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ION PAIRS IN SOLVOLYSIS REACTIONS. KINETIC DEUTERIUM ISOTOPE EFFECTS FOR DEPROTONATION OF CARBOCATION INTERMEDIATES IN AQUEOUS SOLVENT

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ABSTRACT

Solvolysis of 2-X-2-phenylpropane (**1-X**) in 25 vol% acetonitrile in water at 25 °C produces 2-hydroxy-2-phenylpropane (**1-OH**) and 2-phenylpropene (**3**). The carbocationic intermediate discriminates between different nucleophiles; azide anion, acetate anion, and methanol are more efficient nucleophiles than water, k_{N_3}/k_{H_2O} = 42, k_{OAc}/k_{H_2O} = 3, and k_{MeOH}/k_{H_2O} = 2·9 (ratio of second-order rate constants). The fraction of the elimination product **3** increases with increasing basicity of the leaving group X as well as by addition of general bases. The Brønsted parameter for this catalysis is small, β = 0·13, with substituted acetate anions. The kinetic deuterium isotope effect for the dehydronation of the intermediate has been measured (assuming the reaction from intermediate to alcohol is insensitive to isotopic substitution) employing the hexadeuterated substrate **d$_6$-1-X** as $k_3^{H}/k_3^{d_6}$ = 3·5 ± 0·2 for the chloride **1-Cl** with acetate anion, and, without added base, 3.1 ± 0·2 for the acetate **1-OAc**, and 3·1 ± 0·2 for the *p*-nitrobenzoate **1-PNB**, respectively, and ~5 for the protonated methyl ether **1-OMeH$^+$**. The variation in isotope effect with change in leaving group is discussed in terms of elimination from contact ion pairs and 'free' carbocation. The overall kinetic isotope effect for the solvolysis was found to be $k_{obs}^{H}/k_{obs}^{d_6}$ = 1·31 (**1-OMeH$^+$**), 1·38 (**1-OAc**), 1·40 (**1-PNB**), and 5·7 (**1-OH$_2^+$**). These isotope effects consist of the isotope effect $k_{12}^{H}/k_{12}^{d_6}$ for the formation of the substitution product **1-OH** and $k_{13}^{H}/k_{13}^{d_6}$ for production of the olefin **3**. It is concluded that the latter isotope effect is enlarged owing to a branched mechanism in which the deprotonation of the carbocationic intermediate competes with formation of the substitution product. As large an isotope effect as $k_{13}^{H}/k_{13}^{d_6}$ ~6·5 has been measured for **1-OMeH$^+$**.

INTRODUCTION

The abstraction of a β-hydron from a short-lived carbocation or ion-pair intermediate is expected, according to the Hammond postulate, to proceed via a transition state that closely resembles the high-energy intermediate. Partial carbon—hydrogen bond breaking provides stabilization of the intermediate and is expected to have an influence on the product composition as well.[1,2] This hyperconjugation, and not a large degree of proton transfer, should be the factor responsible for the high preference of the more stable olefin that is generally (but not always) seen in elimination reactions of this type.[2,3]

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The elimination product in a solvolysis reaction may derive from the initially formed ion pair (or ion–molecule pair) or from the solvent-equilibrated ('free') ion:

$$\begin{tikzcd}
\mathbf{RX} \arrow[r] & \text{ion pair(s)} \arrow[rr] \arrow[dr, "-HX"'] & & \mathbf{R}^+ \arrow[r, "SOH"] \arrow[dl, "-H^+"] & \mathbf{ROS} \\
& & \text{olefin} & &
\end{tikzcd} \tag{1}$$

Kinetic deuterium isotope effects and Brønsted parameters constitute potential tools for obtaining information about the transition state of the hydron-removal step. Accordingly, the magnitude of the kinetic deuterium isotope effect for this step should be a function of, for example (i) the acidity of the hydron, (ii) structure and solvation of the hydron-abstracting base (which may be the solvent, added base, or the leaving group of the ion pair or ion–molecule pair), (iii) the degree of hyperconjugation of the carbon—hydrogen bond, (iv) the degree of deviation from linearity of the hydron-removal process, (v) the nature of the intermediate (ion pair or free ion). These factors are, of course, correlated but a separation of this kind may make it easier to rationalize and understand the relation between isotope effect and structure.

