Hydrolytic Decomposition of Esters of Nitric Acid. Part III. Kinetic Evidence for Ion Exchange between Anionic Reagents and the Solvent in the Carbonyl Elimination Reaction ($E_{CO}2$).*

By John W. Baker and A. J. Neale.

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The effect of attack by ethoxide ion, resulting from the equilibrium $Y^- + EtOH \rightleftharpoons HY + OEt^-$ (I), on the determined velocity coefficients $kE_{CO}2$ for the strictly bimolecular elimination reaction $Y^- + CH_2Ph{\cdot}O{\cdot}NO_2 \longrightarrow HY + Ph{\cdot}CH{:}O + NO_2^-$ in 100% ethyl alcohol has been studied when $Y^- = p\text{-}MeO{\cdot}C_6H_4{\cdot}O^-$, PhO^-, and *m*- and $p\text{-}NO_2{\cdot}C_6H_4{\cdot}O^-$. In the initial absence of the free conjugate acid HY the value of $kE_{CO}2$ drifts markedly downwards during the reaction because much of the elimination is initially due to the much stronger nucleophilic ethoxide ion, the concentration of which is continuously reduced by a mass-law effect on the equilibrium (I) by HY produced as the reaction proceeds. Initial addition of increasing concentrations of free HY eliminates this drift and gradually reduces the value of $kE_{CO}2$ asymptotically to the true value of this constant for attack by Y^-, which is thus determined. The erroneous values which result from neglect of proton transfer from the solvent to an attacking nucleophilic reagent are illustrated, and values of the equilibrium constants K_b' for the four phenols studied are calculated. A plot of the true log $kE_{CO}2$ values against either pK_b' values or pK_a for the phenols in 95% alcohol gives straight lines upon which the value of EtO^- also fits.

A similar, but less marked effect on the concomitant S_N2 reaction $Y^- + CH_2Ph{\cdot}O{\cdot}NO_2 \longrightarrow CH_2Ph{\cdot}Y + NO_3^-$ is also discussed.

One method for the diagnosis of mechanism in nucleophilic substitutions and their concomitant elimination reactions is to study the effect of changing the nucleophilic power of the attacking reagent on the course and velocity of the reaction (Gleave, Hughes, and Ingold, *J.*, 1935, 236; Ingold, " Structure and Mechanism in Organic Chemistry," Geo.

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* Part II, *J.*, 1952, 1208.

Bell and Sons, London, 1953, pp. 335 *et seq.*). Such nucleophilic reactions have often been studied in proton-donating solvents in which (cf. Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 399) complications may arise owing to proton transfer from the solvent (often alcohol) to the nucleophilic reagent Y^- and the establishment of the equilibrium

$$Y^- + EtOH \rightleftharpoons HY + OEt^- \quad . \; . \; . \; . \; . \; . \; . \quad (I)$$

Such complications were recognised and qualitatively detected by, *e.g.*, Cox (*J.*, 1918, 666; 1922, 493) in his study of the relative reactivities of various alkyl halides with sodium 1- and 2-naphthoxides in alcohol, and by Haywood (*J.*, 1922, **121**, 1904) in similar studies with sodium benzyloxide. There is, however, little or no quantitative information on the magnitude and importance of this effect. Unless the equilibrium (I) were displaced very largely towards the left, the resulting partial replacement of a relatively weak nucleophilic reagent Y^- by the strongly nucleophilic ethoxide ion would cause large increases in the velocity of reaction and thus give quite erroneous values for the velocity coefficients for attack by Y^-.

Clear-cut, quantitative assessment of the magnitude of such ion-exchange with the solvent in kinetic studies might be possible if the following conditions are satisfied. First, the bimolecular reaction studied must be of mechanistic purity throughout the whole range of experiments. Secondly, since it is known that variation in nucleophilic power of different reagents towards hydrogen is usually greater than that towards carbon, a 1 : 2-elimination reaction should demonstrate the effect more markedly than a substitution reaction. Moreover, it would seem (cf. p. 3230) that the lyate-ion effect (Benfey, Hughes, and Ingold, *J.*, 1952, 2488) is much more important in a substitution action, thus giving an abnormally low velocity coefficient for ethoxide ion in ethyl alcohol solution. Finally, the anion Y^- should be a weak base relative to ethoxide ion (if alcohol is the proton-donating solvent), but not so weak that the equilibrium (I) would be displaced almost completely to the left, causing practical exclusion of ethoxide ion from the beginning of the reaction.

