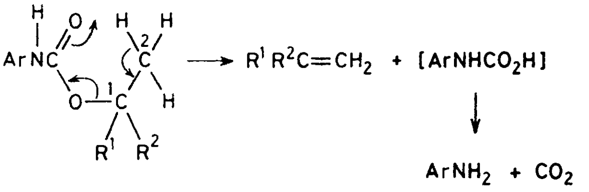
Structure and Isotope Effects upon the Thermal Decomposition of Carbamates of Highly Congested Tertiary Alcohols

By **John S. Lomas**, L'Institut de Topologie et de Dynamique des Systèmes de l'Université de Paris 7, associé au C.N.R.S., 1 rue Guy de la Brosse, 75005 Paris, France
Melanie P. Thorne,* Chemistry Department, University of Keele, Keele, Staffs ST5 5BG

Rate constants have been measured for the thermal decomposition in diphenyl ether at 383—433 K of the carbamates of congested tertiary aliphatic alcohols (1)—(4) which are more reactive than any carbamates previously studied. The effects of structural change among (1)—(4) or of variation in substituent at the tertiary carbon atom are inconsistent with a predominantly carbocation type of mechanism. Kinetic deuterium isotope effects (k.i.e.) upon the methyl derivatives are unambiguously primary (2.2—2.6 at 400 K) and clearly indicate extensive C–H fission in the rate-determining step. These results contrast with the previous interpretation of the k.i.e. in decompositions of $CH_3C_6H_4NHCO_2Bu^t$ for which rate-determining C–O fission was proposed. Reinterpretation of the earlier data in terms of superimposed primary and secondary isotope effects leads to results in agreement with the new data and with the product isotope effects. Phenyl substituents, however, increase the carbocationic character of the transition state, but this mechanistic change does not cause the reactivity to be higher than that of the congested derivatives: there is, therefore no relationship between the isotope effect and the reactivity.

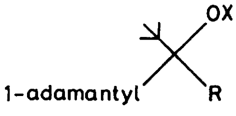
THE thermal decomposition of tertiary carbamates is one of a large series of reactions of acid derivatives which decompose *via* cyclic transition states, usually six-membered.[1] Carbamates of tertiary alcohols are generally agreed to decompose by a mechanism involving transfer of hydrogen to carbonyl oxygen with elimination of olefin, and subsequent fast decomposition of the resultant carbamic acid to give amine and carbon dioxide [2] (Scheme). There is some uncertainty, however, about the degree of advancement of C–H and C–O bond breaking in the transition state.



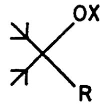
SCHEME

Previous work places this reaction in a series wherein the importance of C–O bond breaking increases in the order: acetate < carbamate < carbonate.[3] Although earlier studies of the kinetic effect of solvent variation and of substituent effects in $ArNHCO_2CMeR^1R^2$ tended to show that a highly charged transition state was unlikely and that the tertiary carbon did not adopt marked carbocation character,[2,4] recent results on kinetic isotope effects (k.i.e.) on the decomposition of the above carbamate where R^1, R^2 = Me or Ph were interpreted as arising from cumulative secondary effects, whereupon the conclusion is that ' the heterolysis of the α-C–O bond is of major importance in the rate-determining step '.[5] Such a paradoxical situation clearly merits further attention.

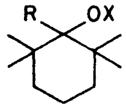
One of the difficulties in studying the mechanism of simple tertiary carbamate pyrolysis through k.i.e.s is that the reaction is necessarily carried out at elevated temperatures, *ca.* 463 K for the most studied t-butyl *N*-*p*-tolylcarbamate decompositions in diphenyl ether, where the maximum theoretical primary isotope effect is small (3.11). Any primary isotope effect which is substantially less than maximum can therefore fall in a range where confusion with secondary effects is possible particularly since complete deuteriation of β-hydrogens involves nine deuterium atoms. In order to avoid this ambiguity we have now investigated a series of highly congested carbamates derived from alcohols (1')—(4'), which are much more reactive than any previously examined, and which have only one CH_3 group capable of providing hydrogens for elimination.