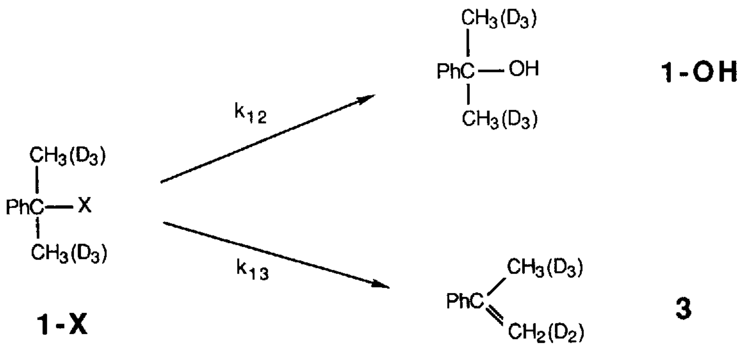
Nearly twenty years ago, Smith and Goon studied the ethanolysis of cumyl derivatives, i.e., 2-X-2-phenylpropane (**1-X**).[4] The kinetic deuterium isotope effect for the dehydronation step was measured for the leaving groups X=Cl, *p*-nitrobenzoate, and thionebenzoate as $k_3^{H}/k_3^{d_3} = 3{\cdot}15$, 2·53, and 1·75, respectively, at 25 °C. (After recalculation of the data in Reference 4 to 25 °C). These values were obtained from product ratios (3,3,3-$^2H_3$)-2-phenylpropene to (1,1-$^2H_2$)-2-phenylpropene employing substrates having one of the methyl groups fully deuterated. Isotope effects may also be calculated from the measured product ratios of olefin to alcohol that, for the dehydronation step, yield $k_3^{H}/k_3^{d_6}$ ~3·3, 2·6, and 2·2, respectively, at 25 °C.[4] The question arises: what is the reason to the variation in isotope effect?

In order to favor diffusional separation to 'free' carbocation relative to reactions occurring directly from the ion pairs (including internal return), cumyl derivatives are solvolyzed in the present work in a highly aqueous medium. Even in this strongly dissociating solvent there is variation in $k_3^{H}/k_3^{d_6}$ with leaving group. The results are discussed in terms of elimination from both ion pairs and free carbocation.

RESULTS

The solvolysis of 2-X-2-phenylpropane (**1-X**) at a constant ionic strength of 0·75 M ($NaClO_4$) in 25 vol% acetonitrile in water at 25 °C yields 2-hydroxy-2-phenylpropane (**1-OH**) and 2-phenylpropene (**3**) (Scheme 1). Weak bases, such as substituted acetate anions, increase the fraction of elimination product. The catalytic effect of AcO^- is shown in Figure 1. However, the main product is the alcohol **1-OH**, even at rather high concentration of other nucleophiles or in the presence of strong bases (Table 1).

Addition of sodium azide (0·75 M) yields a product ratio [**1-N$_3$**]/[**1-OH**] = 0·75, sodium acetate (0·75 M) gives [**1-OAc**]/[**1-OH**] = 0·054, and 25 vol% methanol in water (ionic strength 0 M) gives [**1-OMe**]/[**1-OH**] = 0·44. From these results, the discrimination between water and



$X = Cl, AcO, PNB, Me^+OH, H_2O^+$

Scheme 1

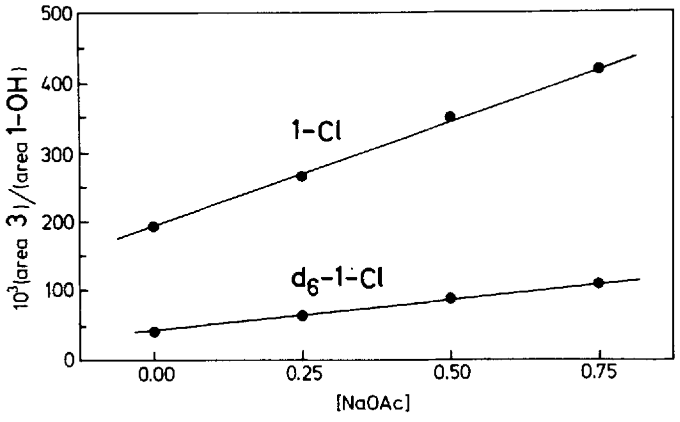


Figure 1. The increase in the olefin/alcohol product ratio for the reaction of **1-Cl** and **d$_6$-1-Cl** with increasing concentration of OAc^- in 25 vol% acetonitrile in water; ionic strength 0·75 M maintained with sodium perchlorate

other nucleophiles for reaction with the carbocationic intermediate can be calculated as $k_{N_3}/k_{H_2O} = 42$, $k_{OAc}/k_{H_2O} = 3$, and $k_{MeOH}/k_{H_2O} = 2{\cdot}9$ (ratio of second-order rate constants).

