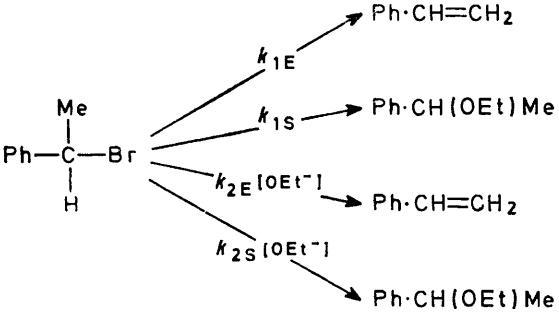
A Re-examination of the ' Unified ' S_N2–$E2$ Mechanism [1]

By **D. J. McLennan,** Department of Chemistry, University of Auckland, Auckland, New Zealand

Rates and product proportions for the reactions of 1-phenylethyl and phenethyl bromides with sodium and potassium ethoxides in ethanol, in the absence and presence of sodium perchlorate, are reported. When consideration of the separate reactions of free ethoxide ions and metal ethoxide ion-pairs is taken, the data can be successfully interpreted in terms of competing $E1$, $E2$, S_N1, and S_N2 processes. The Sneen–Robbins mechanistic alternative, in which is postulated an ion-pair intermediate common to both substitution and elimination processes, gives a less satisfactory account of the results.

BIMOLECULAR elimination ($E2$) and nucleophilic substitution (S_N2) reactions very often compete with each other when alkyl halides *etc.* react with bases in hydroxylic solvents.[2] Olefinic and substitution products may also be formed in apparent first-order ($E1$ and S_N1) reactions.[3] Such a traditional competitive process is shown in Scheme 1 for the reactions of 1-phenylethyl bromide with ethoxide ions in ethanol. It is realised that the k_{1E} and k_{1S} steps are more complex than is depicted here.[4] The important point is that they are first-order reactions.



SCHEME 1

Sneen and Robbins [5] have claimed that this type of mixed first- and second-order scheme does not account for the kinetics observed under pseudo first-order conditions ($[OEt^-] > [CHPhMeBr]$) on the grounds that second-order k_2 values as calculated from equation (1) are not constant as is shown later in Tables 1 and 2 and could not be accounted for by a ' normal ' salt effect. In equation (1) the observed pseudo-first-order rate

$$k_{obs} = k_1 + k_2[OEt^-] \qquad (1)$$

coefficient is presumed to comprise a rate constant k_1 for unimolecular solvolysis and a k_2 term for the competing second-order base-promoted reactions.[5] The competitive process was therefore rejected in favour of a mechanism in which an ion-pair at a steady-state concentration is an intermediate on the path to both olefinic and substitution products which may be formed by both solvent-promoted and base-promoted reactions (Scheme 2).* By employing a single adjustable parameter, Sneen and Robbins have shown that k_{obs} and k'_{ip}, the latter being a theoretical pseudo-first-order rate constant calculated from their equation (10) and pertaining to the mechanism in Scheme 2, are in reasonably good agreement at various ethoxide concentrations.

This ion-pair (' unified ') mechanism is a natural extension of one suggested by Sneen and Larsen [6] to explain the ' borderline ' kinetics observed when added nucleophile and hydroxylic solvents compete in nucleophilic substitutions of substrates such as secondary alkyl sulphonate esters (Scheme 3). In fact it has been suggested [6c] that the traditional S_N2 mechanism, involving a single transition state containing a quinquecovalent carbon atom, may have to be abandoned in favour of an ion-pair mechanism even for substitution at primary carbon atoms ($k'_{-1} \gg k'_S + k'_N[N]$). Such a revolutionary suggestion concerning a mechanism that has long

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* Throughout this paper, primed rate constants will refer to processes suggested by Sneen, whereas unprimed rate constants will refer to competitive processes.

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[4] S. Winstein, B. Appel, R. Baker, and A. Diaz, ' Organic Reaction Mechanisms,' *Chem. Soc. Special Publ.*, 1965, No. 19, p. 109.