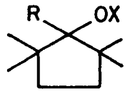
(1')
(1)



(2')
(2)



(3')
(3)



(4') X = H
(4) X = $OCNHC_6H_4CH_3$

a; R = CH_3
a'; R = CD_3
b; R = C_2H_5
c; R = n-C_3H_7

The carbonium ion reactions of both (2') and its corresponding *p*-nitrobenzoates where R = alkyl or aryl have been extensively studied by Lomas and Dubois.[6,7] More limited information is available concerning the acid-catalysed solvolysis of (1'), (3'), and (4') where R = Me or Bu^t.[8] Molecular mechanics calculations indicate that these alcohols are highly strained due to steric crowding and have bond lengths and bond angles about the functionalised tertiary carbon which differ markedly from standard values. *p*-Nitrobenzoates of (2`) have been reported, but no carbamates or other acid derivatives of these alcohols had been synthesised when this work was undertaken.

RESULTS AND DISCUSSION

Carbamate Formation.—Initial attempts to prepare the series of carbamates from (2`) by the conventional procedure of tin(II) 2-ethylhexanoate-catalysed condensation of the alcohol with *p*-tolyl isocyanate in toluene at 60 °C failed except when R = Me, though traces of the ethyl derivatives were obtained by this method. A better procedure was found to consist in stirring the alcohol and isocyanate with catalyst at room temperature without solvent until the mixture solidified; this required from 12 to 60 h. By this means carbamates (1a), (2b,c), (3a—c), and (4a) were prepared in good yields. Nevertheless attempts to obtain carbamates from the Pr^i and Bu^i derivatives of (2`) resulted only in the formation of the trimer of the isocyanate; presumably the steric requirements of these groups render carbamate formation slower than the polymerisation process. The physical data for the new carbamates are given in Table 1.

TABLE 1

Physical data for *N*-*p*-tolylcarbamates of congested alcohols

		% Composition						δ($CDCl_3$) from Me_4Si		
		Found			*Theory*					
Compd	M p (°C)	C	H/D	N	C	H/D	N	$(CH_3)_3C$–C or ring CH_3	CH_3–C–O	NH
(1a)	152	78.0	9.75	3.95	78.0	9.55	3.8	1.13	1.77	6.33
(1a')	154	77.3	9.7	3 65	77.5	9.4	3.75			
(2a)	148	74.5	10.1	4.9	74.2	9.95	4.8	1.10	1.71	6.30
(2a')	148	73.2	9.9	4.8	73.4	10.05	4.75			
(2b)	112	74.7	10.3	4.8	74.7	10.15	4.6	1.17		6.30
(2c)	118	75.3	10.65	4.6	75.2	10.35	4.4	1.17		6.33
(3a)	167 (decomp.)	75.4	9.85	4.75	75.2	9.65	4.6	1.08, 1.04	1.72	6.31
(3a')		74.3	9.85	4.85	74.5	9.65	4.55			
(3b)	147	75.9	9.95	4.35	75.7	9.8	4.4	1.07		6.35
(3c)	129	75.9	10.15	4.45	76.1	10.03	4.2	1.10, 1.06		6.33
(4a)	126	74 9	9.7	4.95	74.7	9.4	4.85	1.08, 1.04	1.49	6.32
(4a')	126	73.6	9.5	4.95	73.9	9.3	4.8			

Structural Effects.—The kinetics of decomposition in diphenyl ether were studied at temperatures in the range 383—433 K, depending on the reactivity of the compound. The reactions were followed by g.l.c. analysis of the evolved carbon dioxide, as in previous work in this area,[2,4] and showed first-order kinetics to at least three half-lives. The first-order rate constants and activation parameters are given in Tables 2 and 3.