The kinetics of the reactions were studied by a sampling high-performance liquid chromatography (HPLC) procedure. The measured rate constants and reaction conditions are shown in Table 2. The chloride **1-Cl** reacts very rapidly and it was not possible to study the rate by HPLC.The isotope effects for the reactions were obtained from kinetic and product data wih (1,1,1,3,3,3-$^2H_6$)-2-X-2-phenylpropane (**d$_6$-1-X**)(Table 2). The calculation of the isotope effect on k_3 is based upon the assumption that the reaction from the common carbocationic intermediate to alcohol is insensitive to isotopic substitution.[1,2]

Table 1. Product compositions and elimination rate constants for the reaction of **1-Cl**, **1-OAc**, **1-PNB**, and **1-OMe** in 25 vol% acetonitrile in water at 25·00 ± 0·03 °C

Substrate	Salt	10^3[**3**]/[**1-OH**]	$10^{-6}k_3$,[a] $\text{M}^{-1}\text{s}^{-1}$
1-Cl	0·75 M $NaClO_4$	<5[b]	<0·6[b,c]
	0·75 M NaOAc	10·9	39
	0·75 M $NaOOCCH_2OMe$	10·1	34
	0·75 M $NaOOCCH_2CN$	8·3	22
	0·75 M $NaOOCCF_3$	6·6	11
	0·75 M NaOH	~30	
1-OAc	0·75 M $NaClO_4$	35	
1-PNB	0·75 M $NaClO_4$	19	
1-OMe	0·71 M $NaClO_4$ 0·04 M $HClO_4$	1	

[a] The elimination from the intermediates(s); based upon the product compositions and the rate constant $k'_{H_2O} = 1{\cdot}2 \times 10^8 \times 41{\cdot}67\ s^{-1}$.

[b] Upper limit; it was not possible to show that **1-Cl** was completely free of **3**.

[c] A water concentration of 41·67 M was used to calculate the second-order rate constant.

Table 2. Rate constants and isotope effects for the reactions of **1-Cl**, **1-OAc**, **1-PNB**, **1-OMe**, and **1-OH** and the (1,1,1,3,3,3-$^2H_6$)-analogues in 25 vol% acetonitrile in water at 25·00 ± 0·03 °C[a]

Substrate[b]	$10^6(k_{12} + k_{13})$, s^{-1}	$(k_{12} + k_{13})^H/(k_{12} + k_{13})^{d_6}$	$k_{13}^H/k_{13}^{d_6}$	$k_3^H/k_3^{d_6}$ [c]
1-Cl, d$_6$-1-Cl				3·5 ± 0·2
1-OAc	5·06	1·38 ± 0·06	4·1 ± 0·2	3·1 ± 0·2
d$_6$-1-OAc	3·66			
1-PNB[d]	105·7	1·40 ± 0·06	4·3 ± 0·2	3·1 ± 0·2
d$_6$-1-PNB[d]	75·3			
1-OMe[e]	110·0	1·31 ± 0·06	~6·5	~5
d$_6$-1-OMe[e]	84·2			
1-OH[f]	0·16		5·7 ± 0·2	
d$_6$-1-OH[f]	0·028			

[a] Ionic strength 0·75 M maintained with sodium perchlorate.

[b] Concentration: 2 mM unless specified.

[c] Based upon equation (2) assuming $k_2^H/k_2^{d6} = 1$.

[d] Concentration: 0·2 mM.

[e] $[HClO_4]$ = 41·7 mM.

[f] $[HClO_4]$ = 83·3 mM.

