2. *Nucleophilic Reactivity. Part IV.*[1] *Competing Bimolecular Substitution and β-Elimination.*

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The rate coefficients and yields of olefin have been measured for the reactions of several alkyl bromides with a series of *para*-substituted phenoxide ions in ethanol at 60°. The changes in the rate coefficients of phenethyl bromide and 4-nitrophenethyl bromide produced by changes of concentration have been analysed, and the influence of the ethoxide ions in equilibrium with various concentrations of phenol and phenoxide ions has been estimated. These analyses, although approximate, establish the general-base-catalysed nature of the E_2 mechanism for phenethyl bromide. The changes in the rates of substitution and elimination with the structure of the phenol are given approximately by the Brönsted catalysis law, and are interpreted in terms of the simple treatment of nucleophilic reactivity discussed previously.

THERE are now three known mechanisms for β-elimination from saturated systems, (1) the E_1 mechanism (2) the bimolecular E_2 mechanism, and (3) a mechanism, E_1CB, involving an intermediate carbanion.[2]

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[1] Part III, Hudson and Loveday, *J.*, 1962, 1068.

[2] Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 657; Ingold, *Proc. Chem. Soc.*, 1962, 265; Bunnett, *Angew. Chem.*, 1962, **74**, 731.

$$(1)\ \mathrm{RR'CH{\cdot}CH_2X} \xrightarrow[\text{Slow}]{} \mathrm{RR'CH{\cdot}CH_2^+} + \mathrm{X^-} \longrightarrow \mathrm{RR'C{:}CH_2} + \mathrm{H^+}$$

$$(2)\ \mathrm{RR'CH{\cdot}CH_2X} + \mathrm{HO^-} \longrightarrow \mathrm{HO{\cdots}H{\cdots}CRR'{\cdots}CH_2X} \longrightarrow \mathrm{H_2O} + \mathrm{RR'C{:}CH_2} + \mathrm{X^-}$$

$$(3)\ \mathrm{RR'CH{\cdot}CH_2X} + \mathrm{HO^-} \rightleftharpoons \mathrm{H_2O} + \mathrm{RR'C^-{\cdot}CH_2X} \xrightarrow[\text{Slow}]{} \mathrm{H_2O} + \mathrm{RR'C{:}CH_2} + \mathrm{X^-}$$

The E_1 reaction (1) can be differentiated from (2) and (3) by the difference in kinetic order, but little attention has been paid to the differentiation between (2) and (3) until recently. Mechanism (2) is known to be general for alkyl bromides and this has been studied widely from the point of view of the relation between structure and yield of olefin.[2] Mechanism (3) is promoted by electron-attracting substituents which stabilise the carbanion, and has been established recently for the elimination of hydrogen fluoride from 1,1,1-trifluoro-2,2-dihalogenoethanes.[3]

Although β-elimination has been widely studied from a mechanistic point of view, no systematic kinetic study of the influence of the nucleophilic reagent has been reported, although it is known that bases other than hydroxide and alkoxide ions may be used.[2] In an early investigation, Hanhart and Ingold [4] found that the yield of olefin produced by the dry distillation of trimethylpropylammonium salts decreases regularly with the basicity of the anion. Although each salt decomposed under different conditions, this suggests that an E_2 reaction is more sensitive to changes in basicity of the nucleophilic reagent than the concomitant S_N2 reaction, a conclusion which is supported by the present investigation. More recently, Cromwell and Hess [5] have shown that, whereas α-bromo-β-methyl-4-phenylpropiophenone undergoes β-elimination with piperidine, predominant substitution occurs with the less basic morpholine.

Since the yield of olefin from an alkyl halide is determined by the relative rate of the competing nucleophilic displacements at the β-hydrogen and α-carbon atoms, our previous interpretation of nucleophilic reactivity [1,6] provides a basis for analysing competing S_N2 and E_2 reactions. These have the added advantage of a common leaving group. In the present paper, the general-base-catalysed β-elimination of phenethyl bromide produced by a series of phenoxide ions is investigated in detail. Several other alkyl bromides have been examined in order to relate the selectivity, represented by the coefficients α_S and α_E of the Brönsted equations for substitution and elimination, respectively, to the structure of the alkyl bromide. The results are interpreted in terms of the simple electrostatic treatment of nucleophilic reactivity advanced previously.[6]

EXPERIMENTAL

All the kinetic measurements were made with ethanol (Fluka puriss) solutions in a thermostat-bath at 60° ± 0·01°. The phenols were recrystallised to constant m. p., identical with recorded values. 4-Nitrophenethyl bromide was prepared [7] by treating phenethyl bromide with fuming nitric acid and formed needles, m. p. 69·5°, from alcohol. The other bromides were redistilled before use.

Products of Reaction between Sodium Phenoxide and Phenethyl Bromide.—Phenethyl bromide (5·55 g., 0·03 mole), phenol (5·65 g., 0·06 mole), and sodium phenoxide (1·38 g., 0·03 mole) in ethanol (50 ml.) were heated under reflux for 44 hr. The concentration of styrene, determined by vapour-phase chromatography (v.p.c.), was 0·27M, corresponding to a total of 0·0135 mole. Only traces of phenethyl bromide were detected. The ethanol and part of the styrene were removed under reduced pressure, and some styrene (b. p. 35°/80 mm.), characterised by the infrared spectrum and refractive index, was recovered. Phenol (4·085 g., 0·0434 mole), b. p. 80°/40 mm., and phenyl phenethyl ether (3·103 g., 0·0156 mole), b. p. 163°/12 mm., n_D^{20} 1·5688 (lit.,[8] n_D^{16} 1·5706), were obtained. (Schorigin [8] records a yield of 45—50% of phenyl phenethyl

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[3] Hine, Wiesboeck, and Ghirardelli, *J. Amer. Chem. Soc.*, 1961, **83**, 1219.
[4] Hanhart and Ingold, *J.*, 1927, 997.
[5] Cromwell and Hess, *J. Amer. Chem. Soc.*, 1961, **83**, 1237.
[6] Hudson, *Chimia* (*Switz.*), 1962, **16**, 173.
[7] Sobotka, *Ber.*, 1929, **62**, 2192.
[8] Schorigin, *Ber.*, 1925, **58**, 2035.

ether from phenethyl chloride and potassium phenoxide in ethanol.) The residue of 3·283 g. was a mixture of sodium bromide (0·03 mole determined by Volhard's method) and a polymer (0·1963 g.), probably polystyrene. The reaction thus gives 45% of styrene and 55% of phenyl phenethyl ether.