[5] R. A. Sneen and H. M. Robbins, *J. Amer. Chem. Soc.*, 1969, **91**, 3100.

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TABLE 1

Reaction of 1-phenylethyl bromide with NaOEt in ethanol

[NaOEt]/M	10^4k_{obs}/s^{-1}	f_E	10^4k_2/$l\ mol^{-1}\ s^{-1}$	10^4k_{2E}/$l\ mol^{-1}\ s^{-1}$	10^4k_{2S}/$l\ mol^{-1}\ s^{-1}$	α [a]
0	1·13 [b]	0·03				
0·114	3·54 [b]	0·165 [c]	21·1	4·82	16·3	0·480
0·121	3·57 [b]	0·170 [c]	20·2	4·74	15·4	0·475
0·362	5·35	0·275	11·7	4·00	7·69	0·352
0·533	6·57 [b]	0·296 [c]	10·2	3·58	6·62	0·287
0·686	7·48 [b]	0·320 [c]	9·2	3·44	5·82	0·243
0·844	8·4	0·323	8·6	3·17	5·44	0·213
1·07	9·8 [b]	0·325 [c]	8·2	2·94	5·16	0·177
1·432	12·0	0·329	7·6	2·67	4·86	
1·714	13·5	0·331	7·2	2·58	4·63	

[a] Degree of dissociation of sodium ethoxide ion-pairs. [b] From ref. 5. [c] From ref. 17.

TABLE 2

Reaction of 1-phenylethyl bromide with KOEt in ethanol

[KOEt]/M	10^4k_{obs}/s^{-1}	f_E	10^4k_2/$l\ mol^{-1}\ s^{-1}$	10^4k_{2E}/$l\ mol^{-1}\ s^{-1}$	10^4k_{2S}/$l\ mol^{-1}\ s^{-1}$	α [a]	$10^4k'_{ip}$ [b]/s^{-1}
0	1·13 [c]	0·03 [d]					
0·0641	2·17	0·180	16·2	5·58	10·6	0·573	2·18
0·0983	2·66	0·205	15·6	5·20	10·3	0·523	2·66
0·144	3·19	0·230	14·3	4·86	9·4	0·486	3·21
0·238	4·26	0·259	13·1	4·49	8·7	0·430	4·14
0·297	4·90	0·269	12·7	4·32	8·4	0·407	4·61
0·360	5·60	0·284	12·4	4·32	8·1	0·387	5·04
0·404	5·95	0·285	11·9	4·11	7·8	0·374	5·31
0·485	6·72	0·288	11·5	3·92	7·6	0·350	5·74

[a] Degree of dissociation of potassium ethoxide ion-pairs. [b] From equation (10) of ref. 5, with $a = 0{\cdot}018$, $b = 0{\cdot}500$, $x = 8{\cdot}5$, and $y = 12{\cdot}5$. [c] From ref. 5. [d] 2,4,6-Collidine present in slight excess.

TABLE 3

Reaction of 1-phenylethyl bromide with NaOEt in ethanol in the presence of $NaClO_4$

[NaOEt]/M	$[NaClO_4]$/M	10^4k_{obs}/s^{-1}	f_E	10^4k_{2E}/$l\ mol^{-1}\ s^{-1}$	10^4k_{2S}/$l\ mol^{-1}\ s^{-1}$	$10^4k'_{ip}$ [a]/s^{-1}
0	0·749	2·16 [b]	0·05 [b]			
0·139	0·610	2·96	0·175	2·95	2·81 [c]	5·90
0·208	0·544	3·52	0·216	3·14	3·41	7·21
0·278	0·472	3·87	0·241	2·96	3·20	8·30
0·347	0·405	4·40	0·260	2·99	3·49	9·24
0·416	0·330	4·81	0·271	2·88	3·50	9·98

[a] From equation (10) of ref. 5 with $a = 0{\cdot}053$, $b = 0{\cdot}500$, $y = 12{\cdot}5$, and $x = 8{\cdot}5$. [b] 2,4,6-Collidine present in slight excess. [c] Larger than usual experimental error of $\pm 0{\cdot}93$. This value was not used in computing an average k_{2S}.