DISCUSSION

The carbocationic intermediate shows a relatively low selectivity toward different nucleophiles. The k_{N_3}/k_{H_2O} value of 42 measured for the chloride **1-Cl** is similar to the value of ~50 obtained in the same medium for the solvolysis of 3-(2-chloro-2-propyl)indene at 35 °C[5] and to the value of 40 measured for the related 1-chloro-1-(4-methylphenyl)ethane in 50% trifluoroethanol in water.[6] The selectivity is, however, considerably larger than that shown under the same reaction conditions as in this work for 9-(2-chloro-2-propyl)fluorene for which a discrimintion ratio of k_{N_3}/k_{H_2O} ~5 has been measured.[1] It was concluded that this small k_{N_3}/k_{H_2O} value reflects nucleophilic attack mainly at the ion pair stage, i.e. diffusional separation does not compete favorably with direct reaction of the highly reactive ion pair.

Assuming a diffusion-controlled reaction of the cumyl cationic intermediate with azide anion, with $k_d = 5 \times 10^9$ M^{-1}s^{-1}, makes it possible to calculate approximate rate constant values for the nucleophilic attack on the cation.[1,5,6] This assumption is in accord with the conclusion that ring-substituted 1-phenylethyl carbocations, which show both larger and smaller selectivities than the cumyl cation, react with the azide anion with diffusion-limited rate constants.[6] Thus the reaction with solvent water to form **1-OH** has a rate constant of about 5×10^9 s^{-1}, i.e. $k_{H_2O} \sim 1{\cdot}2 \times 10^8$ M^{-1}s^{-1}; the reaction with methanol is 2·9 times as fast, $k_{MeOH} \sim 3{\cdot}5 \times 10^8$ M^{-1}s^{-1}. The latter value is somewhat smaller than that measured for the 1-(4-methylphenyl)ethyl cation ($6{\cdot}6 \times 10^8$ M^{-1}s^{-1}).[6] The acetate anion is about 3 times more effective in attacking the intermediate than a water molecule.

The increase in elimination to substitution product ratio with increase in basicity of the leaving group X (Table 1) indicates that X^- is involved in the reaction from intermediate to elimination product. Accordingly, a significant part of the elimination seems to occur directly from the ion pair, presumably with the leaving group acting as the proton abstractor.[1,2,6,7] It is possible that, to some extent, the substitution products are also formed via a one-step reaction from the ion pair. The results of the isotope-effect measurements, which will be discussed in detail below, constitute a strong indication that the elimination and the substitution reactions are not separate, parallel reactions but are couple via a common intermediate, most reasonably of ion-pair type.

Equation (2) shows a simplified mechanism without any explicit indication of diffusional separation of the ion pair. It is kinetically indistinguishable from a more complex reaction scheme involving solvent-separated and free ions that continue rapidly to substitution product.

$$\begin{tikzcd}
\mathbf{RX} \arrow[r, shift left, "k_1"] & \mathbf{R^+X^-} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, "k_3"] & \mathbf{ROH} \\
 & \text{olefin} &
\end{tikzcd} \qquad (2)$$

The small kinetic isotope effects k^H/k^{d_6} on the observed rate constants for X = HOMe$^+$, OAc, or PNB(~1·05/β-D) indicate that the hyperconjugative stabilization effect of the hydrons of the methyl groups is small. Stepwise solvolysis reactions usually show isotope effects of 1·10 ± 0·05/β-D.[8] For example, the hydrolysis of 9-(1,1,1,3,3,3-$^2H_6$)-9-(2-chloro-2-propyl)fluorene under the same reaction conditions as in this work exhibits an isotope effect of $k^H/k^{d_6} = 2{\cdot}2$ (1·14/β-D).[1] The fluorene substituent has a destabilizing effect on the ionization transition state. Accordingly, a large stabilization effect from hyperconjugation is required. On the other hand, it is likely that the small values measured for the **1-X** substrates are attributable to the stabilization effect of the phenyl group that reduces the need for hyperconjugative stabilization from the bonds to the hydrons. The secondary β-deuterium isotope effects measured for carbocation solvolysis of *p*-substituted 1-(chloro-1-phenyl)ethanes in 50% ethanol–water are ~1·05/β-D,[9] the value changing with substituent on the benzene ring.