The highly reactive nature of the congested carbamates can be seen from a comparison of the relative rates of decomposition of (2a) and t-butyl *N*-*p*-tolylcarbamate. At 403 K, the rate constant ratio is 1 050 : 1 per β-hydrogen available for elimination. In contrast the effect of replacing the methyl group by a t-butyl in the gas-phase pyrolysis of the secondary acetates R(Me)-CHOAc, is reported to give a seven-fold rate increase at 403 K.[9]

For the methyl derivatives of the compounds considered in this work, the reactivity increases in the order (4a) < (2a) < (1a) < (3a), the overall rate constant range varying by a factor of *ca*. 14. At 400 K the relative rates are 1 : 3.5 : 6.2 : 14.4. Though the reactivity spread is similar in acid-catalysed solvolysis of the alcohols it is noteworthy that the order is quite different, with the cyclopentyl derivative slowest in the carbamate decompositions but fastest in alcohol solvolysis, where (2a) < (3a) < (1a) < (4a) (relative rates 1 : 3.2 : 10.2 : 26.9).

TABLE 2

Rate constants * (10^4 k/s^{-1}) for decomposition in diphenyl ether of congested carbamates, (1)—(4) at 375—423 K

Compd.	423.2 K	413.1 K	403.2 K	393.0 K	383.2 K	375.5 K
(1a)		7.11	3.27	1.33	0.541	0.270
(1a')		3.63	1.47	0.533	0.234	
(2a)		4.08	1.84	0.690	0.287	
(2a')	3.72	1.74	0.708	0.271		
(2b)	5.69	2.66	1.17	0.461		
(2c)		3.39	1.34	0.518		
(3a)			7.54	3.28	1.51	0.731
(3a')			3.40	1.49	0.603	
(3b)			7.89	3.38	1.63	0.771
(3c)				3.77	1.69	0.791
(4a)	2.87	1.23	0.523	0.216		
(4a')	1.32	0.587	0.224			

* Average of two or three runs.

A second difference in relative rates of carbamate and alcohol or *p*-nitrobenzoate decompositions can be perceived in the albeit foreshortened study of substituent effects carried out on series (2) and (3). Carbamates (2b and c) react at about two-thirds the rate for (2a). Though this might be attributed merely to the statistical effect of replacing one hydrogen atom of the methyl group by an alkyl group, inspection of the results for (3a—c), which react at almost identical rates, indicates that this simple explanation is probably inadequate. However, it is important to notice that the data for carbamates (2a—c) contrast with results for the carbonium ion reactions of the corresponding alcohols and *p*-nitrobenzoates. While the alcohols show only a modest increase in reactivity as R is changed from Me to Et and Pr^n (relative rates 1 : 1.02 : 1.55) the solvolysis rates of the corresponding *p*-nitrobenzoates, which are structurally closer to the carbamates, are enhanced by a factor of *ca.* 16 by the same change (relative rates 1 : 12.4 : 16.6).

TABLE 3

Activation parameters for decomposition in diphenyl ether of congested carbamates (1)—(4)

Compound	E_a/kJ mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta H^‡$/kJ mol^{-1} *	$\Delta S^‡$/J mol^{-1} K^{-1} *	Corr. coef.	No. of points
(1a)	113.20	11.17	109.9	−41.7	0.999	10
(1a')	122.89	12.09	119.7	−24.0	0.998	6
(2a)	117.37	11.45	114.1	−36.3	0.999	11
(2a')	121.41	11.56	117.9	−34.6	0.998	11
(2b)	114.99	10.96	111.6	−45.9	0.999	7
(2c)	125.78	12.43	122.4	−17.8	0.999	6
(3a)	105.78	10.53	102.1	−53.8	0.999	8
(3a')	111.18	10.94	108.0	−46.0	0.999	6
(3b)	102.58	10.18	99.3	−60.6	0.999	10
(3c)	107.35	10.85	104.2	−47.6	0.997	6
(4a)	120.87	11.38	117.5	−38.0	0.979	8
(4a')	123.06	11.31	119.7	−39.2	0.997	5

* Determined from best least squares fit of plots of ln*k*/T *versus* 1/*T*.