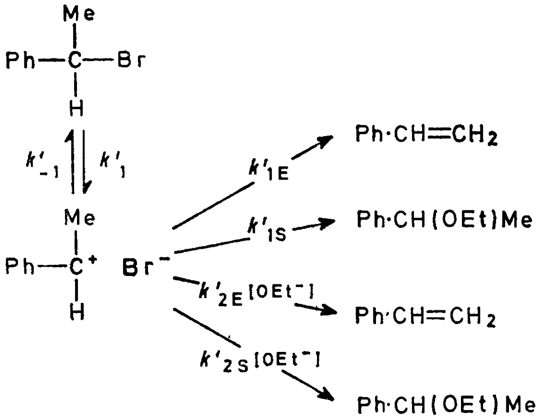
TABLE 4

Reaction of phenethyl bromide with NaOEt in ethanol in the absence and presence of $NaClO_4$

[NaOEt]/M	$[NaClO_4]$/M	10^4k_{obs}/s^{-1}	10^4k_{2E}/$l\ mol^{-1}\ s^{-1}$	α [a]	10^4k_{2E} for CHPhMeBr [b]/$l\ mol^{-1}\ s^{-1}$
0·1			34·2 [c]	0·495	4·90
0·207		6·83	33·0	0·422	4·47
0·362		11·5	31·7	0·352	4·00
0·614		17·7	28·8	0·260	3·49
0·844		24·1	28·6	0·213	3·17
1·041		28·8	27·7	0·179	3·00
0·222	0·525	6·22	28·0		
0·325	0·424	9·00	27·7		
0·404	0·346	11·4	28·2		

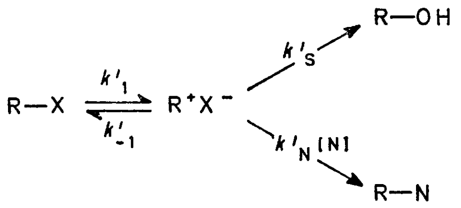
[a] Degree of dissociation of sodium ethoxide. [b] k_{2E} value for 1-phenylethyl bromide at the indicated base concentration, interpolated from data in Table 1. [c] From ref. 25.

been accepted as being concerted must stand up to the closest scrutiny. The idea has not met with widespread approval[7-16] although much of the evidence presented against it has been indirect or inferential. On the credit side, the results of a linear free-energy approach employed by Scott[17] for substitutions of methyl halides are in keeping with the Sneen–Larsen mechanism.



SCHEME 2

In this work we will show that the competitive $E1$–$E2$–S_N1–S_N2 mechanism (Scheme 1) does in fact account for the observed rate and product data for the alkaline ethanolysis of CHPhMeBr and that Sneen's basis for the rejection of this process is erroneous. Further, we will show that the S_N2 and $E2$ components are concerted processes involving nucleophilic attack on covalent substrate.



SCHEME 3

RESULTS

The solvent was dry ethanol. The temperature for all kinetic runs was 50 ± 0·1 °C. Table 1 shows the observed pseudo-first-order rate constants and the overall olefin fractions (f_E) for the reactions of CHPhMeBr with varying amounts of sodium ethoxide. Some of the rate data are those of Sneen and Robbins,[5] and some of the olefin fractions have been interpolated from Taylor's results.[18] The degree of dissociation of sodium ethoxide ion-pairs (α) at each base concentration has been interpolated from Brandstrom's data.[19] Values of k_2 have been calculated from equation (1) (in which k_{obs} at [NaOEt] = 0 has been taken as equal to k_1) and values of k_{2E} and k_{2S} have been calculated from equations (2) and (3) respectively (see Discussion section). k_{2E} and k_{2S}, the second-order elimination and substitution rate coefficients for the competitive process in Scheme 1, are not constant and decrease with increasing base concentration.

Similar data for potassium ethoxide as base are presented in Table 2. Values of k_{2E} and k_{2S} again drift downwards. The agreement between k_{obs} and k'_{ip}, the latter calculated from equation (10) of Sneen and Robbins,[5] is impressive at lower base concentrations but becomes progressively poorer in more concentrated solution.

