Mechanisms of Elimination Reactions. Part IV.[1a] Rates of Elimination from Substituted Phenethyl'onium Salts in Isopropyl Alcohol containing Potassium Isopropoxide

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Rate coefficients for elimination from a number of *p*-substituted phenethyl-dimethylsulphonium and -trimethylammonium ions have been measured in isopropyl alcohol containing potassium isopropoxide. Kinetic deuterium isotope effects were measured using the 2,2-dideuteriophenethyl and phenethyl substrates. Compared with previous results in ethanol, the isotope effects in isopropyl alcohol are larger for both 'onium salts, suggestive of less proton transfer to the base in the transition state in the more basic medium. The Hammett reaction constant for the sulphonium salt eliminations increases markedly as the solvent is changed from ethanol to isopropyl alcohol, consistent with an increase in the carbanion character of the transition state. In contrast, little change in ρ is noted for the ammonium salts. This observation demonstrates the uncertainty in using the changes in ammonium ion eliminations as representative models for eliminations involving other charged leaving groups.

CHANGING the reaction medium from ethanol–ethoxide to t-butyl alcohol–t-butoxide can cause a significant variation in the orientation and stereochemistry of bimolecular elimination[1b–e] from alkyl halides,[2] alkyl sulphonates,[3–5] and alkyl'onium salts.[6] Both *syn*-elimination and the proportion of the Hofmann alkene in the product are promoted by the change to the more basic medium. Steric factors,[2,6,7] ion association phenomena,[8] and variations in the carbanion character of the transition state[1e,9,10] have been invoked to explain the experimental observations.

For quaternary ammonium salts, a change from ethanol–ethoxide to t-butyl alcohol–t-butoxide is assumed to cause a shift to a more reactant-like transition state with an accompanying reduction in the carbanion character of the transition stage for bimolecular elimination. These deductions follow from substituent studies on rates of elimination of 2-arylethyltrimethylammonium ions.[11] However, the kinetics of the elimination reaction in t-butyl alcohol are complicated by medium effects, which are very dependent on the specific cation. In addition, the large isotope effect (k_H/k_D) may contain a contribution from the tunnel effect, encouraged by the bulky t-butoxide ion. Thus, the above deduction concerning trends in carbanion character may be on uncertain grounds. Consequently, we decided to study the elimination of 2-arylethyl'onium salts in isopropyl alcohol–isopropoxide, a reaction medium in which ion-association effects are less pronounced than in t-butyl alcohol.

EXPERIMENTAL

Substrates.—The preparation of the substituted arylethyl-dimethylsulphonium[12] and the -trimethylammonium salts[11] have been described previously. The 2,2-dideuteriated materials (<2% protic impurity by n.m.r. spectroscopy) have been characterised before.[11,13] All compounds had m.p.s in agreement with those already reported.

Solvents and Bases.—Isopropyl alcohol was purified by two distillations from sodium, and was stored and handled only in a dry box. Basic solutions, prepared by dissolving freshly cleaned potassium in isopropyl alcohol, were standardised by titration against standard acid and used for periods of one week only.

Kinetic Measurements.—The rates of elimination of the arylethyl'onium salts were monitored by u.v. spectroscopy. In all cases, the reactions were followed for at least 10 half-lives, and the optical density of the resulting reaction solution was consistent with the formation of a quantitative yield of the substituted styrene within experimental limits. To simplify the kinetics, all reactions were carried out with at least a 10-fold excess of base over substrate and the pseudo-first-order plots constructed were linear for at least three half-lives in most cases.[11,13] In all cases, reactions were carried out in stoppered silica cells, housed continually in the thermostatted cell compartment (±0·1 °C) of a Unicam SP 500 spectrophotometer.

Kinetic Results.—The pseudo-first-order rate coefficients were converted into second-order rate coefficients by division by the base concentration. The variation in the second-order coefficients with base concentration is shown in Table 1. Table 2 lists the rate coefficients for the substituted arylethyl'onium salts at specific base concentrations.

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DISCUSSION

The second-order rate coefficients for elimination from the phenethyl'onium ions decrease with increasing isopropoxide concentration (see Table 1 and Figure). In fact, graphs of log k_{E2} against log [KOPr^i] give slopes (over a 10-fold variation in base concentration) approximating to 0·5, suggesting a dependence of rate coefficient on [KOPr^i]$^{1/2}$. This observation is consistent with either (i) a salt effect on the rate coefficient, increasing ionic strength being expected to decrease the rate coefficient for a reaction between oppositely charged ions,[14] or (ii) a tendency of the base to exist in dimeric aggregates with increasing base concentration. We prefer the latter explanation, as for the sulphonium salt, where a wider range of base concentration was used, the rate coefficient reaches a maximum value at a base concentration of *ca.* $3{\cdot}6 \times 10^{-3}$M, a value which is maintained with a further four-fold decrease in base concentration. These results clearly emphasise the need to use standard base concentrations when comparing rate coefficients for various substituted derivatives. Unlike the situation reported previously for t-butyl alcohol,[11] changing the concentration of the substrate (*i.e.* variation of quaternary