In a study (to be fully reported later) the attack of various nucleophilic reagents on benzyl nitrate in 100% ethyl alcohol solution to determine the effect of changes in the reagent on the velocities and relative importance of the two simultaneous reactions :

$$(a)\quad Y^- + CH_2Ph{\cdot}O{\cdot}NO_2 \longrightarrow CH_2PhY + NO_3^- \qquad (S_N2)$$

$$(b)\quad Y^- + CH_2Ph{\cdot}O{\cdot}NO_2 \longrightarrow Ph{\cdot}CH{:}O + NO_2^- + HY \; (E_{CO}2)$$

(cf. Baker and Easty, *Nature*, 1950, **166**, 156; *J.*, 1952, 1193, 1208), we realised that the attack of various aryloxide ions in the kinetically isolated reaction (*b*) fulfilled the desired conditions. The attack of the phenolic ions (which have the appropriate basic strengths) is at the α-hydrogen atom, and the most significant feature of the carbonyl-elimination reaction (not shared by an olefin elimination) is that it must always be bimolecular, since a rate-determining ionisation $CH_2Ph{\cdot}O{\cdot}NO_2 \rightleftharpoons CH_2Ph{\cdot}\overset{+}{O} + NO_2^-$ is extremely improbable, especially in dry alcohol as solvent. Moreover this conclusion would be unaffected by any intrusion of a unimolecular mechanism in the substitution reaction (*a*) because we have found that this reaction with benzyl nitrate, as with the corresponding halides, is on the borderline S_N2—S_N1 mechanism. Early results (cf. Baker and Neale, *Nature*, 1953, **172**, 583) strongly suggested the incursion of ethoxide ion in these reactions. Thus the velocity coefficients of both the S_N2 and $E_{CO}2$ reactions for attack by equimolecular solutions of either sodium hydroxide (OH^-) or sodium (OEt^-) dissolved in 100% ethyl alcohol were almost identical. This indicated that the attack was essentially by ethoxide ions in both cases and hence that, when $Y^- = OH^-$, the equilibrium (I) is displaced very largely to the right in the presence of small concentrations of water. This conclusion was independently confirmed by Caldin and Long (*ibid.*, p. 583; cf. Williams and Bost, *J. Chem. Phys.*, 1936, **4**, 251).

If, owing to equilibrium (I), aryloxide ions give rise to an appreciable initial concentration of ethoxide ions, there will be two carbonyl-elimination reactions (*b*) proceeding simultaneously, one with aryloxide and the other with ethoxide ion as the nucleophilic reagent. Because of its much greater nucleophilic power, that with ethoxide ion will have much the greater velocity, notwithstanding the low concentration of ethoxide ions. As the reaction with the aryloxide ion proceeds, increasing concentrations of the conjugate acid ArOH are produced and will, by displacement of the equilibrium (I) to the left, continually decrease the concentration of ethoxide ion, which is inversely proportional to the concentration of ArOH. This would lead, as is observed, to a marked downward drift in the experimental value of $kE_{CO}2$ as the reaction proceeds. Bearing in mind the simultaneous occurrence of two substitution reactions (*a*) (with aryloxide and ethoxide ions) and a superimposed solvolysis (for which correction can be made), the task of separately evaluating the velocity coefficients of each of the four simultaneous reactions is rather formidable, requiring determination of at least four entities (*e.g.*, the concentrations of NO_3^-, NO_2^-, ArOH, and $Ph{\cdot}CH_2{\cdot}OAr$) as functions of time. A simpler experimental approach to the problem seemed to be the initial addition of increasing concentrations of the free conjugate acid ArOH, first, to swamp the small concentration changes consequent on the production of a phenol by reaction (*b*) and, secondly, by a mass law effect on the equilibrium (I), ultimately to effect the more or less complete suppression of ethoxide ion from the beginning of the experiment. If these aims could be achieved before the concentration of the phenol is large enough to alter seriously the nature of the medium, such additions of the free phenol in increasing amounts should gradually eliminate the drift in the value of $kE_{CO}2$ throughout any one run and cause successive decreases in $kE_{CO}2$ towards an asymptotic value which is the true value of this coefficient for attack by the reagent OAr^-. Both these expectations have been completely realised in the carbonyl-elimination reaction for