The effect of varying the sodium ethoxide concentration at constant ionic strength is shown in Table 3. Anhydrous sodium perchlorate was used as the 'buffering' electrolyte and the total salt concentration was 0·75M. The non-nucleophilic salt has a much smaller effect on k_{obs} than does sodium ethoxide, but the NaOEt > $NaClO_4$ acceleration order is not observed with reactions of tertiary halides.[9,20] It is clear that, with one exception that can be attributed to a larger than usual experimental error, values of k_{2E} and k_{2S} are constant. Mean values and standard deviations are respectively $(2{\cdot}98 \pm 0{\cdot}03) \times 10^{-4}$ l mol⁻¹ s⁻¹ and $(3{\cdot}40 \pm 0{\cdot}14) \times 10^{-4}$ l mol⁻¹ s⁻¹. Both standard deviations are smaller than the average experimental error of *ca.* 6%.

Pseudo-first-order rate constants for the dehydrobromination of phenethyl bromide promoted by an excess of sodium ethoxide in ethanol are shown in Table 4. Solvolysis accounts for *ca.* 2% of the total reaction at [NaOEt] = 0·207M and less at higher concentrations, and hence was neglected. Styrene was the sole product in all runs. Hence k_{2E} was calculated from equation (2) with $k_1 = 0$ and $f_E = 1{\cdot}00$. As [NaOEt] is increased from 0·1M to 1·0M, k_{2E} decreases by a small amount. The overall decrease is real, being greater than deviations which could be attributed to experimental error, which is *ca.* 3% in these runs.

The effect of using anhydrous sodium perchlorate to buffer the ionic strength at 0·75M for the reaction of phenethyl bromide with NaOEt is also shown in Table 4. There is now discernible drift in k_{2E} and the average value is $28{\cdot}0 \times 10^{-4}$ l mol⁻¹ s⁻¹. The standard deviation is less than the calculated experimental error.

DISCUSSION

Reactions of 1-*Phenylethyl Bromide*.—If k_1 and f_0 are the rate constant and olefin fraction respectively in neutral solvolysis and if it is assumed that they are not subject to salt effects,* then the second-order rate

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* Salt effects on k_1 should be reasonably small in the reasonably polar solvents used. See ref. 2, p. 485 and ref. 14.

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constants for elimination (k_{2E}) and substitution (k_{2S}) in Scheme 1 are given by [1] equations (2) and (3), in which f_E is the total olefin fraction at a given [NaOEt]. However, rate coefficients so calculated decrease with increasing [NaOEt] (Tables 1 and 2). This decrease can be attributed to a salt effect arising from ion-pairing of the base

$$k_{2E} = (f_E k_{obs} - f_0 k_1)/[\text{NaOEt}] \qquad (2)$$

$$k_{2S} = \{(1 - f_E)k_{obs} - (1 - f_0)k_1\}/[\text{NaOEt}] \qquad (3)$$

to its counter-ion. If k_i and k_{ip} are the respective second-order rate constants for attack by free ethoxide ions and by sodium (or potassium) ethoxide ion-pairs, then k_{2E} and k_{2S} can be expressed in terms of equation (4), in which α is the degree of dissociation of the ion-pairs.[19] It follows that a plot of say $k_{2E}/(1 - \alpha)$ against $\alpha/(1 - \alpha)$ should be linear, with slope k_i and intercept

$$k_{2E} \text{ (or } k_{2S}) = \alpha k_i + (1 - \alpha)k_{ip} \qquad (4)$$

k_{ip}, if such a salt effect influences k_{2E}. Data from such plots are shown in Table 5. With the exception of two points in the NaOEt k_{2S} plot (omitted from the calculations for Table 5) these plots are strictly linear for two metal alkoxides of differing degrees of dissociation. Even more satisfactory is the fact that k_i values, which should be independent of the cation, are in good agreement for sodium and potassium ethoxides.