TABLE 1

The influence of base concentration on the second-order rate coefficient for elimination from phenethyl-dimethylsulphonium and -trimethylammonium ions by potassium isopropoxide in isopropyl alcohol

(*a*) At 30 °C

10^3[KOPr^i]/M	k_{E2}/l mol min^{-1} (PhCH$_2$CH$_2\overset{+}{\text{S}}$Me$_2$) *	10^3[KOPr^i]/M	k_{E2}/l mol^{-1} min^{-1} (PhCH$_2$CH$_2\overset{+}{\text{N}}$Me$_3$) *
23·6	93·8 ± 1	111	1·10
17·7	107	95	1·12
11·8	166	71·2	1·69
10·3	171	48·5	2·02
7·08	211	30·6	2·61
4·80	259	23·7	2·85
3·60	293	18·0	3·30
2·52	288 ± 5		
2·36	302		
1·50	310 ± 13		
1·08	332		
0·87	296 ± 2		
0·82	301 ± 5		

(*b*) At 40 °C

10^3[KOPr^i]/M	k_{E2}/l mol^{-1} min^{-1} (PhCH$_2$CH$_2\overset{+}{\text{N}}$Me$_3$) *
48·7	6·59 ± 0·1
24·4	10·8 ± 0·3
12·2	15·5 ± 0·5

(*c*) At 45 °C

10^3[KOPr^i]/M	k_{E2}/l mol^{-1} min^{-1} (PhCH$_2$CH$_2\overset{+}{\text{N}}$Me$_3$) *
49·1	15·1
24·6	24·4 ± 0·2
17·5	28·5
12·7	38·4

* Average deviation listed when more than one run recorded.

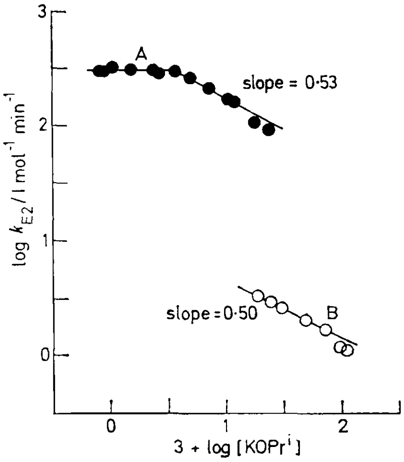
TABLE 2

Rate coefficients for elimination from substituted 2-arylethyl'onium salts (p-XC$_6$H$_4$CH$_2$CH$_2$Y) by potassium isopropoxide in isopropyl alcohol

X	k_{E2}/l mol^{-1} min^{-1} (Y = $\overset{+}{\text{S}}$Me$_2$)	k_{E2}/l mol^{-1} min^{-1} (Y = $\overset{+}{\text{N}}$Me$_3$)
(*a*) At 30 °C		
H	301 ± 5 [a] 288 ± 5 [b]	3·21 ± 0·07 [c]
H *	42·9 ± 1·6 [b]	0·846 ± 0·012 [c]
Cl	2370 ± 50 [a]	30·5 ± 0·2 [c]
Me	101 ± 2 [a]	0·906 ± 0·024 [c]
OMe	42·3 ± 0·2 [a]	0·346 ± 0·007 [c]
(*b*) At 40 °C		
H		10·8 ± 0·3 [c]
H *		2·99 ± 0·13 [c]
(*c*) At 45 °C		
H		24·4 ± 0·4 [c]
H *		6·97 ± 0·06 [c]

* Refers to the 2,2-dideuteriophenethyl-Y.

The base concentration was [a] $8{\cdot}2 \times 10^{-4}$M; [b] $2{\cdot}52 \times 10^{-3}$M; [c] $2{\cdot}42 \times 10^{-2}$M.



Elimination from phenethyl'onium ions in isopropyl alcohol containing potassium isopropoxide at 30 °C. Graph of log k_{E2} against 3 + log [KOPr^i] for A, dimethylsulphonium salt; B, trimethylammonium salt

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ammonium ion concentration) did not affect the second-order rate coefficients.