Our first conclusion is therefore that structural effects on carbamate decompositions do not resemble those upon the carbonium ion reactions of related derivatives. These results confirm the earlier work of Ashcroft and Thorne[2,4] on substituent effects at the tertiary carbon, where it was found that there was a much closer analogy with the gas-phase pyrolysis of acetates, well known to occur *via* a semi-concerted cyclic process, than with solvolysis reactions occurring through carbonium ion intermediates.

The olefin product distribution from decompositions of (2a—c) is also consistent with a predominantly concerted, rather than a carbonium ion reaction. Whereas substantial amounts of rearranged olefins are produced in elimination reactions of congested tertiary alcohols and their corresponding *p*-nitrobenzoates, including pyrolysis of the latter, all of which go through carbonium ions,[6,7] analysis of the products from carbamate decompositions shows that the normal olefin predominates, with $<2\%$ rearrangement. Though non-rearranged olefin can be formed from carbonium ions, particularly when R = Me, the fact that 1,2-methyl migration occurs to such a small extent also argues against significant charge development at C-1.

Kinetic Isotope Effects.—Four carbamates (1a')—(4a') fully deuteriated on the tertiary methyl group were synthesised from appropriate alcohols. Decomposition rates were *ca.* 2.2—2.6 times slower than those of the normal compounds (Table 2). The k.i.e.s calculated from the Arrhenius data (Table 3) are given in Table 4, so that errors in any individual determination are minimised. From Table 4 two points may be noted. First, the k.i.e. for the 1,1-di-t-butylethyl carbamate is substantially higher than those of the other compounds and, secondly, there is a marked temperature dependence in all compounds.

These k.i.e. values are greater than that of 1.44 (455 K) found previously for the *N*-*p*-tolylcarbamate of 1,1-diphenylethanol and its trideuteriated analogue. This compound is only slightly less reactive than (4a) (the least reactive of the present work) and is also the only other tertiary carbamate studied having only one methyl group, in which therefore, the value of the k.i.e. per CD_3 is unambiguous.

Potentially there are three kinetic deuterium isotope effects upon carbamate decomposition: a primary effect upon C–H bond stretching, and α- and β-secondary effects upon charge development at C-2 and C-1, respectively. According to Amin and Taylor,[10] in gas-phase acetate and carbonate pyrolysis the observed overall k.i.e.s include contributions from both primary and secondary effects, the contribution of the secondary effect becoming greater as the degree of carbocation formation at C-1 increases (and hence the kinetic significance of C–H bond breaking decreases) with changes in substituents. These authors observed k.i.e.s for t-butyl acetate and 1-phenylethyl phenylcarbonate of 2.285 and 2.11, respectively, and estimate that the secondary effect contribution in the acetate pyrolysis is 1.03 per D, assuming that the primary effect is the same for both esters, since their reactivities are similar.

TABLE 4

Kinetic isotope effects for decomposition of carbamates in diphenyl ether * at 385—423 K

Compound	423 K	400 K	385 K
(1a,a')	1.94	2.28	2.55
(2a,a')	2.42	2.60	2.75
(3a,a')	2.04	2.23	2.38
(4a,a')	2.15	2.24	2.34

* Calculated from $k_H/k_D = A_H/A_D \exp (E_D - E_H)/RT$.

The k.i.e.s for decompositions in diphenyl ether of 1-phenylethyl and t-butyl carbamates containing one, two or, in the case of the latter compound, three CD_3 groups appeared to be cumulative (1.40 and 1.31 per CD_3, respectively)[5] and to show only slight temperature dependence and this, together with the value of 1.44 for the 1,1-diphenylethyl carbamate, led one of us to conclude that the effects were almost totally secondary with C–O bond-breaking kinetically the most significant process in all three compounds.