The mechanistic scheme shown in equation (2) corresponds to the following relations between phenomenological and microscopic rate constants:

$$k_{12} = k_1k_2/(k_{-1} + k_2 + k_3) \tag{3}$$

$$k_{13} = k_1k_3/(k_{-1} + k_2 + k_3 \tag{4}$$

$$k_{12} + k_{13} = k_1(k_2 + k_3)/(k_{-1} + k_2 + k_3) \tag{5}$$

The expressions for the isotope effects are:

$$k^{\mathrm{H}}_{12}/k^{\mathrm{D}}_{12} = (k^{\mathrm{H}}_1/k^{\mathrm{D}}_1)(k^{\mathrm{H}}_2/k^{\mathrm{D}}_2)(k^{\mathrm{D}}_{-1} + k^{\mathrm{D}}_2 + k^{\mathrm{D}}_3)/(k^{\mathrm{H}}_{-1} + k^{\mathrm{H}}_2 + k^{\mathrm{H}}_3) \tag{6}$$

$$k^{\mathrm{H}}_{13}/k^{\mathrm{D}}_{13} = (k^{\mathrm{H}}_1/k^{\mathrm{D}}_1)(k^{\mathrm{H}}_3/k^{\mathrm{D}}_3)(k^{\mathrm{D}}_{-1} + k^{\mathrm{D}}_2 + k^{\mathrm{D}}_3)/(k^{\mathrm{H}}_{-1} + k^{\mathrm{H}}_2 + k^{\mathrm{H}}_3) \tag{7}$$

$$(k^{\mathrm{H}}_{12} + k^{\mathrm{H}}_{13})/(k^{\mathrm{D}}_{12} + k^{\mathrm{D}}_{13}) = (k^{\mathrm{H}}_1/k^{\mathrm{D}}_1)[(k^{\mathrm{H}}_2 + k^{\mathrm{H}}_3)/(k^{\mathrm{D}}_2 + k^{\mathrm{D}}_3)][(k^{\mathrm{D}}_{-1} + k^{\mathrm{D}}_2 + k^{\mathrm{D}}_3)/(k^{\mathrm{H}}_{-1} + k^{\mathrm{H}}_2 + k^{\mathrm{H}}_3)] \tag{8}$$

Reaction branching in accord with equation (2) may cause enlarged and attenuated isotope effects. Let us assume for simplicity that internal return is slow ($k_{-1} << k_2, k_3$). For example, the isotope effect $k^{\mathrm{H}}_{13}/k^{\mathrm{D}}_{13}$ (equation (7)) has a maximum value of $(k^{\mathrm{H}}_1/k^{\mathrm{D}}_1) \times (k^{\mathrm{H}}_3/k^{\mathrm{D}}_3)$ for $k_2 >> k_3$ and $k^{\mathrm{H}}_2 \sim k^{\mathrm{D}}_2$, i.e. the isotope effect is a product of the secondary isotope effect on ionization and the primary isotope effect on hydron abstraction. If the secondary isotope effect is large, the result may be a considerable elimination isotope effect $k^{\mathrm{H}}_{13}/k^{\mathrm{D}}_{13}$. The isotope effect on k_{12} is equal to the ionization isotope effect under these conditions, $k^{\mathrm{H}}_{12}/k^{\mathrm{D}}_{12} = k^{\mathrm{H}}_1/k^{\mathrm{D}}_1$. On the other hand, a considerable amount of elimination causes a decrease in $k^{\mathrm{H}}_{12}/k^{\mathrm{D}}_{12}$ (cf. equation (6)) as well as a smaller than maximum $k^{\mathrm{H}}_{13}/k^{\mathrm{D}}_{13}$.

Branching as the cause of unusually large and unusually small kinetic isotope effects has been discussed previously for reactions that are coupled via a common carbanion intermediate[10] and for solvolysis reactions;[1,2,11] A solvolytic system that is not accompanied by substitution but by return may also exhibit an enlarged overall elimination isotope effect owing to the competition between return and dehydronation of the carbocation intermediate that follows a common ionization step.[12]

The large values of $k^{\mathrm{H}}_{13}/k^{\mathrm{D}}_{13}$ (Table 2) strongly indicate that the substitution and elimination reactions employ a common intermediate, the ion pair and/or the solvent equilibrated carbocation. The ion-molecule pairs formed from the protonated ether and alcohols may be intermediates provided that they have lifetimes long enough ($k < 10^{13}\,\mathrm{s}^{-1}$); otherwise they are only encounter complexes for the reverse reaction, the nucleophilic attack on the carbocation.[13]

As is exemplified by the reaction of **1-OH$_2^+$**, the competing reaction does not have to be visible to cause enlarged isotope effects. Such a reaction is the degenerate nucleophilic trapping of the intermediate with solvent water that gives back starting material. Owing to this competition from a common intermediate, the isotope effect on k_{13} is enlarged. If the reactions had been parallel instead, an isotope effect on k_{13} equal to $k^{\mathrm{H}}_1/k^{d_6}_1$ would have been measured (assuming slow internal return, equation (7)). Accordingly, this type of competition, a kind of 'external return', has the same effect on $k^{\mathrm{H}}_{13}/k^{d_6}_{13}$ as that of internal return.