The values for the primary kinetic isotope effect, k_H/k_D, for elimination from the phenethyl'onium ions with isopropoxide ion are listed in Table 3, along with results reported previously for other basic media. The rate ratio, $k(\mathrm{PhCH_2CH_2Y})/k(\mathrm{PhCD_2CH_2Y})$, contains a contribution from a secondary isotope effect, but these are generally close to unity[15] and therefore the figures reflect mainly the primary effect. As the solvent is changed from EtOH ⟶ $\mathrm{Pr^{i}OH}$ ⟶ $\mathrm{Bu^{t}OH}$, the magnitude of the isotope effect increases markedly. The result for elimination of the ammonium salt in ethanol, when considered in conjunction with other kinetic evidence,[1,11] is clearly consistent with a transition state in which the proton is extensively transferred to the base. Thus, the rise in the isotope effect along the series EtOH ⟶ $\mathrm{Pr^{i}OH}$ ⟶ $\mathrm{Bu^{t}OH}$ indicates a gradual reduction in the extent of proton transfer as the medium basicity increases, in agreement with the Hammond[16] and Swain–Thornton postulates.[17] As already reported for ethanol, the isotope effect is larger for the sulphonium than ammonium salt in isopropyl alcohol, consistent with less proton transfer in the transition state for elimination involving the better leaving group.

TABLE 3

Kinetic isotope effects for elimination from phenethyl'onium salts with various alkoxide bases

Temp. (°C)	Solvent [a]	k_H/k_D [c] $Y = \overset{+}{N}Me_3$ [d]	k_H/k_D [c] $Y = \overset{+}{S}Me_2$ [d]	Reference
30	$\mathrm{Pr^{i}OH}$	$3{\cdot}80 \pm 0{\cdot}10$	$6{\cdot}73 \pm 0{\cdot}28$	This work
40	$\mathrm{Pr^{i}OH}$	$3{\cdot}61 \pm 0{\cdot}17$		This work
45	$\mathrm{Pr^{i}OH}$	$3{\cdot}50 \pm 0{\cdot}07$		This work
30	EtOH	$3{\cdot}5$ [e]	$5{\cdot}70 \pm 0{\cdot}22$	*f*, 11
50	EtOH	$2{\cdot}98 \pm 0{\cdot}08$		*f*
30	$\mathrm{Bu^{t}OH}$	$6{\cdot}96 \pm 0{\cdot}14$		11
50	H_2O	$3{\cdot}02 \pm 0{\cdot}09$ [b]		*f*
60	H_2O		$4{\cdot}71 \pm 0{\cdot}09$	*f*
30	H_2O		$5{\cdot}93$ [e]	*f*

[a] Base is the lyate ion in each case. [b] 50% v/v $\mathrm{EtOH{-}H_2O}$. [c] Ratio of rates for elimination of $\mathrm{PhCH_2CH_2Y{-}PhCD_2CH_2Y}$. [d] For definition of Y, see Table 2. [e] Values interpolated from data at higher temperatures. [f] W. H. Saunders, jun., and D. H. Edison, *J. Amer. Chem. Soc.*, 1960, **82**, 138.

The rates of elimination of trimethylphenethylammonium ion proceed *ca.* 300—800 times faster in isopropyl alcohol than in ethanolic basic media.[11] For the more basic medium, a reduction in the activation energy is expected,[16,17] and the activation entropy is also slightly more positive (Table 4). The ratio of the pre-exponential factors A_H/A_D, of the Arrhenius equation for elimination from the protic and deuteriated substrates in isopropyl alcohol has a value of 0·71, significantly greater than the lower limit of 0·5 expected in the absence of tunnelling.[18] Thus, it seems fairly certain that the isotope effect for elimination from trimethylphenethylammonium ion in isopropyl alcohol is not complicated by a tunnelling contribution.

TABLE 4

Activation parameters for elimination from trimethylphenethylammonium ion and its 2,2-dideuterio-analogue in isopropyl alcohol and ethanol at 50 °C

Substrate	Solvent [a]	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}
$\mathrm{PhCH_2CH_2\overset{+}{N}Me_3}$	EtOH	$27{\cdot}5$ [b]	$13{\cdot}7$ [b]
$\mathrm{PhCH_2CH_2\overset{+}{N}Me_3}$	$\mathrm{Pr^{i}OH}$ [c]	$24{\cdot}8 \pm 2{\cdot}2$	$17{\cdot}4 \pm 7{\cdot}3$
$\mathrm{PhCD_2CH_2\overset{+}{N}Me_3}$	$\mathrm{Pr^{i}OH}$ [c]	$25{\cdot}8 \pm 2{\cdot}3$	$18{\cdot}1 \pm 7{\cdot}6$

[a] Base is the lyate ion. [b] From ref. 11. [c] Rate coefficients for $2{\cdot}42 \times 10^{-2}$M-$\mathrm{KOPr^{i}}$ used in the calculation of the activation parameters, for which the standard deviations are cited.