While values up to 1.44 per CD_3 can reasonably be attributed to β-D secondary isotope effects upon partial carbocation formation, though a little high compared with Shiner's data on t-butyl chloride solvolysis,[11] the new values reported here are well outside the range of plausible secondary effects and must contain at least an important contribution from a primary isotope effect upon C–H bond stretching. This conflicts with the previous conclusions that for t-butyl as well as for the phenyl-substituted carbamates, the k.i.e. should be attributed to cumulative secondary β-D effects solely.

We have found that it is possible to interpret the earlier results in a completely different manner, which leads to conclusions significantly different from our original position, and which gives a direct determination of the contribution of primary and secondary effects to the decomposition rates of t-butyl *N*-*p*-tolylcarbamates.

This new approach can be demonstrated most clearly in the case of $[^2H_3]$-, $[^2H_6]$-, and $[^2H_9]$-t-butyl *N*-*p*-tolylcarbamates for which k.i.e.s of 1.288, 1.750, and 2.59 at 463 K can be calculated from the Arrhenius parameters derived from the data in ref. 5. Isotopic substitution will have the following kinetic effects: a primary effect from differences in C–H (D) stretching; a small α-secondary effect from each of the other two deuteriums in the CD_3 group involved in elimination; and a β-secondary effect, from all the deuterium atoms, due to differences in interaction between H or D and the partial positive charge at C-1. [The γ-effect due to non-reacting CD_3 groups on C–H (D) stretching will be negligible.] Designating these effects as *a*(per D), *b*(per D), and *c*(per CD_3) respectively, we can write equations (1)—(3) which can be solved to give $c = 1.052$

$$\frac{k_{\mathrm{D}_3}}{k_{\mathrm{H}_9}} = \frac{2}{3c} + \frac{1}{3ab^2c} = 0.776 \qquad (1)$$

$$\frac{k_{\mathrm{D}_6}}{k_{\mathrm{H}_9}} = \frac{1}{3c^2} + \frac{2}{3ab^2c^2} = 0.571 \qquad (2)$$

$$\frac{k_{\mathrm{D}_9}}{k_{{}^1\mathrm{H}_9}} = \frac{1}{ab^2c^3} = 0.385 \qquad (3)$$

and $ab^2 = 2.232$. A simple calculation shows that the term ab^2 corresponds to the product isotope effect (p.i.e.) in the case of a concerted reaction. Redetermination of the olefin product distribution, at 463 K, by a more accurate n.m.r. analysis gives values of 2.23 and 2.26 for the $[^2H_3]$ and $[^2H_6]$ compounds respectively. (Previously reported as 2.30 and 2.26 at 472.2 K). Consequently the k.i.e. values for the t-butyl carbamates are seen to be consistent with a scheme involving a large primary isotope effect (assuming b^2 to be close to unity) and a small secondary effect (1.02 per D at 463 K).

For the monophenyl derivative we can write analogously two equations (4) and (5) only, which have the

$$\frac{k_{\mathrm{D}_3}}{k_{\mathrm{H}_6}} = \frac{1}{2c} + \frac{1}{2cab^2} = 0.703 \qquad (4)$$

$$\frac{k_{\mathrm{D}_6}}{k_{\mathrm{H}_6}} = \frac{1}{ab^2c^3} = 0.494 \qquad (5)$$

solutions, $c = 1.402$, $ab^2 = 1.029$; or $c = 1.44$, $ab^2 = 0.971$. The former, more likely solution would suggest that the introduction of one phenyl group produces a dramatic change in transition state character with the secondary isotope effect upon partial carbocation formation dominant and C–H stretching unimportant. If this is so, then the product and rate-determining transition states will be different and consequently ab^2 will no longer bear any relationship to the p.i.e. This is borne out by the value of 2.21 which we have recently obtained for the p.i.e. from the product distribution in the decompositions of 1-$[^2H_3]$methyl-1-phenylethyl *N*-*p*-tolylcarbamate at 463 K, indicating that transfer of the hydrogen occurs after breaking of the C–O bond. It should be pointed out, however, that the solution of these equations is very sensitive to the k.i.e. values. A 1% adjustment, well within experimental error, of the above values leads to $c = 1.17$ and $ab^2 = 1.44$ and, therefore to a rather different description of the transition state.