TABLE 5

Quantities derived from plots of $k_{2E}/(1 - \alpha)$ against $\alpha/(1 - \alpha)$

Base	NaOEt [b]	KOEt [b]
$10^4 k_i$(elim.)/l mol^{-1} s^{-1}	$7{\cdot}95 \pm 0{\cdot}07$	$8{\cdot}56 \pm 0{\cdot}13$
$10^4 k_{ip}$(elim.)/l mol^{-1} s^{-1}	$1{\cdot}88 \pm 0{\cdot}14$	$1{\cdot}45 \pm 0{\cdot}11$
r(elim.) [a]	0·999	0·999
$10^4 k_i$(subst.)/l mol^{-1} s^{-1}	$17{\cdot}0 \pm 0{\cdot}8$	$16{\cdot}8 \pm 0{\cdot}2$
$10^4 k_{ip}$(subst.)/l mol^{-1} s^{-1}	$2{\cdot}47 \pm 0{\cdot}28$	$2{\cdot}56 \pm 0{\cdot}18$
r(subst.) [a]	0·994	0·999

[a] Correlation coefficient for relevant plot. [b] Uncertainties expressed as standard deviations.

The deviant points pertain to the 0·114M and 0·121M-NaOEt runs (Table 1). They should perhaps be considered as a single point since the two observed rate constants are probably within experimental error of each other. In this case in particular, k_{2S} is subject to a large experimental error in that it is calculated from a small difference between two comparable quantities. However this consideration does not completely account for the deviation. Neither are models based on linear negative salt effects on k_1 (lyate ion effects [21]) completely satisfactory, either quantitatively or scientifically, since they involve the use of an unprovable hypothesis.[9] We note however that KOEt k_{2S} values do not give rise to any significant deviation in the plot of $k_{2S}/(1 - \alpha)$ against $\alpha/(1 - \alpha)$. Salt effects on k_1 will not affect k_{2E} to any extent since $f_0 k_1$ is insignificant in comparison with $f_E k_{obs}$ at most base concentrations.

Thus when normal salt effects are taken into consideration, k_{2E} and k_{2S} values for a competitive $E1$–$E2$–S_N1–S_N2 situation are satisfactorily constant. The ion-pairing origin of such salt effects has been questioned by Sneen and Rolle,[22] and their ionic strength suggestion may well be correct for the low nucleophile concentrations employed in their study. However, plots of log k_{2E} and log k_{2S} against $I^{\frac{1}{2}}$ and $(\alpha I)^{\frac{1}{2}}$, where I is the ionic strength, are non-linear.

It has been shown [23] that the degree of dissociation of a salt may be kept constant while the salt concentration is varied by ' buffering ' the ionic strength of the solution with an inert salt having a common cation. Such buffering should also cause salt effects on k_1 to be minimal. So if the above ion-pairing hypothesis is correct, buffering should result in k_{2E} and k_{2S} values being independent of [NaOEt], and the results in Tables 3 and 4 show that this is the case. The values of k_{2E} and k_{2S} are sensibly constant up to [NaOEt] = 0·4M, whereas they decrease by *ca.* 25% over this concentration range in the unbuffered runs. It is noteworthy that while the k'_{ip} rate coefficients calculated on the basis of the Sneen–Robbins mechanism agree tolerably well with the observed rate constants when the total salt concentration is varied (Table 2 and ref. 5) they bear no resemblance to k_{obs} values at constant ionic strength (Table 3).

We can now show that the second-order reactions do *not* involve rate-determining attack of base on a preformed ion-pair. The solvolysis should proceed at least partly *via* the intermediacy of ion-pairs,[4,24] and if the second-order reactions have Sneen-type mechanisms [see equation (5)] they must involve reaction of ethoxide with these same ion-pair intermediates. However, if our claim that the solvolyses and base-promoted reactions are separate processes is correct, they cannot therefore involve common intermediates. Attack of base on covalent substrate *via* the single transition state $E2$ and S_N2 mechanisms is strongly implied.

Reactions of Phenethyl Bromide.—While we were reasonably confident as to the essential correctness of the above-mentioned ion-pairing origin of drifting k_{2E} and k_{2S} values derived from a competitive situation, we decided to check the validity of the explanation in another way.