Table 5 lists the Hammett reaction constants for elimination from the substituted phenethyl'onium salts in a variety of basic media. The present results show that the value of ρ increases in going from H_2O ⟶ EtOH ⟶ $\mathrm{Pr^{i}OH}$, but then decreases in passing to $\mathrm{Bu^{t}OH}$. The magnitude of ρ has generally been attributed as a measure of the carbanion character of the β-carbon atom in the transition state for elimination,[1] increasing carbanion character being indicated by an increasing value of ρ. In all the solvents, the ρ values for the eliminations from the sulphonium salts are smaller than those observed for the ammonium salts, in line with less carbanion character in the transition state for elimination from the former series. This observation is in line with the higher primary isotope effects (k_H/k_D) for the eliminations from the sulphonium salts, and the larger leaving-group isotope effects reported previously for the sulphonium than the ammonium compounds.[19]

TABLE 5

Hammett reaction constants for elimination from substituted 2-arylethyl'onium (p-$\mathrm{XC_6H_4CH_2CH_2Y}$) ions in various protic solvents at 30 °C

	$Y = \overset{+}{S}Me_2$		$Y = \overset{+}{N}Me_3$		
Solvent [a]	ρ [b]	r [c]	ρ [b]	r [c]	Ref.
H_2O	$2{\cdot}21 \pm 0{\cdot}08$ [d]				*f*
EtOH	$2{\cdot}64 \pm 0{\cdot}16$ [d]	0·996	$3{\cdot}77 \pm 0{\cdot}21$	0·997	11, 12
			$3{\cdot}94 \pm 0{\cdot}55$ [e]	0·990	11
$\mathrm{Pr^{i}OH}$	$3{\cdot}47 \pm 0{\cdot}19$ [d]	0·998	$3{\cdot}87 \pm 0{\cdot}16$ [d]	0·998	This work
$\mathrm{Bu^{t}OH}$			$3{\cdot}04 \pm 0{\cdot}03$ [e]	0·998	11

[a] The lyate ion is the base. [b] Calculated by the least squares method, with standard deviation. [c] Correlation coefficient. [d] X = H, p-Cl, p-Me, or p-OMe. [e] X = H, p-Me, or p-OMe. [f] W. H. Saunders, jun., C. B. Gibbons, and R. A. Williams, *J. Amer. Chem. Soc.*, 1958, **80**, 4099.

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The most interesting aspect of the results in Table 5 concerns the relatively small change in ρ as the solvent is changed from ethanol to isopropyl alcohol for the ammonium ion eliminations (3·77 ⟶ 3·87), but the substantial variation noted for the sulphonium ion series (2·64 ⟶ 3·47). It could be argued that the large value of 3·77 observed for the ammonium salts is already near the carbanion extreme, and therefore is in an insensitive region. Even if the carbanion character of the transition state did not change with variation in the reaction medium, it is unlikely that ρ would remain constant as it generally increases with a decrease in the dielectric constant of the medium.[20] Thus, the slight increase in ρ (3·77 ⟶ 3·87) in passing from ethanol to isopropyl alcohol, for the elimination from the ammonium salts is negligible. Bearing in mind that the hydrogen isotope effect increases and the activation energy decreases, it would seem reasonable to interpret the results as indicating a slight decrease in carbanion character as the reaction medium becomes less polar and more basic. Thus, these results for the ammonium ion eliminations in isopropyl alcohol confirm the earlier prediction based on results in ethanol and t-butyl alcohol; namely, that the carbanion character of the transition state decreases as the medium becomes less polar but more basic.

The results for the sulphonium salts seem at variance with this latter hypothesis. Clearly, the increase in ρ in passing from ethanol to isopropyl alcohol (2·64 ⟶ 3·47) seems too large to be attributed solely to a medium effect and implies a definite increase in carbanion character of the transition state for elimination. Bearing in mind the increase in k_H/k_D (5·07 ⟶ 6·73), indicating less proton transfer in isopropyl alcohol, this apparent increase in carbanion character should be reflected by a greater decrease in α-C–$\overset{+}{S}Me_2$ bond breaking in the more basic medium. Hopefully, this situation will be verified by studies of the leaving-group isotope effect in isopropyl alcohol. In addition, further elimination studies in n-butanol, a solvent with intermediate properties (dielectric constant and lyate ion basicity) to those of isopropyl and t-butyl alcohols, may yield a sulphonium ion elimination giving a greater ρ value than the corresponding ammonium ion elimination.

In two earlier papers, we illustrated the different behaviour towards solvent effects of eliminations involving uncharged leaving groups. Addition of dimethyl sulphoxide to t-butyl alcohol caused no change in the magnitude of the Hammett reaction constant for elimination from substituted phenethyl bromides,[21] but brought about substantial increases for a series of substituted sulphonates.[1a,22] In this paper, the danger of assuming that changes in ρ with reactions conditions for ammonium ion eliminations are typical for all eliminations involving charged leaving groups has been highlighted.

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