Total Rate of Reaction.—A solution, of known concentration, of phenethyl bromide in ethanol (100 ml.), and a mixture of phenol and sodium ethoxide of known concentration in ethanol (100 ml.), were placed in a thermostat-bath at 60° ± 0·01° for 20 min., then mixed rapidly. The rate of reaction was determined by titration of the bromide ion in 10-ml. samples. A correction was applied to account for the difference in volume of the solvent at 20° and 60°. Reactions were carried out with equal concentrations of phenethyl bromide and phenoxide, so that the simplified second-order rate equation may be used, $k_2 = x/at(a - x)$. Detailed examples of the calculation of k_2 are given in Tables 1 and 2. A summary of the rate constants is given in Tables 4 and 5.

TABLE 1.

Rate of reaction between phenethyl bromide and *p*-cresol in ethanol at 60°.

a (initial concns. of phenethyl bromide, sodium *p*-tolyloxide, and *p*-cresol) = 0·0958 mole/l.

t (sec.)	$x = [Br^-]$ (mole l.$^{-1}$)	10^4k_2 (l. mole^{-1} sec.$^{-1}$)	t (sec.)	$x = [Br^-]$ (mole l.$^{-1}$)	10^4k_2 (l. mole^{-1} sec.$^{-1}$)
1·920	0·00720	4·94	6·420	0·0221	4·87
2·820	0·0112	4·89	7·320	0·0244	4·87
3·720	0·0143	4·92	8·220	0·0267	4·90
4·620	0·0171	4·90	9·120	0·0287	4·89
5·520	0·0197	4·89	10·020	0·0306	4·88

$k_2 = 4{\cdot}89 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

Three other experiments gave $10^4k_2 = 4{\cdot}72$, 4·73, and 4·63 l. mole^{-1} sec.$^{-1}$, severally giving an average $k_2 = 4{\cdot}74 \pm 0{\cdot}15 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

TABLE 2.

Rate of reaction between 4-nitrophenethyl bromide and *p*-bromophenol in ethanol at 60°.

Initial concns. of 4-nitrophenethyl bromide and sodium *p*-bromophenoxide = 0·0958 mole/l.

t (sec.)	$[Br^-]$ (mole l.$^{-1}$)	10^2k_2 (l. mole^{-1} sec.$^{-1}$)	t (sec.)	$[Br^-]$ (mole l.$^{-1}$)	10^2k_2 (l. mole^{-1} sec.$^{-1}$)
100	0·0170	2·25	280	0·0381	2·46
160	0·0261	2·44	340	0·0426	2·46
220	0·0326	2·44	400	0·0459	2·40

$k_2 = 2{\cdot}41 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

Two other determinations gave $10^2k_2 = 2{\cdot}32$ and 2·43 l. mole^{-1} sec.$^{-1}$, which give an average $k_2 = 2{\cdot}39 \pm 0{\cdot}07 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

Analysis of Olefin.—Three methods were used depending on the nature of the olefin and on the reaction conditions: (*a*) This method was used for investigating phenethyl bromide, 4-bromoheptane, and octyl bromide. When phenethyl bromide was used, the styrene was measured by vapour-phase chromatography on a column (Q Apiazon) at 150°, with a flow of helium at a pressure of 1·5 kg./cm.[2] Standard solutions of styrene were used to calibrate the height of the peaks which were found to be proportional to concentration. After a known time, the reaction mixture was cooled, and 5 µl. were taken for analysis. At least three injections were made each time and the average peak height was used in calculating the styrene concentration. The remaining solution was used for the Volhard titration, which gave the extent of reaction. The following is a typical example for the reaction between phenethyl bromide (0·3 mole) and sodium phenoxide (0·3 mole) in the presence of phenol (0·3 mole): after 16 hr. at 60°, the solution was cooled, and four injections of the solution (5 µl.) gave the following heights of the v.p.c. peaks: 42·76, 45·80, 42·40, and 46·76 cm., giving an average of 44·43 cm. From the calibration factor of 0·00189, the amount of styrene was found to be 0·0843 mole. The solution (10 ml.) had a concentration of bromide of 0·1862 mole (Volhard), giving a value of 45·3% of olefin. With octyl bromide, and 4-bromoheptane, a column of polyethylene glycol at 70° was used. A control experiment showed that only 28% of hept-3-ene was lost by polymerisation in 16 days at 60°. The results of these olefin estimations are given in Tables 11 and 12.

(*b*) The second method was developed for 4-nitrophenethyl bromide, as in this case v.p.c.

analyses could not be made because the 4-nitrostyrene is destroyed at high temperature. In this method the remaining phenol in the reaction mixture was titrated after a certain reaction time. The mixture (10 ml.) was added to a 0·1M-solution of sodium hydroxide (20 ml.), water (50 ml.), and carbon tetrachloride, leaving sodium phenoxide and sodium bromide only in the aqueous layer. The phenol was titrated with bromine in the usual way.[9] The difference between this titre and the initial titre of phenol is equal to the quantity of substitution product formed. The extent of reaction was determined separately by titration of bromide, and hence the yields of substitution product and olefin were found. The results of this method are given in Table 13.