It is difficult to draw any conclusion about the amount of internal return. A sizeable fraction of elimination combined with an increasing isotope effect on $k_{12} + k_{13}$ with increasing basicity of the leaving group should have been a strong indication for the importance of internal return. However, the amount of elimination product is very small for all the leaving groups

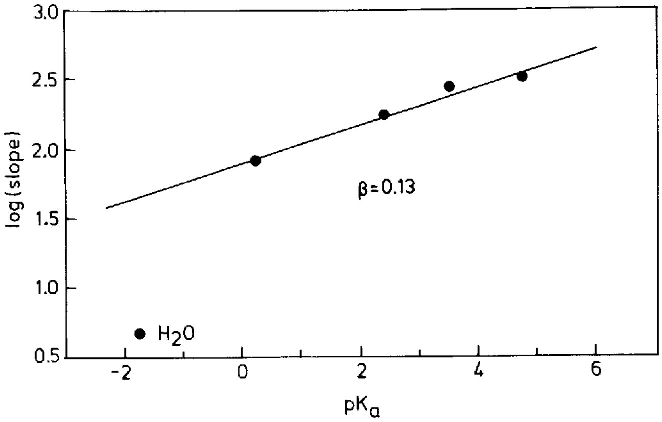


Figure 2. Brønsted plot for the deprotonation of the carbocationic intermediate(s) formed from **1-Cl** in 25 vol% acetonitrile in water; ionic strength 0·75 M maintained with sodium perchlorate. The pK_a values refer to water.[14] The log (slope) of the ordinate is obtained from plots of olefin/alcohol product ratios versus base concentration as shown in Figure 1

besides H_2O^+, which gives an intermediate that undergoes external return, i.e. a 'degenerate' substitution reaction with solvent water that gives back the starting material. Comparison with data for the other leaving groups indicates that this trapping of the cation with water is fast. Accordingly, the present results may be rationalized without invoking internal return.

Smith and Goon have measured $k^{H}_{obs}/k^{d_6}_{obs}$ for ethanolysis of **1-Cl**, **1-PNB**, and **1-thionebenzoate** as 1·46 (25 °C), 1·63 (100 °C), and 1·94 (50 °C), respectively.[4] Since these reactions yield a considerable amount of elimination product, which increases with the increase in k^{H}_{obs}/k^{d6}_{obs}, the variation in isotope effect on k_{obs} is presumably the result of partially reversible ionization combined with a variation in the fraction of elimination product (cf. equation (8)). These results argue against rapid internal return in the much more strongly ionizing solvent employed in the present work.

Figure 2 shows a Brønsted plot for the deprotonation of the carbocationic intermediate formed from **1-Cl** with substituted acetate anions. The deprotonation by water is about one magnitude less effective. The value of 0·13 indicates an 'early' transition state for the deprotonation step. The value of the Brønsted parameter is similar to that measured for 1-chloro-1-(4-methylphenyl)ethane in 50% trifluroethanol in water (β = 0·14)[6] as well as to β = 0·14 and 0·16, for formation of the Hofmann and Saytzev olefin, respectively, in the solvolysis of 3-(2-chloro-2-propyl)indene.[2] As discussed above, the intermediates formed in these reactions show similar reactivity toward nucleophiles as the cumyl cation. A considerably smaller value (β = 0·05) has been obtained for the highly unstable ion pair formed from 9-(2-chloro-2-propyl)fluorene.[1]

Based upon the low yield of olefin, it is concluded that the proton abstraction is activation limited. Accordingly, the calculated rate constants for the proton abstraction are low (Table 1). The rate for deprotonation by acetate anion is about 600 times slower than the corresponding reaction in the solvolysis of 9-(2-chloro-2-propyl)flourene,[1] and approximately three times faster per proton than the proton removal from the (4-methylphenyl)ethyl cation.[6] The diffusional separation of the ion pair is expected to be much faster than the deprotonation; the rate constant should be $\sim 10^{10}\,s^{-1}$.