In the case of the diphenyl derivative there is only one reliable datum, $ab^2c = 1.44$, from which the only reliable conclusion is that neither ab^2 nor c is likely to exceed 1.44, though it is reasonable to assume that $c \geqslant 1.40$ if $c = 1.40$ for the monophenyl compound.

A plausible interpretation of all these results is that there is a spectrum of transition states for tertiary carbamate decompositions in solvent ranging from largely concerted for the aliphatic systems to carbocation-like in the diphenyl compound. The current view of solvolysis mechanisms also provides for a spectrum of transition states ranging from S_N2 through various types of ion-pairs to S_N1. For example Robertson *et al.*[12] have recently postulated that solvolysis of $ArCH_2X$ involves a rate-determining transition state $ArH_2\overset{\delta+}{C}\cdots\overset{\delta-}{X}$, wherein the $C\cdots X$ separation is greatest when the positive charge is most readily delocalised. The transition state for the carbamate decompositions may be written in an analogous way with the δ+ varying from zero to nearly unity. Maccoll [13] first proposed an intermediate of this type for acetate pyrolysis, but this has been largely ignored in recent years.

Maximum primary isotope effects are observed for hydrogen transfers involving symmetrical, linear transition states. Observed k.i.e. values of less than maximum may indicate therefore that the hydrogen is less, or more, than half-way transferred or that the six-membered ring is not planar, or both. The small primary k.i.e. and the p.i.e. of 2.21 for the monophenyl carbamate indicate that the C–H bond is not much altered in the rate-determining step but that H or D is eliminated from the incipient carbocation in just the same way as in the concerted reaction.

The assumption that these decompositions involve formation of the unstable (unknown) arylcarbamic acid (scheme) has been based solely on the analogy with acetate pyrolysis, without experimental evidence. We now find, however, that for carbamates of both tertiary alkyl alcohols and their phenyl-substituted derivatives the mass spectra obtained at ionization potentials (12—14 eV) just above the appearance potentials show, besides peaks due to the molecular ion, peaks at *m/e* 151 (or 152 for deuteriated compounds), 107 (or 108, 109), and at values attributable to the olefin fragments. The *m/e* 151 (152) and 107 (108, 109) peaks correspond to CH_3-$C_6H_4NHCO_2H$ (D) and $C_6H_3C_6H_4NH_2$ (HD,D_2) respectively. This, the first physical evidence for formation of arylcarbamic acids supports the view that hydrogen is transferred to the carbonyl oxygen in the thermal decompositions. Borrell first showed that photolytic, pyrolytic, and electron-impact induced eliminations of acids from esters follow the same mechanisms, and this has since been confirmed by other workers.[14]

Our theory of a spectrum of transition states accommodates not only our new data on highly congested systems, where the k.i.e.s can be considered as due largely to differences in the C–H and C–D bond fission, but also Kwart and Slutsky's work on t-butyl *NN*-dimethylcarbamate [2] where a k.i.e. close to the theoretical maximum was observed.

Isotope Effects, Reactivity, and Mechanism.—It has been suggested [3] that the reactivity of an ester is an indication of the degree of concertedness, the most reactive esters having the more carbocation-like transition states, and, more specifically, that the importance of C–H stretching and, consequently, of the primary k.i.e. will decrease with increasing reactivity. These ideas have been used as guide-lines for interpreting k.i.e.s relating to the decomposition of different types of ester, acetates, and carbonates, for example.[10]

Now our results indicate that (1) major structural changes such as replacement of two phenyl by two t-butyl groups result in gross mechanistic changes in which the less reactive of the two carbamates has the most ionic mechanism, and (2) even within a single series of closely related compounds the reactivity cannot be correlated directly with the isotope effect. Factors other than C–H stretching or C–O heterolysis must contribute to the reactivity.