In several cases, methods (*a*) and (*b*) were compared. A typical example of method (*b*) is: 4-bromoheptane (0·1 mole), phenol (0·2 mole), and sodium ethoxide (0·1 mole) reacted for 45 hr. at 60°, the solution was cooled, and then (1) Volhard gave 0·0501 mole of bromide ion, (2) titration of phenoxide with hydrochloric acid gave 0·0498 mole, and (3) 10 ml. of solution in 100 ml. of 0·05N-sodium hydroxide were extracted three times with carbon tetrachloride, the aqueous phase being titrated with bromine to give 0·1782 mole of PhOH + PhONa. The concentration of phenyl 1-propylbutyl ether is then equal to 0·2 (initial titre of phenol + phenoxide) $-$ 0·1782 $=$ 0·0278 mole, and heptene $=$ 0·0501 (% of reaction) $-$ 0·0278 $=$ 0·0223 mole. From the phenol titration, the yield of hept-3-ene $=$ 0·0223/0·0501 $=$ 44·5%. Method (*a*) (v.p.c.) gave 0·0226 mole of heptene, from comparison with calibration samples of 0·2, 0·1, and 0·05 mole of heptene, giving a yield of 100 × 0·0226/0·0501 $=$ 45·0% of hept-3-ene.

The two methods were also tested for the reaction recorded in Table 3. From the value (A),

TABLE 3.

Reaction of $Ph\cdot CH_2\cdot CH_2Br$, *p*-$NO_2\cdot C_6H_4\cdot ONa$, and *p*-$NO_2\cdot C_6H_4\cdot OH$ (all 0·1N).

Compounds analysed	Method	Concentrations Initial	 Final
p-$NO_2\cdot C_6H_4\cdot O^-$ ($+EtO^-$)	HCl (titr.)	0·100	0·0590
p-$NO_2\cdot C_6H_4\cdot O^-$ + *p*-$NO_2\cdot C_6H_4\cdot OH$	Br_2	0·213	0·1799 (A)
p-$NO_2\cdot C_6H_4\cdot O^-$ + *p*-$NO_2\cdot C_6H_4\cdot OH$	HCl (titr.) *	0·2053	0·1733 (B)
Br^-	Volhard	—	0·0405
$Ph\cdot CH{:}CH_2$	V.p.c.	—	0·00687 (C)

* This analysis was made by addition of an excess of sodium hydroxide and back-titration with hydrochloric acid (automatic titrator).

% substitution $=$ (0·213 $-$ 0·1799)/0·0407 $=$ 81·3, *i.e.*, elimination $=$ 18·7%; from (B), % substitution $=$ (0·2053 $-$ 0·1733)/0·0407 $=$ 78·6, *i.e.*, elimination $=$ 21·4%. In this case, the elimination is given directly by v.p.c. analysis (C) from 0·00687/0·0407 $=$ 16·9%. The agreement between the methods is not very close, but is reasonable in view of the experimental difficulties.

The elimination determined by method (*b*) (titration of phenol) includes possible substitution by ethoxide ions, since this reaction liberates phenol. The influence of this in the cases studied here is negligible, since ethoxide gives 100% elimination in the reaction reported in Table 3.

(*c*) In the reactions with sodium ethoxide, in the absence of phenol, the yield of olefin could be determined by titration of the double bond by bromine in the usual way.[10]

RESULTS

Total Rate Constants: Effect of Concentration.—In all cases, satisfactory second-order rate plots were obtained up to 40—50% reaction. The calculated rate constants, however, varied considerably with initial concentration as shown in Table 4. This shows that k_2 varies significantly at high concentrations of phenol, where the concentration of ethoxide ions in equilibrium is very low. Moreover, these variations are comparable for phenols of widely different pK_a. It is highly likely that k_2 is affected by the changing medium under these conditions rather than by the change in ethoxide-ion concentration. To investigate this, butyl bromide was studied in the same way (Table 5). Phenols give no olefin with this bromide within the limits of experimental detection and, moreover, the rate constant for the reaction with sodium ethoxide is almost the same as that obtained with sodium phenoxide in the presence of phenol (Table 6).

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[9] Stone, " Determination of Organic Compounds," McGraw-Hill, Vancouver, 1956, p. 124.

[10] Ref. 9, p. 16.

TABLE 4.

Influence of concentration changes on the total rates (k_2, l. mole^{-1} sec.$^{-1}$) of reaction. [Bromide] = [Phenoxide] = [X]; [Phenol] = [Y].

Phenethyl bromide

[X]	[Y]	10^5k_2
Phenol		
0·01	—	201
	0·01	101
	0·03	70·1
	0·07	51·6
0·02	—	131
	0·02	67·1
	0·06	48·8
	0·14	39·4
0·1	0·1	29·9
	0·3	27·7
0·2	0·2	25·0
	0·6	17·9
p-*Bromophenol*		
0·1	0·1	15·2
	0·3	12·7
p-*Acetoxyphenol*		
0·1	0·1	4·27
0·2	0·2	4·15
	0·6	2·63

4-Nitrophenethyl bromide

[X]	[Y]	10^3k_2
Phenol		
0·02	—	270
	0·02	164
	0·06	92·0
0·05	—	135
	0·05	88
0·1	—	80·3
	0·1	53·2
	0·3	35·1
p-*Bromophenol*		
0·1	—	23·9
	0·1	15·4
p-*Nitrophenol*		
0·1	—	0·513
	0·1	0·357
	0·3	0·246

TABLE 5.

Influence of concentration changes on the total rate (k_2, l. mole^{-1} sec.$^{-1}$) of reaction of butyl and octyl bromide with sodium phenoxide in the presence of phenol. (For X and Y see Table 4.)

