Kinetic Hydrogen Isotope Effects in the Thermal Decomposition of t-Butyl *N-p*-Tolylcarbamates

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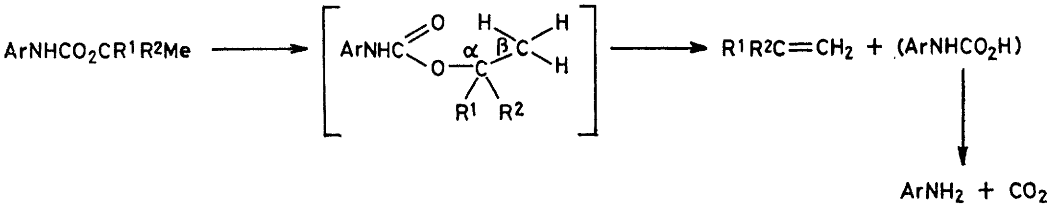
Kinetic isotope effects for the thermal decomposition of t-butyl-, [$^2H_3$]t-butyl-, [$^2H_6$]t-butyl-, and [$^2H_9$]t-butyl-*N-p*-tolylcarbamates have been determined in the range 473 ± 10 K. Multiple isotopic substitution leads to almost cumulative effects with $k_H : k_D$ per CD_3 *ca.* 1.31, indicating that these are secondary rather than primary isotope effects. Hyperconjugation of the CH_3 groups with the forming partial positive charge at the α-carbon atom is considered to be the major source of the isotope effects.

CARBAMATES of tertiary alcohols undergo thermal decomposition in inert solvents [1,2] or in the gas phase to yield olefins.[3-5] Kinetic studies of substituent effects have shown that the mechanisn is similar to that proposed for pyrolysis of other esters, *viz* a 6-membered cyclic transition state (see Scheme) and, from comparison of the rates of decomposition and the relative effects of substituents in different esters, it has been proposed that the importance of C–O bond-breaking increases (relative to C–H bond-breaking) in the order acetates < carbamates < carbonates.[6,7]



SCHEME

A few kinetic hydrogen isotope studies have been used to provide some information concerning the amount of C–H bond-breaking occurring in the transition state in ester decompositions. For ethyl acetate $k_H : k_D$ equal to 90% of the theoretical maximum * has been reported.[8] $k_H : k_D$ Values of *ca.* 80% theoretical were found by Taylor [9] for 1-phenylethyl and 1,2-diphenylethyl acetates. DePuy *et al.*[10] report similar results for pyrolysis of 1-methylcyclohexyl acetate and its [2,2,6,6-$^2H_4$]-isomer. All these effects have been interpreted as primary effects. However, both Blades [8] and DePuy [10] measured the intra- rather than the inter-molecular isotope effects and thus primary effects are to be expected.

In the carbamate series, Kwart and Slutsky [5] found $k_H : k_D$ values equal to the theoretical maximum for the

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* Calculated according to Wiberg's [11] method, assuming C–H bond fully broken and no tunnelling. For carbamates in this study ν_H = 2 980, ν_D = 2 335 cm^{-1}.

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

[4] N. J. Daly and F. Ziolkowski, *J.C.S. Chem. Comm.*, 1972, 911.

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

[7] M. P. Thorne, *J.C.S. Perkin II*, 1977, 879.

[8] A. T. Blades and P. W. Gilderson, *Canad. J. Chem.*, 1960, **38**, 1401, 1407.

[9] R. Taylor, *J.C.S. Perkin II*, 1972, 165.

[10] C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, 1959, **7**, 123.

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

t-butyl *NN*-dimethylcarbamate and its fully deuteriated isomers. They interpreted these results as implying complete C–H bond-breaking in the transition state. In an earlier publication [3] we reported a $k_H : k_D$ value of *ca.* 82% theoretical for decomposition of t-butyl and [$^2H_9$]t-butyl *N*-*p*-tolylcarbamates in diphenyl ether and a somewhat lower value for the gas-phase decomposition of these compounds.

However, although these values appear at first sight to be large enough to be interpreted as primary isotope effects, the possibility that they are cumulative secondary effects due to the multiple deuteriation cannot be ruled out. To decide upon these alternatives and hence to establish more precisely the relative importance of the α-C–O and β-C–H bond-breaking processes in decomposition of tertiary carbamates, the kinetic isotope effects for the series of *N*-*p*-tolylcarbamates of t-butyl alcohol and the three of its deuteriated isomers which have one, two, and three methyl groups fully deuteriated respectively have been investigated.

RESULTS AND DISCUSSION

Rate constants and $k_H : k_D$ ratios for the carbamate decompositions are given in Tables 1 and 2. The isotope effects show a small temperature variation and for the most highly deuteriated compound this is about the same as the temperature dependance of the theoretical values, so that $k(H_9) : k(D_9)$ is always *ca.* 82% of the theoretical maximum. In comparison with $k_H : k_D$ for 1-methylcyclohexyl acetate (81% of theory) our results seem somewhat high for a primary effect, since other evidence clearly points to a greater degree of C–O bond heterolysis in tertiary carbamates than in tertiary acetates and therefore less C–H bond rupture in the rate-determining step.