TABLE 1. *Values of* kS_N2 *and* $kE_{CO}2$ *(both corrected) for the reaction between* Y^- *and* $PhCH_2{\cdot}O{\cdot}NO_2$ *in dry ethyl alcohol at* 60·2° *in the presence of varying concentrations of free* HY.

Expt	Y^-	Excess of HY, (mole l.$^{-1}$)	Initial concn. (mole l.$^{-1}$)		10^5k_2 (l. mole^{-1} sec.$^{-1}$)	
			$[CH_2Ph{\cdot}ONO_2]$	$[Y^-]$	S_N2	$E_{CO}2$
1	EtO^-	—	0·0400	0·1026	100 ± 10	1345 ± 10
2	*p*-$MeO{\cdot}C_6H_4O^-$	0·0019	0·0500	0·0970	122 ± 5	99·2 → 74·5
3	,,	0·0382	0·0529	0·1021	116 ± 2	34·1 → 32·0
4	,,	0·0622	0·0516	0·1000	114 ± 2	23·5 ± 0·3
5	,,	0·0967	0·0529	0·1024	112 ± 2	17·3 ± 0·1
6	,,	0·2025	0·0530	0·0990	103 ± 0·5	11·1 ± 0·05
[7	,,	0·5015	0·0597	0·1097	83·2 ± 0·6	6·38 ± 0·02]
8	$C_6H_5{\cdot}O^-$	0·006	0·0480	0·0927	74 ± 2	48·8 → 36·8
9	,,	0·0252	0·0505	0·0935	68·7 ± 1	26·7 → 22·6
* 10	,,	0·0333	0·0536	*0·0286*	(74·8 ± 1)	21·6 → 20·2
* 11	,,	0·0674	0·0896	*0·2095*	(63·4 ± 1)	12·8 ± 0·1
12	,,	0·0701	0·0510	0·0993	66·3 ± 1	12·7 ± 0·1
* 13	,,	0·1010	0·0530	*0·0400*	(70·2 ± 1)	9·9 ± 0·1
14	,,	0·1080	0·0477	0·0915	64·3 ± 1	9·7 ± 0·1
15	,,	0·2275	0·0514	0·1000	59·1 ± 1	6·30 ± 0·1
16	,,	0·3087	0·0478	0·0897	59·1 ± 1	5·28 ± 0·1
[* 17	,,	0·7244	0·0541	*0·0468*	(48·1 ± 1)	2·97 ± 0·03]
[18	,,	0·9202	0·0502	0·0888	43·6 ± 1	2·44 ± 0·02]
19	*m*-$NO_2{\cdot}C_6H_4{\cdot}O^-$	0·001	0·0545	0·0898	25·4 ± 1	2·35 → 1·55
20	,,	0·1589	0·0519	0·0988	20·5 ± 0·2	0·584 ± 0·007
21	,,	0·2572	0·0528	0·1004	18·1 ± 0·2	0·440 ± 0·005
22	,,	0·4138	0·0565	0·1019	16·1 ± 0·2	0·360 ± 0·004
[23	,,	0·9986	0·0543	0·1013	10·5 ± 0·2	0·143 ± 0·003]
24	*p*-$NO_2{\cdot}C_6H_4{\cdot}O^-$	—	0·0564	0·0983	7·2 ± 0·10	0·20 → 0·15
25	,,	0·0628	0·0514	0·1064	6·07 ± 0·10	0·122 ± 0·01
26	,,	0·0963	0·0489	0·1034	5·51 ± 0·07	0·108 ± 0·01
27	,,	0·1882	0·0537	0·1108	5·38 ± 0·03	0·100 ± 0·01
[28	,,	0·3937	0·0508	0·1081	4·39 ± 0·10	0·076 ± 0·01]
† 29	$C_6H_5O^-$	0·0297	0·0541	0·1039	14·9 ± 0·1	3·75 → 3·38
† 30	,,	0·0464	0·0513	0·1036	14·9 ± 0·1	2·72 ± 0·06
† 31	,,	0·0908	0·0531	0·1032	14·4 ± 0·1	1·77 ± 0·03
† 32	,,	0·2121	0·0555	0·1373	13·3 ± 0·1	1·08 ± 0·01