The degree of proton transfer from the intermediate in the reaction of **1-Cl** is also expressed by the isotope effect $k_3^H/k_3^D = 3{\cdot}5$ (Table 2). This value is somewhat larger than those obtained with the more basic leaving groups OAc^- and PNB^- (Table 2) but is smaller than that measured for **1-OMeH$^+$**. The isotope effect of 5 may seem very large. However, since the methyl groups are triple-deuterated, a normal secondary isotope effect is exerted on k_3 by the two non-abstracted hydrons in addition to the primary isotope effect. For instance, if this secondary effect is 10% per deuterium, the primary isotope effect k_3^H/k_3^{d6} for **1-OMeH$^+$** is $5/1{\cdot}1^2 = 4{\cdot}1$. It was not possible to measure the isotope effect on k_3 for **1-OH$_2^+$** but it is reasonably large owing to the large isotope effect $k_{13}^H k_{13}^{d_6}$ of 5·7. A significantly larger isotope effect on the deprotonation step for $X = OH_2^+$ than for $X = Cl$ has been found previously.[2] A plausible explanation is that, with a less basic leaving group like OH_2 and MeOH, the elimination does not occur at the ion-pair stage but from a more dissociated species. The chloride anion may be a somewhat more efficient base which, to some extent, abstracts a proton before it diffuses away from the carbocation. Added chloride anion has been found to be a more efficient catalyst than solvent water for abstraction of a proton.[1] However, the cation intermediate formed from 1-chloro-1-(4-methylphenyl)ethane yields a smaller fraction of elimination than the corresponding protonated alcohol.[6] Accordingly, the measured isotope effect $k_3^H/k_3^{d_6}$ of 3·5 for **1-Cl** may consist of a small isotope effect of ~3 for deprotonation by Cl^- and an isotope effect of ~4–5 for deprotonation of the 'free' carbocation. The smaller isotope effects on k_3 measured in ethanol[4] are in accord with this interpretation. Furthermore, only small isotope effects have been reported for the dehydronation step in reactions showing rate-limiting hydron abstraction from ion pairs.[15] A reason for a higher isotope effect with the free ion than with the ion pair may be difference in linearity and/or symmetry of the transition state.

Dehydronation of carbocations stabilized by one or two ferrocenyl groups has been studied by Bunton and coworkers.[16] These carbocations are so stable that they can be isolated as salts. An isotope effect k^H/k^D as large as 6·7 and $\beta = 0{\cdot}32$ have been measured for these ions with tertiary amines in 50% water–acetonitrile. A large kinetic deuterium isotope effect on the deprotonation step has also been measured for a solvolytic 1,4-elimination of acetic acid from 3-(2-acetoxy-2-propyl)indene.[2]

The ion pair **1^{+-}OAc** is formed in the solvolysis of **1-OAc** but is also an intermediate in the reaction of the cumyl cation with acetate anion to give the ester. However, formation of this specific ion pair (possibly with the acetate anion in approximately correct position for formation of the ester) is probably not required in the base-promoted reaction step giving olefin. Data for the acetate-promoted solvolytic elimination of HCl from 3-(2-chloro-2-propyl)indene support this hypothesis that the base-promoted deprotonation of a cation may occur via an encounter complex (or ion pair) with a geometry different from that of the ion pair producing the ester.[2]

EXPERIMENTAL SECTION

General. The ^1H-NMR analyses were performed with a JEOL FX 100 spectrometer equipped with a 5 mm dual probe (^1H,^{13}C) or 5 mm ^1H probe. The high-performance liquid-chromatography (HPLC) analyses were carried out with a Hewlett-Packard 1084B liquid chromatograph equipped with a variable-wavelength detector on a C8 reversed-phase column (3·0 × 200 mm). The mobile phase was a solution of methanol in water. The reactions were studied at constant temperature in a HETO 01 PT 623 water thermostat.

Materials. Acetonitrile (Fluka, for UV spectroscopy) was used as a solvent without further purification. Methanol used for preparation of reaction solutions was of spectroscopic quality, otherwise of HPLC grade. All other chemicals were of reagent grade and were used without further purification. A stock solution of sodium perchlorate was prepared from perchloric acid and sodium hydroxide solution. The pH values of the stock solutions of the acetate anions were adjusted to *ca.* 7.