The fact that the highly congested compounds are substantially more reactive than the simpler homologues can be attributed to steric acceleration. This expression implies that the energy of the initial state of the reaction is enhanced, relative to an unstrained system, rather more than is that of the corresponding transition state. Consequently the activation energy decreases. Although non-bonding interactions elongate the C–C-1 bonds and probably the O–C-1 bond also, there is no evidence from our results that this leads to a transition state of enhanced carbocationic character.

Even within the series under investigation the data do not appear to conform to any sort of relationship between reactivity and C–H stretching. The isotope effects for (2)—(4) are of the same order of magnitude as that calculated for the t-butyl carbamate, which is *ca.* 300—600 times less reactive. The calculated value of 2.68 at 423 K for this latter compound indicates a primary effect of *ca.* 2.30 (assuming the secondary effect is temperature independent). A secondary effect of the same magnitude in (2) indicates a primary effect of 2.30 also. For the two systems with cyclic substituents, (3) and (4), the k.i.e.s are about equal but are somewhat smaller than that of (2) and yet the reactivity order is (4) < (2) < (3).

The magnitude of the primary isotope effect will depend, *inter alia*, on the geometry of the six-membered ring system. It is known from molecular mechanics calculations that the Bu^t–C–Bu^t angle in structure (2) is rather greater than the normal tetrahedral angle, whereas in the cyclic analogues the opening of the corresponding angle is restricted by the ring. The angle O–C-1–C-2 will therefore tend to be smaller in (2) than in (3) and (4). It is possible that the smaller O–C-1–C-2 angle leads to greater planarity in the transition state and thus to greater linearity in the hydrogen transfer between the C-2 and carbonyl-O atoms than is possible for the more rigid tetramethyl cyclic systems. While this reasoning accounts for the similarity of the k.i.e.s it does not explain the difference in reactivities (*ca.* 14 times) of the two series (3) and (4). In the absence of specific information about the geometrical requirements of the transition state or the energetics of the reaction we are unable at present to rationalise satisfactorily either the isotope effects or the relative rates. It seems for this reason all the more unwise to assume that reactivity and C–H stretching are inter-related. Our data do not support this assumption nor do we have the means whereby to ' explain away ' this ' anomaly ', if it is to be considered as such.

In conclusion, our results demonstrate that the transition state for saturated tertiary alkyl carbamate decomposition, even in highly strained systems, is not carbocation-like. A self-consistent interpretation of new and previous k.i.e.s in terms of a spectrum of transition states ranging from highly concerted to more nearly carbocationic, in the case of the diphenylethyl derivative is proposed. An intriguing feature of this interpretation is that, contrary to expectation, the proposed mechanistic shift is not accompanied by large rate enhancements.

EXPERIMENTAL

Alcohols.—The tertiary alcohols were synthesised by reaction of the appropriate ketone with an ethereal solution of alkyl-lithium as described in ref. 8.

Carbamates.—The alcohols (0.03 mol) were stirred with *p*-tolyl isocyanate (0.03 mol) and tin(II) 2-ethylhexanoate (0.1 g) at room temperature until the mixture solidified (up to 60 h). The carbamate was extracted with light petroleum (b.p. 60—80°) and recrystallised from light petroleum. For the adamantyl derivative the alcohol was first dissolved in the minimum of toluene.

Kinetic Experiments.—Decomposition rates were followed by heating the carbamates (0.2—0.3 g) in diphenyl ether (20 ml) to within ± 0.4 °C of the required temperature in a silicone oil bath. The effluent gases were carried over to the gas-sampling loop (10 ml) attached to the g.l.c. and analysed periodically, as fully described in refs. 2 and 4.

Product analyses on (2a—c) were carried out by sealing small samples (5 mg) of the carbamate in diphenyl ether (0.2 ml) in Pyrex tubes and heating at 425 K for 10—15 half-lives. G.l.c. comparison with authentic samples on 10% Apiezon L obtained by pyrolysis of the corresponding *p*-nitrobenzoates gave the following yields of rearranged olefins: (2a), 0—1%, (2b), 0—1%, (2c), 1—2%, the remainder, more than 98% in all cases, consisting of the 1,1-di-t-butylalkene.