* Determined at a different [NaOPh] which (p. 3230) causes some change in kS_N2 (values in parentheses). † At 45°.

attack by four different aryloxide ions on benzyl nitrate in 100% ethyl alcohol as solvent, *viz.*, $OAr^- = p\text{-}MeO{\cdot}C_6H_4{\cdot}O^-$, OPh^-, *m*- and $p\text{-}NO_2{\cdot}C_6H_4{\cdot}O^-$, and, in the case of phenoxide, at two temperatures. The effects of addition of increasing amounts of the corresponding free phenol on the separate values of kS_N2 and $kE_{CO}2$ (corrected for the solvolysis of benzyl nitrate in 100% alcohol, which gives no elimination) are in Table 1. When a drifting velocity coefficient was obtained the limits of the (regular) drift from the initial to the final readings are indicated; where no such significant drift occurred, the mean deviation from the mean is shown. It was shown that the presence of 0·994M-phenol caused only a ~7% rise in the velocity of the solvolysis of benzyl nitrate in dry ethyl alcohol ($10^5k_1^{60\cdot2°}$ increased from 0·119 to 0·127 $sec.^{-1}$) which makes no significant difference to the small correction for solvolysis. The observation that, at constant concentration of phenol, the experimental value of $kE_{CO}2$ is independent of the initial aryloxide ion concentration, shows that the elimination by this ion is a true second-order reaction.

Before a quantitative analysis of the results is given attention may be directed to a few general features. In agreement with the postulated effect of the free phenol on the equilibrium (I) it is found that, as the basic strength of the aryloxide ion decreases ($p\text{-}MeO{\cdot}C_6H_4{\cdot}O^- > OPh^- > m\text{-} > p\text{-}NO_2{\cdot}C_6H_4{\cdot}O^-$) the observed drift in $kE_{CO}2$ in the absence of excess of phenol becomes less marked (Table 1, Expts. 2, 8, 19, 24) and this initial value is closer to the value observed in the presence of a moderate excess of phenol, *i.e.*, as the acid strength of the phenol increases, the initial equilibrium (I) lies further to the left so that much smaller concentrations of ethoxide ion are initially present. As expected, gradual replacement of ethoxide ion by aryloxide ion has a much smaller effect on kS_N2 than on $kE_{CO}2$. The results of Quayle and Royals (*J. Amer. Chem. Soc.*, 1942, **64**, 227) for the action of 0·05M-sodium phenoxide in dry ethyl alcohol on *n*-butyl bromide provide a further illustration of the relatively small effect on a substitution reaction. Extrapolation of their data gives $10^5k_2^{55°} = 26{\cdot}8$ l. $mole^{-1}$ $sec.^{-1}$. For the similar attack by sodium ethoxide the value is $10^5k_2^{55°} = 43{\cdot}9$ l. $mole^{-1}$ $sec.^{-1}$ (Dhar, Hughes, Ingold, and Masterman, *J.*, 1948, 2055). From our calculation (p. 3230) of the equilibrium constant between phenoxide ion and ethyl alcohol (at 60°), the initial concentration of ethoxide ion in Quayle and Royals's experiment would be ~0·005M, whence the true value of $10^5k_2^{55°}$ for phenoxide can be calculated to be 24·9 l. $mole^{-1}$ $sec.^{-1}$, representing only about a 7% error in their recorded value.

