and tertiary acetates the values of k_{rel} determined by Lum and Smith at 650 and 570 K, respectively, have been extrapolated to 463 K by assuming the acetates obey the Taft equation,[15] $\log k_{rel} = \rho\sigma^*$, and hence that $\log(k_{rel})_{T_1}/\log(k_{rel})_{T_2} = \rho_1/\rho_2 = T_2/T_1$.* All the results are corrected statistically for the number of β-hydrogen atoms available.

TABLE 2

Activation parameters for decomposition of *N*-tolylcarbamates, $p\text{-MeC}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CMeR}^1\text{R}^2$, in diphenyl ether

R^1	R^2	E_a/ kJ mol^{-1}	log (A/s^{-1})	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}
Ph	Ph	110.5 ± 2.2 [a]	9.82	106.9	-68.4 ± 1.2
Ph	Me	128.1 ± 1.9	11.22	124.2	-41.5 ± 1.0
$CH{:}CH_2$	Me	128.6 ± 4.9	11.33	124.7	-39.8 ± 10.7
Me	Me	136.8 ± 2.0	11.39	133.0	-38.9 ± 1.0

[a] Standard errors calculated from all points included in data in Table 1 [J. Topping in ' Errors of Observation and their Treatment,' 3rd edn., Chapman and Hall (for Institute of Physics and the Physical Society), London, 1962, p. 105].

In both tertiary series the vinyl and phenyl groups each have about the same effect on the rate, but in secondary acetates the vinyl is considerably less rate-enhancing than the phenyl. The k_{rel} value for the carbamates, although small as compared with ionic reactions, is larger than for the acetates, as would be expected for the more heterolytic reactions. Here the resonance interactions of the phenyl and vinyl substituents (both show $-I$, $+M$ effects) will interact more strongly with the incipient carbocation. The σ_I and σ_R values [17] for a phenyl group are 0.10 and —0.11, compared with 0.15 and —0.23 for vinyl, [18] so that the greater polarisability of the vinyl group can be expected to cause it to activate more strongly, relative to phenyl, as the carbocation character of the α-carbon atom increases (Table 3).

By the same reasoning, an ethynyl group (σ_I 0.20, σ_R +0.03) [19] can be expected to have a small deactivating effect on the reaction. In fact k_{rel} values (at 463 K, per β-H) calculated from earlier data [1,3] for decomposition of $RC_6H_4\cdot NH\cdot CO_2CMe_2X$ (X = Me or C⋮CH) in diphenyl ether are 1.02, 1.02, and 1.3 for R = H, *p*-Cl, or *m*-Cl, respectively. Thus it is the resonance effect rather than the inductive effect which determines the activating

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* Extrapolation of the Arrhenius equation (ref. 11) to 463 K gives k_{rel} for $RMe_2C\cdot OAc$ (R = Me, Ph, or $CH{:}CH_2$) as 1 : 5.6 : 5.0, respectively. For $RMeCH\cdot OAc$, k_{rel} values are 1 : 10 : 5.6. Results of Taylor [8,16] for secondary acetates where R = Me or Ph agree more closely; *viz.* k_{rel} 1 : 5.0 ($\rho_1 T_1 = \rho_2 T_1$) or 1 : 4.7 (Arrhenius).

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[18] G. B. Ellam and C. D. Johnson, *J. Org. Chem.*, 1971, **36**, 2284.

[19] C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 859; see also ref. 18.

influence of the substituents. In addition, as the hybridisation at the α-carbon changes to sp^2, the phenyl and vinyl compounds will be subject to steric acceleration effects; these effects will not be significant with the small ethynyl substituent. The k_{rel} values at 450 and 463 K in Table 3 differ by a factor of 1.2 instead of 1.03 as predicted by the $\rho_1 T_1 = \rho_2 T_2$ relationship. Calculation of k_{rel} at intermediate temperatures shows a steady decrease in the values and in the ratio of calculated to predicted value. Clearly other factors are also influencing the rates, although the influence of these other effects on k_{rel} is only slight.

TABLE 3

Relative rates of pyrolysis of α-substituted esters

R	MeCH(OAc)R [a] k_{rel} [c] (463 K)	$Me_2C(OAc)R$ [a] k_{rel} [c] (463 K)	$Me_2C(O_2C{\cdot}NH{\cdot}C_6H_4Me\text{-}p)R$ [b] k_{rel} (463 K)	 k_{rel} (450 K)
Me	1	1	1 (8.82)	1 (2.80)
Ph	4.9	5.5	10.0 (58.9)	12.1 (22.5)
$CH{:}CH_2$	2.1	5.05	11.3 (66.7)	13.61 (25.4)
d			77.0 (227.0)	106.1 (99.0)

[a] Data from ref. 11; see text. [b] This work; values of $10^5k/s^{-1}$, calculated from Arrhenius data, given in parentheses. [c] All k_{rel} values corrected statistically for number of β-hydrogen atoms. [d] $Ph_2MeC{\cdot}O_2C{\cdot}NH{\cdot}C_6H_4Me\text{-}p$.

Previously it has been shown [9] that for decompositions of $RC_6H_4{\cdot}NH{\cdot}CO_2Bu^t$ in the gas phase and in diphenyl ether, solvation increased the rates by an estimated factor of 8, but the ratio of the ρ factors at 548.8 K (gas phase) and 450.7 K (solvent) was 0.85, compared factor of 8, but the ratio of the ρ factors at 548.8 K (gas phase) and 450.7 K (solvent) was 0.85, to be compared with the 0.825 predicted from the $\rho_1 T_1 = \rho_2 T_2$ relationship. In this case substituents at the α-carbon atom were constant and therefore solvation and steric effects were, presumably, also constant.

It is likely that deviations from the log $k_{\mathrm{rel}} = \rho\sigma^*$ relationship encountered in the present work are due to solvation rather than to steric effects since the $(k_{\mathrm{rel}})_{463}$ values calculated for the gas-phase tertiary acetate decompositions using $\rho_1 T_1 = \rho_2 T_2$ agree closely with the calculations using the Arrhenius data.

Solvation differences can also account for the differences in $\Delta S^\ddagger$ throughout the series. Even when these values are adjusted to account for the number of methyl groups [*i.e.* increased by $R \ln 2$ (*ca.* 5.8) or $R \ln 3$ (*ca.* 9.1)], they are sufficiently large to be considered significant. For the gas-phase tertiary acetate series, $\Delta S^\ddagger$ is the same, for all three substituents, within the limit of experimental error.[11] Evidently, as the incipient carbocation is more fully developed, the solvation by the slightly polar diphenyl ether increases, thus making the entropy change on going from reactant to transition state greater. This effect is also shown in the value of $\Delta S^\ddagger$ for the αα-diphenyl carbamate.

The influence of a second phenyl substituent at a tertiary α-carbon atom on ester decompositions has not hitherto been reported. Table 3 shows that the additional phenyl group produces considerable additional rate enhancement, despite the increased steric requirement. Over the temperature range 440—463 K the rate enhancement due to the second phenyl group increases steadily from 61 to 77% of the enhancement due to one phenyl. This change, if real, could be due to a lessening of steric strain between the bulky substituents as the temperature increases.

Additional, direct evidence is required concerning the relative importance of C–O and C–H bond-breaking in the rate-determining steps. It is hoped that a report of a kinetic isotope study to provide some of this information will be presented at a later date.

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