TABLE 1

Rate constants for decomposition of isotopically substituted *N*-*p*-tolylcarbamates in diphenyl ether

T/K	$10^5k(H_9)$/ s^{-1} *	$10^5k(D_3)$/ $s^{-1\,a}$	$10^5k(D_6)$/ $s^{-1\,a}$	$10^5k(D_9)$/ $s^{-1\,a}$
463.5	9.22		5.20	3.55
465.9	10.92	8.03	6.30	4.21
468.5	13.66	10.44	7.80	5.31
472.7	19.46	14.80	11.40	7.65
479.0	29.99	22.82	17.56	11.91
484.0				16.26

* $k(H_9)$ = rate constant for protium compound; $k(D_3)$, $k(D_6)$, $k(D_9)$ = rate constants for carbamates containing 1, 2, and 3 CD_3 groups respectively.

Values are averages from two or three experiments.

TABLE 2

Isotope effects in the decomposition of isotopically substituted t-butyl *N*-*p*-tolylcarbamates in diphenyl ether

	$(CH_3)_2C(CD_3)$·carb.*		$(CH_3)C(CD_3)_2$·carb.		$(CD_3)_3C$·carb.	
T/K	$k(H_9) : k(D_9)$	K.i.e. per CD_3	$k(H_9) : k(D_6)$	K.i.e. per CD_3	$k(H_9) : k(D_9)$	K.i.e. per CD_3
463.5			1.77	1.33	2.59	1.37
465.9	1.36	1.36	1.73	1.32	2.59	1.37
468.5	1.31	1.31	1.75	1.32	2.57	1.37
472.7	1.31	1.31	1.71	1.31	2.54	1.36
479.0	1.31	1.31	1.71	1.31	2.52	1.36

* carb. = $O_2CNHC_6H_4CH_3$. Maximum error in k.i.e. determinations = ±6%.

The intramolecular isotope effect for the [$^2H_6$]t-butyl carbamate, obtained from the yields of $CH_2{=}C(CD_3)_2$ and $CD_2{=}C(CH_3)CD_3$ determined by n.m.r. spectroscopy, was found to be *ca.* 2.26 (472.7 K). A similar value (2.30) was also found for the [$^2H_3$]t-butyl carbamate, though this result is less reliable, as the signal for the $=CH_2$ protons was small compared with the signal for the $C{-}CH_3$ protons. These are primary effects and are *ca.* 72% of the theoretical maximum.

If the observed intermolecular isotope effects are primary effects, the observed rate constants $k(D_3)$ and $k(D_6)$ for the two partially deuteriated carbamates contain contributions from both C–H and C–D bond-breaking eliminations, since the analytical method to determine the rate constants did not allow for a distinction to be made between the two decomposition pathways. The ' true ' isotope effects can be calculated from the equations $[k(D_3) : k(H_9)]_{obs} = (2 \times 1 \div 3) + (1 \div 3a)$ and $[k(D_6) : k(H_9)]_{obs} = (1 \div 3) + (2 \div 3b)$, where a and b are the $k_H : k_D$ values for deuteriation of one and two methyl groups respectively. Unless the non-reacting CD_3 groups in the $^2H_6$ and $^2H_9$ compounds contribute to the kinetic isotope effect by secondary effects, a, b, and $k(H_9)/k(D_9)$ should be the same, if the isotope effect is primary. Insertion of the values for $k(D_3) : k(H_9)$ at 472.7 K gives $a = 3.45$ and $b = 2.65$ [*cf.* $k(H_9) : k(D_9) = 2.55$].

Thus multiple deuteriation leads to different values for $k_H : k_D$, which are, in turn, different from the (primary) intramolecular isotope effect. Moreover the calculated value for the $^2H_3$ compounds (3.25) is greater than the theoretical maximum (3.11) at that temperature. The rate reduction produced by isotopic substitution must, therefore, be due in whole or in part to secondary effects.

The cumulative nature of secondary isotope effects in the solvolysis of Bu^{t}Cl and its $^2H_3$, $^2H_6$, and $^2H_9$ isomers (298 K; 60% aqueous ethanol) has been convincingly demonstrated by Shiner [12] *et al.*, who showed that $[k(H_9) : k(D_9)]^{\frac{1}{3}} = [k(H_9) : k(D_6)]^{\frac{1}{2}} = k(H_9) : k(D_3)$. A similar cumulative effect is observed in the carbamate decompositions (Table 2) although the values of $k_H : k_D$ per CD_3 for the $^2H_9$ compound are consistently a little higher than those for the other two deuteriated compounds. It would appear, therefore, that the observed rate retardation arises mainly from secondary effects of β-deuterium substitution on the formation of the partial positive charge at the α-carbon.