2-Phenethyl bromide ($PhCH_2{\cdot}CH_2Br$) is a model substrate for second-order eliminations in that 100% styrene is formed and the kinetics are strictly of the second-order within runs where base and substrate concentrations are comparable.[25-27] If this elimination proceeds *via* a Sneen-type mechanism [equation (5)], the

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observed pseudo-first-order rate constant should be given by equation (6) and so k_{obs}/[NaOEt] should be constant. This is not so (Table 4), when whatever is the mechanism of the dehydrobromination of phenethyl bromide, the observed second-order rate coefficient is subject to a negative salt effect.

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}Br} \underset{k''_{-1}}{\overset{k''_1}{\rightleftharpoons}} \mathrm{Ph{\cdot}CH_2{\cdot}CH^+{}_2Br^-}\text{—}k''_{\mathrm{E}}[\mathrm{OEt^-}] \longrightarrow \mathrm{Ph{\cdot}CH{=}CH_2} \quad (5)$$

$$k_{obs} = k''_1 k''_{\mathrm{E}}[\mathrm{NaOEt}]/k''_{-1} \quad (6)$$

Again a plot of $k_{2E}/(1 - \alpha)$ against $\alpha/(1 - \alpha)$ is linear ($r = 0{\cdot}999$) whence $k_i = (45{\cdot}0 \pm 0{\cdot}7) \times 10^{-4}$ l mol^{-1} s^{-1} and $k_{ip} = (23{\cdot}9 \pm 0{\cdot}4) \times 10^{-4}$ l mol^{-1} s^{-1}. Such an ion-pairing interpretation is less ambiguous in this case as we are now dealing with a pure k_{2E} process. It is thus satisfying that a plot of the k_{2E} values pertaining to the suggested competitive reactions of 1-phenylethyl bromide against k_{2E} for phenethyl bromide at corresponding base concentrations is linear ($r = 0{\cdot}989$). This is of course not a linear free-energy relationship and the non-unit slope is merely a reflection of the fact that, relative to the reactivity of free ethoxide ions, the sodium ethoxide ion-pair is more reactive with phenethyl than with 1-phenylethyl bromide. Thus the salt effect that we claim is affecting the competitive k_{2E} values for CHPhMeBr is quantitatively comparable with the salt effect on the unambiguous second-order rate constants for dehydrobromination of $\mathrm{PhCH_2{\cdot}CH_2Br}$.

The effect of using sodium perchlorate to buffer the ionic strength while the base concentration is varied is to remove the small drift in k_{2E} for $\mathrm{PhCH_2{\cdot}CH_2Br}$ (Table 4). This is again in line with expectations based on an ion-pairing origin for the salt effect [23] and with the effect observed with CHPhMeBr.

We now examine another consequence of Sneen's second-order elimination mechanism as exemplified by equation (5). The transition state of higher energy must necessarily be that intervening between the ion-pair and the olefin, and as this conversion should be highly exo-energetic, the transition state should resemble the ion-pair.[28] Thus the C_β–H bond should be but little broken and the electrons in the incipient p-orbital formed by such partial heterolysis should be delocalised into the empty p-orbital at C_α (in the absence of stereochemical constraint) to form a partial π-bond. Thus there should be little if any excess of negative charge on C_β in the transition state.

This consequence of the Sneen mechanism is contrary to fact, both in the phenethyl bromide system and in general. In the former case, primary deuterium isotope effect studies indicate a well-sundered C_β–H bond,[29] and the reasonably large Hammett ρ value (*ca.* 2·25 with $\mathrm{OEt^-}$ in EtOH) is indicative of significant carbanionic charge at C_β.[25,26] For the Sneen–Robbins mechanism [equation (5)] $\rho_{obs} = \rho_{eqbm} + \rho_{rate}$, and since ρ_{eqbm} for ion-pair formation is likely to be negative, ρ_{rate} must be even greater than ρ_{obs}, meaning that the transition state should be zwitterionic. Such an implausible formulation does not fit general observations either, since a wide variety of studies have clearly established that elimination transition states may have considerable β-carbanionic character in suitable cases.[30]

Our kinetic observations together with the above considerations lead us to the conclusion that there is no compelling reason for accepting the Sneen–Robbins ' unified ' mechanism.