[X]	[Y]	10^4k_2
	Butyl bromide	
0·01	0·01	4·93
	0·03	5·24
	0·07	4·85
0·02	—	5·14
	0·02	4·45
	0·06	4·02
0·05	0·05	3·70
	0·15	3·51
	0·35	2·90
0·20	—	3·22
	0·2	2·77
	0·6	2·15

[X]	[Y]	10^4k_2
	Butyl bromide	
0·10	—	3·86
	0·1	3·12
	0·3	2·88
	0·7	2·01
	Octyl bromide	
0·02	—	5·65
	0·02	5·35
0·1	—	5·28
	0·1	3·44
0·1	0·1	0·273 *

* Reaction with *p*-nitrophenoxide.

It is unlikely, therefore, that sodium ethoxide influences k_2 significantly in this case and so the variations in k_2 refer only to the replacement reaction with sodium phenoxide.

The effect of concentration on k_2 may be analysed by considering the acid–base equilibrium in the solution: $PhO^- + EtOH \rightleftharpoons PhOH + EtO^-$, and the equilibrium constant $1 \gg K = [EtO^-][PhOH]/[PhO^-]$. The influence of ethoxide ions may be investigated in principle by making two kinds of regular change: (*a*) With a constant phenol–phenoxide concentration ratio, the concentration of ethoxide ions remains constant with variation in the concentration of sodium phenoxide. (*b*) Variation in the concentration of phenol, for a given value of the phenoxide-ion concentration, produces a proportional change in ethoxide-ion concentration, since $[EtO^-] \propto [PhO^-]/[PhOH]$ when $K \ll 1$. These relations will only hold approximately in the concentration range employed in the present investigations, owing to the variations in activity coefficients. However, the variations can be largely taken into account by using butyl bromide as a reference, as explained below. It is instructive to compare the variation in rate for the several bromides with change in concentration, *e.g.*, in terms of the ratio of the rate constants by using 0·02N-PhO⁻ + 0·02N-PhOH, and 0·1N-PhO⁻ + 0·1N-PhOH, as reported in Table 6. Since the first two bromides shown in Table 6 give no olefin under these conditions, the decreases in k_2 with increasing concentration (given by the similar factors of 1·43 and 1·55) are attributed to deviations from ideality. The greater changes in k_2 for the other bromides follow the increased effect of OEt⁻, as represented in Table 6 by the values of $k(\text{EtO}^-)/k(\text{PhO}^-)$, and are, therefore, probably due in part to the influence of the equilibrium concentration of ethoxide ions, which becomes more important at the higher concentrations.

TABLE 6.

	Bu^nBr	$C_8H_{17}Br$	$Ph{\cdot}CH_2{\cdot}CH_2Br$	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Br$
k_2 ratio *	1·43 (1·47) ‡	1·55	2·2	3·1
Olefin (%)	0	0	46	100
$k(\text{EtO}^-)/k(\text{PhO}^-)$ †	2·44	2·28	27·8	138

* k_2 when [PhOH] = [PhO⁻] = 0·02N, divided by k_2 when [PhOH] = [PhO⁻] = 0·1N. † Rate constants for initial 0·1N-concns. of EtO⁻ and PhO⁻. ‡ Corresponding rate ratio for the reaction with ethoxide ions.

Variation of Phenol Concentration.—According to the equilibrium involving phenoxide and ethoxide ions, an increase in phenol concentration, [PhOH], would decrease [EtO⁻], thus reducing the rate if elimination produced by the latter were important. However, an increase in [PhOH] would also reduce the activity coefficient of phenoxide ions (by association), thus reducing the rate, and this effect is shown by the results (Table 7) for butyl bromide. Here the ratios of the rate constants when [PhOH] = [PhO⁻], and when [PhOH] = 3[PhO⁻], are recorded for various initial concentrations of PhO⁻. For butyl bromide the two values of k_2 are similar over the 0·01—0·1N concentration range, *i.e.*, the ratios in Table 7 are close to unity, the ratios at the higher concentrations being similar for the two alkyl bromides. The rate ratios increase again for phenethyl bromide in the lower concentration range, indicating that the reaction of this bromide with ethoxide ions becomes appreciable, in agreement with the calculations in the following section.

TABLE 7.

[PhO⁻]		0·01	0·02	0·05	0·1	0·2
k_2 ratio *	$Ph{\cdot}CH_2{\cdot}CH_2Br$	1·44	1·35	—	1·08	1·39
	Bu^nBr	0·95	1·11	1·05	1·08	1·31

* The ratio of k_2 for initial concentrations [PhOH] = [PhO⁻] and [PhOH] = 3[PhO⁻] given in Table 4.

In view of the fact that the change in k_2 with phenol concentration is a minimum at *ca.* 0·1M, this concentration was chosen arbitrarily to compare the rate constants for the various reactions shown in Table 8.

For reaction of bromides with sodium ethoxide (0·1N) in ethanol at 60°, the following rate constants (k_2, l. mole⁻¹ sec.⁻¹) were observed: phenethyl bromide, $8{\cdot}36 \times 10^{-3}$ ($12{\cdot}4 \times 10^{-3}$

TABLE 8.

Total rate constants (l. mole⁻¹ sec.⁻¹) for the reactions of various alkyl bromides with *para*-substituted phenols in ethanol at 60°. The initial concentrations of alkyl bromide, phenol and phenoxide were 0·0958M in each case.