[12] V. J. Shiner, jun., B. L. Muir, and G. Heineman, *J. Amer. Chem. Soc.*, 1963 **85**, 2413.

Secondary isotope effects for unimolecular S_N1–E_1 reactions of Bu^{t}Cl have usually been attributed to the decrease in hyperconjugation with the carbonium ion resulting from substitution of CD_3 for CH_3. If this is the case in carbamate decompositions, more reactive carbamates (in which carbonium ion formation is, presumably, further advanced) would be expected to show larger isotope effects. This is precisely what is found for t-butyl *N*-phenylcarbamate and its [$^2H_9$]t-butyl isomer. In diphenyl ether at 468 K the *N*-phenylcarbamate decomposes *ca.* 1.38 times as fast as the corresponding *N-p*-tolylcarbamate and gives a kinetic isotope effect of 2.80.

It is somewhat surprising that the $k(H_9) : k(D_9)$ values for the carbamate eliminations are of the same magnitude as those for solvolysis of Bu^{t}Cl, in view of the difference in temperature at which the reactions are done and the fact that carbonium-ion formation is not very far advanced in the transition state of the carbamate reactions, as evidenced by the small substituent and solvent effects and the yields of but-1-ene and but-2-ene from t-pentyl carbamates.[2] In the solvolysis reactions, Shiner[13] has shown that the isotope effects are larger when the ratio of elimination to substitution is larger. Thus $k(H_9) : k(D_9)$ for elimination reactions at room temperature is presumably considerably in excess of the reported values (2.30—2.62 depending on solvent) which contain contributions, from both S_N1 and E_1 reaction pathways.

Nevertheless, for secondary effects our results might be considered somewhat high if hyperconjugation differences are the sole cause. In these reactions, contributions to the isotope effect may also arise from differences in the C–H and C–D bond lengths, which will lead to different energy requirements for formation of the cyclic transition state.

Some stretching of the β-C–H bond must also occur in the transition state, so that small contributions to the isotope effect can arise from differences in the vibrational frequencies of the C–H and C–D bonds. This may account, in part, for the departure from cumulative behaviour of the isotope effects observed for the $^2H_3 \longrightarrow {}^2H_9$ compounds.

The values of $k_H : k_D$ per CD_3 are consistently larger for the $^2H_9$ compound. The estimated maximum error in determination of the kinetic isotope effects is ±6%, which could lead to overlap of the three sets of $k_H : k_D$ values. However, application of Student's *t* test[14] to the data indicates a 99% confidence level that the differences shown in Table 2 are real.

Solvation effects are also important in these decompositions[3] and may contribute in a non-cumulative manner to the isotope effects.

The overall pattern presented here, however, clearly supports the view that in decompositions of t-butyl N-*p*-tolylcarbamates heterolysis of the α-C–O bond is of major importance in the rate-determining step.

EXPERIMENTAL

2-*Methyl*[1,1,1-$^2H_3$]*propan*-2-*ol* was prepared from CD_3I (Aldrich Chem. Co. Ltd. 99+ atom % D) and analytical grade acetone *via* a Grignard reaction, as described by Shiner;[12] yield 40%.

2-*Methyl*[1,1,1,3,3,3-$^2H_6$]*propan*-2-*ol* was prepared in the same manner as the preceding compound except that CH_3I and $(CD_3)_2C{=}O$ (Aldrich Chem. Co. Ltd. 99.5 atom % D) were used; yield 40%.

2-[$^2H_3$]*Methyl*[1,1,1,3,3,3-$^2H_6$]*propan*-2-[$^2H_1$]*ol* was obtained commercially (Aldrich Chem. Co. Ltd. 99+ atom % D). The hydroxylic deuterium exchanged with protium during the carbamate preparation so that the final compound contained deuterium in the t-butyl group only.

Carbamates. These compounds were prepared by treating the alcohol (0.1 mol) with *p*-tolyl isocyanate (0.11 mol) in toluene at 333 K in the presence of tin(II) 2-ethylhexanoate as described in ref. 15. After recrystallisation from light petroleum (b.p. 60—80 °C) the carbamates were sublimed *in vacuo*; n.m.r. spectroscopy (JEOL JNM-FX100) showed that the deuterium content was better than 99% of the expected value.

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

Kinetic Method.—The carbamates (0.4 g) in diphenyl ether (20 ml) were heated to within ±0.5 °C of the required temperature using a silicone-oil bath. Helium at a constant flow rate was used to carry over the effluent gases. The first-order reaction rates were obtained by periodic analysis of these gases using g.l.c. as described fully elsewhere.[1,2]

The intramolecular isotope effect for the [$^2H_6$]t-butyl carbamate was obtained by trapping the olefinic products in $(CD_3)_2C{=}O$ using solid CO_2–acetone. The solution was transferred to an n.m.r. tube and sealed.

The relative yields of the two olefins were calculated from the averages of four integrations of each of the proton n.m.r. signals after making appropriate statistical corrections. A similar method was used for the [$^2H_3$]t-butyl carbamate.

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