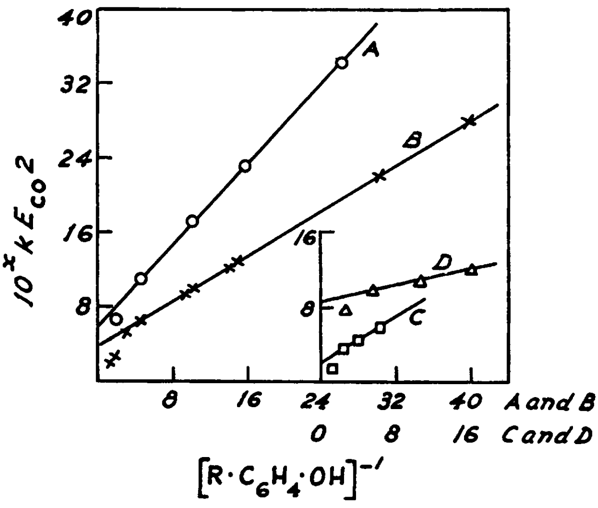

FIG. 1. *Variation of* $kE_{CO}2$ *in the reaction of* $PhCH_2{\cdot}NO_3$ *with* $R{\cdot}C_6H_4O^-$ *in the presence of varying* $[R{\cdot}C_6H_4{\cdot}OH]$ *in* 100% EtOH *at* 60·2°.

A, R = *p*-MeO; *x* = 5.
B, R = H; *x* = 5.
C, R = *m*-NO_2; *x* = 6.
D, R = *p*-NO_2; *x* = 7.

When the concentration of added phenol becomes very large (Table 1, Expts. 7, 17, 18, 23, 28) effects due to the medium and other disturbing factors enter. In Expt. 18, for example, the solvent contains ~6 moles % (~10% by weight) of phenol and abnormally large falls in both kS_N2 and $kE_{CO}2$ are observed. When such experiments are omitted, a plot of $kE_{\mathrm{CO}}2$ against the reciprocal of the phenol concentration gives a good straight line (Fig. 1), extrapolation of which to $[\mathrm{ArOH}]^{-1} = 0$ should give the *true* value of $kE_{\mathrm{CO}}2$ for the particular aryloxide ion. The values so obtained at 60·2° are :

$\mathrm{ArO^-}$ =	p-$\mathrm{MeO{\cdot}C_6H_4{\cdot}O^-}$	$\mathrm{OPh^-}$	m-$\mathrm{NO_2{\cdot}C_6H_4{\cdot}O^-}$	p-$\mathrm{NO_2{\cdot}C_6H_4{\cdot}O^-}$
True $10^5kE_{\mathrm{CO}}2$ (l. mole^{-1} sec.$^{-1}$)	5·63	3·80	0·22	0·085
,, $10^5kS_{\mathrm{N}}2$ (l. mole^{-1} sec.$^{-1}$)	110	60	13·7	5·0

$10^5kE_{\mathrm{CO}}2$ for phenoxide at 45° = 0·7 l. mole^{-1} sec.$^{-1}$.

The large error introduced by neglecting proton-exchange between the solvent and an attacking nucleophilic anion of moderate basic strength is thus clearly demonstrated. For phenoxide in the reaction studied the uncorrected value of $kE_{\mathrm{CO}}2$ is ~13 times the true value, which suggests that it is necessary to re-examine results previously obtained in which this factor has been ignored. We have not yet examined how important is the equilibrium $\mathrm{NR_3 + EtOH \rightleftharpoons N^+HR_3 + OEt^-}$ in the case of attack by neutral bases, but Betts and Hanmett's results (*J. Amer. Chem. Soc.*, 1937, **59**, 1568) show that it is significant in the case of ammonia.