Bromide	R in $R{\cdot}C_6H_4{\cdot}OH$	10^4k_2 *	Bromide	R in $R{\cdot}C_6H_4{\cdot}OH$	10^4k_2 *
$Ph{\cdot}CH_2{\cdot}CH_2$	*p*-MeO	4·88 ± 0·12	Pr^n_2CH	H	1·04 ± 0·07
	p-Me	4·74 ± 0·15		*p*-Br	0·655
	H	2·99 ± 0·11		*p*-NO_2	0·130
	p-Br	1·52 ± 0·04	C_8H_{17}	H	3·44
	p-Ac	0·427 ± 0·04		*p*-NO_2	0·273
	p-NO_2	0·179 ± 0·012	Bu^n	H	3·12
$4\text{-}NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2$	H	532		*p*-NO_2	0·234
	p-Br	154			
	p-NO_2	3·57			

* The rate constants are the average of several determinations, and maximum deviations are given when more than two experiments were made.

when the initial concentration of NaOEt was 0·02N); 4-nitrophenethyl bromide, ~7·3 (by extrapolation); butyl bromide, $7·60 \times 10^{-4}$; octyl bromide, $7·83 \times 10^{-4}$; 4-bromoheptane, $2·97 \times 10^{-4}$.

Variation of Phenoxide Concentration with Constant Ratio [PhO⁻]/[PhOH].—Reference to Table 4 shows that the changes of k_2 with [PhO⁻], with a constant ratio [PhO⁻]/[PhOH], are considerably greater for phenethyl bromide than for butyl bromide in concentrations less than 0·1N, but are similar for higher concentrations. This agrees with the conclusion in the previous section, that the deviations in k_2 for phenethyl bromide are due to activity-coefficient changes at high concentration and to the incursion of the elimination produced by ethoxide ions at the lower concentrations. If we assume that the changes in k_2 produced by activity-coefficient variations are the same for the several bromides, and that changes in the observed rate constant for butyl bromide are due to activity-coefficient changes only, the observed rate constants for phenethyl bromide and 4-nitrophenethyl bromide may be analysed further. The observed rate, r, is given in terms of true bimolecular constants k_2^0 and k_0 for the reactions with phenoxide and ethoxide ions, respectively, by:

$$r = k_2^0[\mathrm{RBr}][\mathrm{PhO^-}]\mathrm{f}(\mathrm{RBr})\mathrm{f}(\mathrm{PhO^-})/\mathrm{f}_* + k_0[\mathrm{RBr}][\mathrm{EtO^-}]\mathrm{f}(\mathrm{RBr})\mathrm{f}(\mathrm{EtO^-})/\mathrm{f}_*',$$

where f refers to the activity coefficient of a reactant and f_* and f_*' to the activity coefficients of the transition states of the reactions with phenoxide and ethoxide ions, respectively. The concentration of ethoxide ions can be found from the equilibrium,

$$K = [\mathrm{EtO^-}][\mathrm{PhOH}]\mathrm{f}(\mathrm{EtO^-})\mathrm{f}(\mathrm{PhOH})/[\mathrm{PhO^-}]\mathrm{f}(\mathrm{PhO^-}),$$

which gives

$$k_2 = \frac{r}{[\mathrm{RBr}][\mathrm{PhO^-}]} = k_2^0\left[\frac{\mathrm{f}(\mathrm{RBr})\mathrm{f}(\mathrm{PhO^-})}{\mathrm{f}_*}\right] + k_0'\left[\frac{\mathrm{f}(\mathrm{RBr})\mathrm{PhO^-}}{\mathrm{f}_*'}\right]\cdot\frac{1}{[\mathrm{PhOH}]\mathrm{f}(\mathrm{PhOH})},$$

where $k_0' = k_0K$.

If we assume that changes in f_* and f_*' with changes in [PhOH] and [PhO⁻] are similar to the corresponding changes in f_*'' for the reaction of butyl bromide with phenoxide ions, *i.e.*, that

$$\mathrm{f}(\mathrm{BuBr})\mathrm{f}(\mathrm{PhO^-})/\mathrm{f}_*'' \approx \mathrm{f}(\mathrm{RBr})\mathrm{f}(\mathrm{PhO^-})/\mathrm{f}_* \approx \mathrm{f}(\mathrm{RBr})\mathrm{f}(\mathrm{PhO^-})/\mathrm{f}_*',$$

then the changes in these activity quotients are given by the changes in the observed rate constant, k_2(BuBr) for butyl bromide, since

$$k_2(\mathrm{BuBr}) = k_2^0(\mathrm{BuBr})\mathrm{f}(\mathrm{BuBr})\mathrm{f}(\mathrm{PhO^-})/\mathrm{f}_*'',$$

where k_2^0 [BuBr] is the corresponding rate constant at infinite dilution.

It follows that

$$k_2(\mathrm{corr.}) \equiv k_2\left[\frac{k_2^0[\mathrm{BuBr}]}{k_2[\mathrm{BuBr}]}\right] = k_2^0 + \frac{k_0'}{[\mathrm{PhOH}]\mathrm{f}(\mathrm{PhOH})}.$$

If the changes in the activity coefficient, f(PhOH) are neglected, since the variations will be small in comparison with the variations in the activity coefficients of the ions, it follows that

$$k_2\ (\mathrm{corr.}) \approx k_2^0 + k_0'/[\mathrm{PhOH}].$$

Values of k_2(corr.) for phenethyl bromide and 4-nitrophenethyl bromide are given in Table 9. From the relation between k_2(corr.) and 1/[PhOH] (Fig. 1), the following values of k_2^0 and k_0' were obtained (in units of u): for phenethyl bromide, $k_2^0 = 0·88$, $k_0' = 0·012$; for 4-nitrophenethyl bromide, $k_2^0 = 1·25$, $k_0' = 0·051$. These figures enable the ratio $F = 100\,k_0'/(k_0' + k_2^0[\mathrm{PhOH}])$, *i.e.*, the amount of olefin produced by the equilibrium concentration of ethoxide ion, to be calculated.