We note that in a Hammett equation study of the reactions of 1-arylethyl bromides with ethoxide in ethanol, Oae and his co-workers [31] have calculated k_{2E} values in the manner presented here, and have found the same downward drift with increasing [NaOEt]. However they have not evaluated k_i as we have done, but have chosen k_{2E} values at a particular base concentration in order to construct their Hammett plot. This is only in order if the relative sensitivity of each compound in the series to free ion and ion-pair attack is the same,[7] and the scatter in the curved Hammett plot may perhaps be evidence that this is not so.

EXPERIMENTAL

Phenethyl bromide was a commercial product and 1-phenylethyl bromide was prepared from 1-phenylethanol. Both were purified by fractional distillation. Absolute ethanol was dried with magnesium. Anhydrous sodium perchlorate was recrystallised from dry acetone. Sodium and potassium ethoxide solutions were prepared, stored (for no longer than a week), and dispensed under dry nitrogen. They were standardised by acid–base titration with a Radiometer Titrigraph automatic titrator.

TABLE 6

Reaction of 0·01242M-1-phenylethyl bromide with 0·297M-KOEt in EtOH at 50·0 °C

Time/s	$\mathrm{AgNO_3}$ [a]/ml	$10^4 k_{obs}$/s^{-1}
0	0·043	
200	0·127	4·99
390	0·199	4·97
600	0·261	4·74
900	0·350	4·78
1560	0·516	4·95
1950	0·582	4·88
2580	0·674	4·91
3990	0·801	4·99
10 Half-lives	0·922	
13 Half-lives	0·920	

Mean = $(4{\cdot}90 \pm 0{\cdot}10) \times 10^{-4}$ s^{-1}

An infinity sample diluted 10-fold had an absorbance of 0·264 (282 nm) whence $f_E = 0{\cdot}268$. A further infinity sample diluted 100-fold had an absorbance of 0·462 (248 nm) whence $f_E = 0{\cdot}270$.

[a] 10 ml samples titrated with 0·1349M-$\mathrm{AgNO_3}$ with a 1·0 ml syringe burette.

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The reactions of 1-phenylethyl bromide were followed by automatic silver nitrate titration of acidified aqueous extracts of reaction mixture following extraction of organic material with CCl_4 and ether. The 2,4,6-collidine present in solvolytic runs was also extracted before titration. Infinity titres were always within 1% of the value expected from the original concentration of CHPhMeBr (*ca.* 0·01M). Plots of log $(V_\infty - V_t)$ against time were strictly linear up to at least 75% reaction. The fraction of elimination was estimated by observing the u.v. absorbance of suitably diluted infinity samples at 248 ($\varepsilon_{\text{styrene}}$ 1·38 × 10^4) [25] and 282 nm ($\varepsilon_{\text{styrene}}$ 7·94 × 10^2).[32] Only the latter wavelength, at which ethyl 1-phenylethyl ether absorbs negligibly, was used to estimate f_E for solvolyses. Undiluted infinity samples in these runs were analysed and the blank cell contained 2,4,6-collidine and 2,4,6-collidinium bromide at the same concentrations as those calculated to pertain to the infinity sample. Separate values of f_E for a given run differed by no more than 0·4%. Details of a typical run are in Table 6.

The reactions of phenethyl bromide ($[PhCH_2{\cdot}CH_2Br]_0$ = *ca.* 10^{-4}M) were followed by u.v. spectrophotometry at 248 nm. Infinity absorbances corresponded to (100 ± 0·7)% elimination. Plots of log $(A_\infty - A_t)$ against time were linear up to at least 80% reaction. This is the appropriate logarithmic quantity to use [33] even though phenethyl bromide itself absorbs weakly at 248 nm. Standard deviations in k_{obs} were generally of the order of 4% for titrimetric runs and 3% for spectrophotometric runs.

I thank Mr. R. J. Wong for least-squares computations and Mr. O. R. Jackson for discussions.

[2/186 *Received*, 28*th January*, 1972]

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