Product isotope effect determinations on $[^{2}H_{3}]$- and $[^{2}H_{6}]$-t-butyl carbamate are described in ref. 5. Decompositions of 1-$[^{2}H_{3}]$methyl-1-phenylethyl carbamate in diphenyl ether were carried out in n.m.r. tubes, heated in the oil bath in a specially designed outer jacket to prevent loss of olefin products due to volatilisation. The jacket consists of a bulb (length 30 mm) containing silicone oil and attached to a water-cooled reflux condenser (150 mm) whose internal diameter is just large enough to allow the n.m.r. tube to be inserted into the bulb so that its liquid contents could be heated, while the volatiles were cooled. The ratio of $C_6H_5(CD_3)C{=}CH_2$ to $C_6H_5(CH_3)C{=}CD_3$ after one and then ten half-lives was obtained using a Hitachi–Perkin-Elmer R24B n.m.r. spectrophotometer from the average of ten sets of integrations. The product ratio did not vary with time. Interference from the diphenyl ether solvent was minimised by running the spectra from high to low field.

This work was undertaken jointly under the European Science Exchange Programme. We thank our respective Universities for permission to partake in the scheme and the Centre National de la Recherche Scientifique, France, (J. S. L.) and the Royal Society for travel and maintenance awards.

[1/842 *Received, 27th May*, 1981]

REFERENCES

[1] R. Taylor, in ' Chemistry of the Functional Groups,' ed. S. Patai, Suppl. Vol. on Acid Derivatives, Wiley, New York, 1979, ch. 15.

[2] S. J. Ashcroft and M. P. Thorne, *Can. J. Chem.*, 1972, **50**, 3478; N. J. Daly and F. Ziolkowski, *J. Chem. Soc., Chem. Commun.*, 1972, 911; H. Kwart and J. Slutsky, *ibid.*, p. 552; R. Taylor and M. P. Thorne, *J. Chem. Soc., Perkin Trans. 2*, 1976, 799.

[3] R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1025.

[4] M. P. Thorne, *J. Chem. Soc., Perkin Trans. 2*, 1977, 879.

[5] M. P. Thorne, *J. Chem. Soc., Perkin Trans. 2*, 1978, 716; *J. Chem. Res.* (*S*), 1978, 222.

[6] J. E. Dubois, J. S. Lomas, and D. S. Sagatys, *Tetrahedron Lett.*, 1971, 1349; J. S. Lomas, D. S. Sagatys, and J. E. Dubois, *ibid.*, p. 599.

[7] J. S. Lomas, D. S. Sagatys, and J. E. Dubois, *Tetrahedron Lett.*, 1972, 165; J. E. Dubois and J. S. Lomas, *ibid.*, 1973, 1791.

[8] J. S. Lomas, P. K. Luong, and J. E. Dubois, *J. Org. Chem.*, 1979, **44**, 1647.

[9] G. Chuchani and I. Martin, *J. Chem. Soc., Perkin Trans. 2*, 1973, 663.

[10] H. B. Amin and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1090.

[11] V. J. Shiner, Jun., B. L. Muir, and G. Heineman, *J. Am. Chem. Soc.*, 1963, **85**, 2413.

[12] M. Ahson, R. E. Roberton, M. J. Blandamer, and J. H. W. Scott, *Can. J. Chem.*, 1980, **58**, 2142.

[13] A. Maccoll, *Adv. Phys. Org. Chem.*, 1965, **3**, 117.

[14] P. Borrell, *Nature*, 1960, **188**, 1002; also see for example, M. M. Green, J. M. Moldowan, and J. G. McGrewll, *J. Org. Chem.*, 1974, **39**, 2166; W. S. Briggs and C. Djerassi, *ibid.*, 1968, **33**, 1612; W. Benz and K. Biemann, *J. Am. Chem. Soc.*, 1964, **86**, 2375.