From these values of k_2^0 and k_0', and from the yield of olefin obtained for given initial concentrations, the contributions from the various reactions may be calculated (Table 10). This Table shows that, for initial concentrations of phenol and phenoxide greater than 0·2M, the ethoxide ions contribute only a few percent to the total reaction. Moreover, over the 0·2—0·4M-concentration range, the variation in the yield of olefin is relatively small, and within the limits of experimental error of the analyses recorded in Table 11.

TABLE 9.

Estimation of the yields of olefin produced by the equilibrium concentration of ethoxide ions for different concentrations of phenoxide ions when [PhO$^-$] = [PhOH].

		Ph·CH$_2$·CH$_2$Br			p-NO$_2$·C$_6$H$_4$·CH$_2$·CH$_2$Br		
[PhOH]	k_2 (BuBr)	k_2	k_2 (corr.)	F *	k_2	k_2 (corr.)	F *
0·01	4·93	10·1	2·05 u	58	—	—	—
0·02	4·45	6·71	1·51 u	41	16·4	3·69 u	67
0·05	3·70	—	—	—	8·8	2·38 u	45
0·10	3·12	2·99	0·958 u	12·5	5·3	1·70 u	29
0·20	2·77	2·50	0·901 u	6·6	—		

* F gives the yield of olefin produced by ethoxide ions, *i.e.*, $F = 100k_0'(k_0' + k_2^0[\text{PhOH}])$. The symbol, u, represents the value of k_2^0(BuBr). These results give values of 5×10^{-4} and 3×10^{-4} for K.

TABLE 10.

Contribution of the S_N2 and E_2 reactions of phenoxide, and the E_2 reaction of the equilibrium ethoxide, to the total reaction of phenethyl bromide.

	Olefin (%)			S_N2 reaction
[PhO$^-$]	From PhO$^-$	From EtO$^-$	Total	of PhO$^-$
0·01	19·0	58	77·0	23
0·02	26·8	41	67·8	32·2
0·1	39·7	12·5	52·2	47·8
0·2	42·2	6·6	48·8	51·2
0·4	43·6	3·4	47	53

Yields of Olefin.—These are recorded in Tables 11—13.

TABLE 11.

Yield of olefin [method (*a*)] for the reactions of phenethyl bromide (X) and *para*-substituted phenols.

[X] (M)	[PhO$^-$] (M)	[PhOH] (M)	Reaction (hr.)	Olefin (%)
		p-MeO·C$_6$H$_4$·OH		
0·3	0·3	0·3	2·5	50·19
0·3	0·3	0·3	5	48·49
0·3	0·3	0·3	7	49·27
0·3	0·3	0·3	24	47·73
0·2	0·4	0·4	5	46·98
0·2	0·5	0·1	6	47·78
			Mean 48·4 ± 1·7	
		p-Me·C$_6$H$_4$·OH		
0·3	0·3	0·3	2·5	49·86
0·3	0·3	0·3	5	49·90
0·3	0·3	0·3	7·5	47·56
0·3	0·3	0·3	19	48·16
0·2	0·4	0·4	5	45·30
0·2	0·5	0·1	6	47·93
			Mean 48·1 ± 2·8	
		PhOH		
0·3	0·3	0·3	4	46·09
0·3	0·3	0·3	7	43·94
0·3	0·3	0·3	16	45·27
0·3	0·3	0·3	28	43·59
0·2	0·4	0·4	8	46·21
0·2	0·5	0·1	16	47·96
0·4	0·4	0·4	3	47·11
0·4	0·4	0·4	4	45·8
0·4	0·4	0·4	4	47·8
0·4	0·4	0·4	18	47·8
			Mean 46·2 ± 4·3	

[X] (M)	[PhO$^-$] (M)	[PhOH] (M)	Reaction (hr.)	Olefin (%)
		p-Br·C$_6$H$_4$·OH		
0·3	0·3	0·3	7	33·34
0·3	0·3	0·3	19	33·53
0·3	0·3	0·3	24	32·91
0·3	0·3	0·3	49	32·87
0·2	0·5	0·1	22	38·1
			Mean 34·0 ± 4·0	
		p-Ac·C$_6$H$_4$·OH		
0·3	0·3	0·3	24	22·33
0·3	0·3	0·3	48	22·25
0·3	0·3	0·3	69	21·73
0·3	0·3	0·3	100	22·19
0·2	0·4	0·4	45	25·60
0·2	0·5	0·1	52	26·0
			Mean 23·2 ± 2·8	
		p-NO$_2$·C$_6$H$_4$·OH		
0·1	0·1	0·1	116	16·9
0·3	0·3	0·3	44	17·35
0·3	0·3	0·3	72	17·09
0·3	0·3	0·3	120	16·68
0·2	0·4	0·4	76	14·62
0·3	0·3	0	146	17·28
			Mean 16·7 ± 2·0	

TABLE 12.

Yields of olefin [method (*a*)] obtained from 4-bromoheptane and *para*-substituted phenols with equal initial concentrations (0·1M) of 4-bromoheptane, phenol, and sodium phenoxide.

PhOH			*p*-Br·C_6H_4·OH			*p*-NO_2·C_6H_4·OH		
Reaction (%)	Olefin (%)		Reaction (%)	Olefin (%)		Reaction (%)	Olefin (%)	
73	41·3	44·2	61	40·8	40·7	19	25·9	24·0
71	46·2		52	38·8		42·6	22·0	
50	45·1		72·7	42·6				

Similar analyses showed that less than 1·0% of olefin was formed from octyl bromide and phenol, with the following concentrations of phenoxide and phenol, respectively: 0·02N and no phenol; 0·02N and 0·02N; 0·1N and no phenol; 0·1N and 0·1N.

TABLE 13.