Analysis of our data gives further interesting information. By using the value $k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2 = 1345 \times 10^{-5}$ (Table 1, No. 1) and the true value of $k^{\mathrm{OPh^-}}E_{\mathrm{CO}}2 = 3{\cdot}8 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$, it is possible to calculate, in any one experiment, the concentrations of phenoxide and ethoxide ions present at each stage of the reaction. The equation representing total carbonyl elimination, determined by the amount of nitrite ion produced at time t, is :

$$\mathrm{d[NO^-_2]/d}t = k^{\mathrm{OPh^-}}E_{\mathrm{CO}}2\,.[\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2}][\mathrm{OPh^-}] + k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2\,.[\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2}][\mathrm{OEt^-}] \quad \text{(II)}$$

If the initial concentration of benzyl nitrate = a, the total alkali concentration = b, and, at time t, the amount of total second-order reaction (substitution + elimination) = x, and the instantaneous values of the concentrations of phenoxide and ethoxide ions are, respectively, p and e, then

$$p + e = (b - x)$$

and $$\mathrm{d[NO_2^-]/d}t = k^{\mathrm{OPh^-}}E_{\mathrm{CO}}2\,.\,(a - x)(p) + k^{\mathrm{OEt}}\,E_{\mathrm{CO}}2\,.\,(a - x)(e)$$

whence $$\mathrm{d[NO_2^-]/d}t(a - x) = \text{(say) } M = k^{\mathrm{OPh^-}}E_{\mathrm{CO}}2\,.\,p + k^{\mathrm{OEt}}\,E_{\mathrm{CO}}2\,.\,(b - x - p)$$

therefore, $$p = [M - k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2\,.\,(b - x)]/[k^{\mathrm{OPh^-}}E_{\mathrm{CO}}2 - k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2]$$

The value of $\mathrm{d[NO_2^-]/d}t$ can be obtained from the tangent at time t to the curve obtained by plotting $[\mathrm{NO_2^-}]$ against t, whence M and thus p and e can be determined. Application of this method to Expt. 8 (no appreciable excess of phenol initially present) shows that, at the beginning of the run, the ratio $\{[\mathrm{OPh^-}]\}/\{[\mathrm{OPh^-}] + [\mathrm{OEt^-}]\} = 0{\cdot}97$, *i.e.*, about 3% of the total alkali present is ethoxide ion. This amount gradually decreases throughout the run until, towards the end, it has been reduced to ~2%. Because of the much larger value of $k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2$ this means that ~85% of the total carbonyl elimination is due to ethoxide ion and only 15% to phenoxide. Even in Expt. 16, approximately 10% of the carbonyl elimination is still due to ethoxide.

The results also permit an assessment to be made of the values of the equilibrium constant $K_b' = [\mathrm{ArOH}][\mathrm{OEt^-}]/[\mathrm{OAr^-}][\mathrm{EtOH}]$ for each of the phenols. The relation (II) can be rewritten as

$$\begin{aligned}\mathrm{d[NO_2^-]/d}t = {} & k^{\mathrm{OAr^-}}E_{\mathrm{CO}}2\,.\,[\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2}][\mathrm{OAr^-}] \\ & + k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2\,.\,[\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2}][\mathrm{OAr^-}]K_b'[\mathrm{EtOH}]/[\mathrm{ArOH}]\end{aligned}$$

whence $$\begin{aligned}\mathrm{d[NO_2]/d}t[\mathrm{Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2}][\mathrm{OAr^-}] &= k^{\mathrm{OAr^-}}E_{\mathrm{CO}}2 + k^{\mathrm{OEt^-}}E_{\mathrm{CO}}2\,.\,K_b'[\mathrm{EtOH}]/[\mathrm{ArOH}] \\ &= kE_{\mathrm{CO}}2 \text{ experimental} \quad . \ . \ . \ . \ . \ . \ . \ . \quad \text{(III)}\end{aligned}$$

since, in the presence of excess of ArOH, the ethoxide ion concentration is small and no serious error is introduced if the measured alkali concentration is substituted for [OAr^-]. Thus the slope of the straight line obtained by plotting $kE_{CO}2$ (experimental) against $[ArOH]^{-1}$ (p. 3228) gives $k^{OEt^-}E_{CO}2 \,.\, K_b'[EtOH]$ whence K_b' (in terms of concentration, not of activities) is obtained, the concentration of ethyl alcohol at 60° being taken as 16·4M. The values (at 60·2°) thus obtained are :

ArOH =	p-MeO·C_6H_4·OH	PhOH	m-NO_2·C_6H_4·OH	p-NO_2·C_6H_4·OH
$10^7K_b'$	493	276	26	0·9