2-Hydroxy-2-phenylpropane (**1-OH**) was purified by recrystallization of commercially available material (Aldrich) from pentane.

*2-Phenylpropene (***3***)* (Fluka) was purified by fractional distillation at reduced pressure.

2-Chloro-2-phenylpropane (**1-Cl**) was prepared from 50 mg of **1-OH** dissolved in 5 ml of dichloromethane containing anhydrous calcium chloride. Dry hydrogen chloride was bubbled through the ice-cold solution for 5 minutes. The filtered product solution was diluted with 20 ml of pentane and half of the volume was evaporated by a stream of nitrogen. Finally, a further portion of 10 ml of pentane was added. This stock solution was stored in the freezer.

Phenyldimethylcarbinyl p-nitrobenzoate (**1-PNB**) was prepared from **1-OH** and *p*-nitrobenzoyl chloride in pyridine.[17]

Phenyldimethylcarbinyl acetate (**1-OAc**) was prepared by $ZnCl_2$-catalyzed acetylation of **1-OH** with acetic anhydride (5 min). The method has been used previously for preparation of other acetates.[1,18] Semi-preparative HPLC gave pure material.

2-Methoxy-2-phenylpropane (**1-OMe**) was prepared by methanolysis of **1-Cl** or by solvolysis of **1-OH** in a mixture of conc. hydrochloric acid (1 part) and methanol (10 parts). The ether was purified by semipreparative HPLC.

(1,1,1,3,3,3-$^2H_6$)-2-Hydroxy-2-phenylpropane (**d_6-1-OH**) was synthesized from (1,1,1,3,3,3-$^2H_6$)-acetone (Ciba, 99·5% ^{2}H) and phenylmagnesium bromide.[4] The deuterium content, after recrystallization of the product from pentane, was > 99 atom% as determined by mass spectroscopy. This purified alcohol was used for the synthesis of **d_6-1-Cl, d_6-1-PNB, d_6-1-OAc**, and **d_6-1-OMe** by the methods described above for the protium compounds.

Kinetics and product studies. The reactions were run at constant ionic strength in solutions prepared by mixing three volumes of water solution of the salt(s) with one volume of the organic solvent at room temperature, *ca.* 22 °C. The reaction vessel was either a 2 ml HPLC flask sealed with a tight PTFE septum which was placed in an aluminium block in the water thermostat or, in the slower reactions, a 4 ml pear-shaped flask, equipped with a PTFE stopcock (high vacuum type). The reactions were initiated by rapid addition of the substrate dissolved in acetonitrile with a spring-loaded syringe. The substrate solution of the chloride was prepared just before use by evaporation of the pentane from an aliquot of the stock solution and dissolving the residue in dry acetonitrile. The concentration of the substrate was about 2 mM in all runs except those for measuring the rate constants with **1-PNB**, in which the concentration was 0·2 mM. At appropriate intervals, samples (400 μl) of the reaction solution were transferred by means of a thermostated syringe (water-jacketed) to an HPLC flask (in some experiments containing a mixture of aqueous sodium hydrogen carbonate and methanol to neutralize the sample) and analyzed. The components of the reaction were chromatographically well separated. The mol% of the starting material and each of the products was measured by means of the relative response factors, which were determined in separate experiments. The rate constants were calculated from plots of ln(area starting material) vs. time and product compositions. The azide adduct **1-N$_3$** was not isolated; the response factor was assumed to be the same as that of **1-OH**. Corrected total peak areas in experiments with and without azide did not differ significantly, indicating similar response factors.

Rate constants for the reactions with **1-OMe** were obtained in the following way. The rate constant k_{23} measured in kinetic runs with **1-OH**

$$\begin{tikzcd}
\textbf{1-OMe} \arrow[rr, "k_{12}"] \arrow[dr, "k_{13}"'] & {} \arrow[d, phantom, "H^+"] & \textbf{1-OH} \arrow[dl, "k_{23}"] \\
& \textbf{3} &
\end{tikzcd} \tag{9}$$

was used for simulation of the reactions from **1-OMe**. Accordingly, the measured mol% of each of the reaction components were compared with the simulated mol% obtained from the integrated rate equations of equation (9).[19] The rate constants k_{12} and k_{13} that gave the best fit to the experimental data are recorded in Table 2.

The estimated errors are considered as maximum errors derived from maximum sytematic errors and random errors.

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