Yields of olefin [method (*b*)] in the reaction between 4-nitrophenethyl bromide and *para*-substituted phenols.

Phenol	[PhOH]	$[PhO^-]$	Olefin (%)	Phenol	[PhOH]	$[PhO^-]$	Olefin (%)
PhOH	—	0·1	98·5 ± 1·5	*p*-NO_2·C_6H_4·OH	—	0·1	89·5 ± 1·2
	0·1	0·1	97 ± 3		0·1	0·1	91 ± 2
	0·3	0·1	100		0·3	0·1	95
p-Br·C_6H_4·OH...	—	0·1	96·4 ± 2·5				
	0·1	0·1	97				

The following yields of olefin were obtained in the reaction of sodium ethoxide (0·1N) and several alkyl bromides (0·1N) by method (*c*): Phenethyl bromide, 98·5 ± 1·6% (7); 4-nitrophenethyl bromide, 100% (1); butyl bromide, 7·3 ± 0·7 (8); octyl bromide 6·4 ± 0·1% (2); 4-bromoheptane 95·5 ± 2% (2) (the number of separate experiments performed is given in parentheses).

DISCUSSION

Theoretical Interpretation.—As discussed previously,[1,6] the change in rate constant, k_2, with the basicity of the nucleophile is given approximately by the Brönsted equation, $\log k_2 = \alpha . pK_a + \text{Constant}$, when a series of similar nucleophiles is considered. Although more accurate free-energy relations of the kind proposed by Hammett and discussed by Taft [11] may be derived, we have considered, for reasons given elsewhere,[6] that the simple Brönsted relation is the most suitable when an interpretation of the reaction parameter α is required.

We have shown [12] that the selectivity coefficient, α, for the reaction between thiophenols and 4-substituted benzyl bromides increases regularly with the electrostatic field at the electrophilic centre, and subsequently found similar behaviour for a wide range of displacements.[1] Values for the selectivity coefficients have also been calculated by assuming reasonable transition-state structures for various types of reaction, and by representing the interaction energy between the nucleophile and the electrophilic centre by Coulomb forces. The case of competing S_N2 and E_2 reactions is particularly suitable for treatment since the displaced group is the same for both reactions. In order to set up the transition states, the following simplifying assumptions were made: (*a*) The C–Br bond extensions and charge distributions are the same in the S_N2 and the E_2 transition state. (*b*) The nucleophile N and leaving group X share the negative charge, *i.e.*, there is no accumulation of charge in the rest of the molecule. (*c*) For simplification, a symmetrical transition state is assumed, *i.e.*, one with formal charges of 0·5, on the groups N and X (cf. Baugham and, Polanyi [13]). (*d*) The N–H and N–C distances, r and r_1^1, in the transition states are taken to be the mean values of the ionic and the covalent distances (cf. Baughan and Polanyi [13]). These assumptions lead to the following transition states illustrated. The interaction

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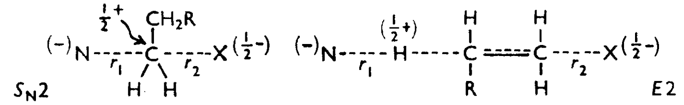
[11] Taft, *J. Phys. Chem.*, 1960, **64**, 1812.
[12] Hudson and Klopman, *J.*, 1962, 1062.
[13] Baughan and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 648.

energies involving the nucleophile are assumed to be given by Coulomb forces (cf. Ri and Eyring [14]).



In the general case, if the charge on the nucleophilic atom (*i.e.*, the oxygen atom of the phenoxide ion) is Z, and that on the electrophilic centre is δ, the activation energy ΔE^* is given by $\Delta E^* = (Z\delta/r_1D) + E_2$, where E_2 is the energy required to stretch the C–X bond, and D is the effective dielectric constant between N and the reaction centre. Similarly for the combination of N with a proton, $\Delta H = Z/r_0D$, where r_0 is the equilibrium separation distance in HN. These two equations give $\Delta E^* = (r_0/r_1)\delta\Delta H$ + Constant, or, by neglecting entropy differences, $\log k = (r_0/r_1)\delta\ .\ pK_a$ + Constant. Thus, from r_0, r_1, and the assumed transition-state structures, values of $(r_0/r_1)_S\delta$ and $(r_0/r_1)_E\delta$ may be calculated and compared with the experimental values α_S and α_E obtained from the corresponding Brönsted relations (Table 14).

TABLE 14.

Comparison of experimental values * of α_S and α_E for several alkyl bromides with the calculated values.

		α (observed)				
	calc.	Pr^n_2CHBr	$C_8H_{17}Br$	Bu^nBr	$Ph\cdot CH_2\cdot CH_2Br$	p-$NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2Br$
S_N2	0·26	0·27	0·36	0·37	0·35	—
E_2	0·37	0·39	—	—	0·56 (0·54) †	0·72 (0·67) †

* From total rate constants for 0·1M-solutions. † Correction applied for olefin produced by EtO^- in equilibrium with PhO^- (see Table 10), giving these minimum values.

Interpretation of Results.—As discussed in the Experimental section, accurate values of the rate constants for substitution and elimination could not be obtained owing to the influence of the equilibrium concentration of ethoxide ions, the sensitivity of the experimental rate constants to changes of concentration in the experimentally accessible region, and the difficulty in analysing accurately the yield of olefin in the presence of phenols. The rate constants quoted in this section are, therefore, approximate, although their relative values are more significant. It should also be noted that the difference in the selectivity coefficients, $\alpha_E - \alpha_S$, is independent of the total rate constants, k_2, as shown by the equations:

$$\text{For elimination, } \log k_E \equiv \log k_2C = \alpha_E\ .\ pK_a + C_1;$$
$$\text{For substitution, } \log k_S \equiv \log k_2(1 - C) = \alpha_S\ .\ pK_a + C_2,$$

where C is the fraction of the reaction leading to olefin. It follows that $\log [C/(1 - C)] = (\alpha_E - \alpha_S)\ .\ pK_a$ + Constant. Thus, although the absolute values of α_S and α_E (see Table 14) are only approximate, the differences, $\alpha_E - \alpha_S$, give the true values.

By using the total rate constants obtained for initial 0·1M-concentrations, the rate constants k_S and k_E may be calculated and related to pK_a of the corresponding phenol, as shown in Fig. 2. For this purpose the pK_a values of the phenols in 95% aqueous ethanol obtained by Schwarzenbach [15] were used, in view of the difficulty of obtaining reliable values in 100% ethanol. From the approximately linear relations, values of α_S and α_E were calculated for the various bromides (Table 14).

Although the values of α are only approximate, they are in good agreement with the predictions of the general interpretation of nucleophilic reactivity, as shown by the following comparisons: (1) The values of α_S for the primary bromides (0·35—0·37) are fairly close to the calculated value of 0·26, bearing in mind the approximations and inaccuracies involved.

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[14] Ri and Eyring, *J. Chem. Phys.*, 1940, **8**, 433.
[15] Schwarzenbach and Rudin, *Helv. Chim. Acta*, 1939, **22**, 360.

These values are significantly higher than the value of 0·22 previously recorded for 3-bromopropanol in water, in agreement with the prediction [6] that a more polar solvent increases the polarity of the S_N2 transition state. The interaction between the nucleophile and the reaction centre is thereby reduced (*i.e.*, a tendency towards a more S_N1-like transition state,) producing a reduction in α. Similarly, the change from primary to secondary bromide produces an appreciable decrease in α_S, owing to the reduced field at the central carbon atom brought about by dispersion of charge in the incipient carbonium ion (see ref. 6, p. 178). (2) The value of $\alpha_E - \alpha_S$ for 4-bromoheptane is close to the calculated value given in Table 14, but the value of α_E increases regularly with conjugation at the β-carbon atom. This may be attributed to the distribution of negative charge in the incipient carbanion, as in (A), which promotes further charge transfer from PhO^- to the hydrogen atom in order to reach the required charge separation in the C–Br bond of the transition state. According to the general interpretation of nucleophilic reactivity given elsewhere,[6] this produces an increase in α.

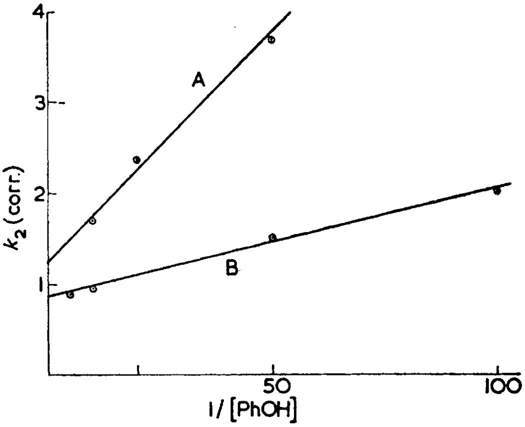


FIG. 1. Relation between k_2 (corr.) (given in μ units) of the equation k_2 (corr.) $= k_2^0 + k_0^1/[PhOH]$ for 4-nitrophenethyl bromide (A) and phenethyl bromide (B).

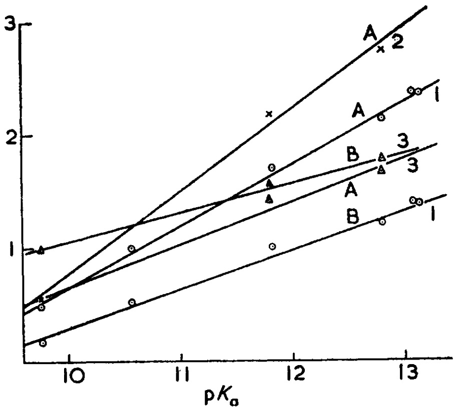
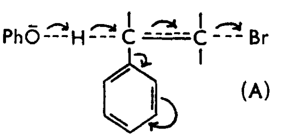


FIG. 2. Relation between log k_2 and pK_a for β-elimination (A) and S_N2 substitution (B), with phenoxide ions, of (1) phenethyl bromide, (2) 4-nitrophenethyl bromide, and (3)4-bromoheptane.



(A)

This interpretation is reasonable, since further stabilisation of the transition state would lead to an intermediate carbanion * (*i.e.*, mechanism E_1CB), in which case $\alpha = 1$, and the reaction becomes specific-base-catalysed. The value of $\alpha \approx 0{\cdot}72$ in Table 14 for 4-nitrophenethyl bromide shows, however, that this limiting transition-state structure is not reached in this case. According to recent analyses of the influence of substituents in the phenyl nucleus, the carbanion character is more advanced in the sulphonium ions † than in the corresponding phenethyl bromide,[16] and the influence of this on the stereochemistry of the elimination is now realised.

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* The E_1CB mechanism has recently been demonstrated kinetically [17] for *erythro*-44′-dichlorochalcone dichloride ($p\cdot Cl\cdot C_6H_4\cdot COCl\cdot CHClC_6H_4\cdot p\cdot Cl$), the carbanion being stabilised in this case by the α-carbonyl group.

† This is to some extent supported by recent studies of deuterium isotope effects with β-phenethyl derivatives.[18]

[16] Saunders and Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 3712; Saunders and Edison, *ibid.*, 1960, **82**, 138.

[17] Crowell, Wall, Kemp, and Lutz, *J. Amer. Chem. Soc.*, 1963, **85**, 2521.

[18] Steffa and Thornton, *J. Amer. Chem. Soc.*, 1963, **85**, 2680.