It must be remembered that all the errors, both in the isolation of $kE_{CO}2$ from the total second-order coefficient, and in the extrapolation of $kE_{CO}2$ to $[ArOH]^{-1} = 0$, cumulatively affect this determination of K_b', yet a Brönsted plot of log $kE_{CO}2$ against pK_b' approximates closely to a straight line (Fig. 2) upon which ethoxide also falls into place. If instead of our pK_b', the recorded values of pK_a for the phenol in 95% aqueous alcohol (Schwarzenbach and Rudin, *Helv. Chim. Acta*, 1939, **22**, 360) (or in water) are used a better straight-line plot results.

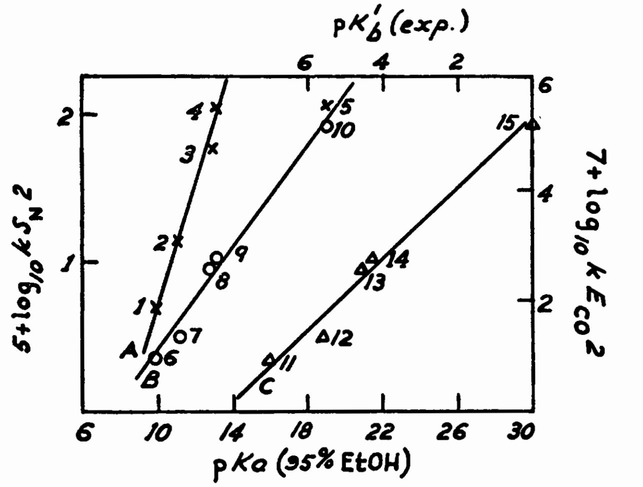

FIG. 2. *Brönsted plots of* kS_N2 *and* $kE_{CO}2$ *for the reaction of* $PhCH_2·NO_3$ *with* RO′ *in* 100% EtOH *at* 60·2°.

Curves : $A = kS_N2$.
B and C, $kE_{CO}2$.

Experimental points :
1, 6, 11. p-NO_2·C_6H_4·O^-.
2, 7, 12. m-NO_2·C_6H_4·O^-.
3, 8, 13. PhO^-.
4, 9, 14. p-MeO·C_6H_4·O^-.
5, 10, 15. EtO^-.

Theoretically, similar analyses could be applied to the data for kS_N2, but reasons have already been given why less clear-cut results might be expected in the substitution reaction. In practice we have found evidence of other disturbing factors. The decrease in kS_N2 caused by increasing concentrations of the free phenol is expressed by an equation $kS_N2 =$ constant $+ A/[ArOH]$, of the same type as (III), and the values of kS_N2 obtained by extrapolation to $[ArOH]^{-1} = 0$ are given above (p. 3228). The observed decrease is, however, larger than would be expected if $A = k^{OEt^-}S_N2 \,.\, K_b'$, when the previously-determined values of K_b', from the elimination reaction, are used. Compared with that for phenoxide, the value of kS_N2 for ethoxide is abnormally low. This may be accounted for, at least partly, by the lyate-ion effect discussed by Benfey, Hughes, and Ingold (*loc. cit.*). The absence of such an effect in the elimination is understandable since it is only another hydrogen nucleus and not carbon which is attacked. Other abnormalities cannot be so explained. Unlike the constancy observed for $kE_{CO}2$, the value of kS_N2 at constant phenol concentration decreases slightly with increasing concentration of sodium aryloxide, *e.g.*, with sodium phenoxide in 100% ethyl alcohol and a 0·07M-excess of phenol :

[NaOPh] (M)	0·04	0·1	0·2
10^5kS_N2 (l. mole.$^{-1}$ sec.$^{-1}$)	70·8	66·3	63·4

Another anomally was observed in the effect of increasing the ionising power of the solvent by addition of water to the alcohol. Whereas increase in the water content of the solvent causes a small *decrease* in the values of both kS_N2 and $kE_{CO}2$ for attack by hydroxide ion, in agreement with the Hughes–Ingold theory (*J.*, 1935, 244) for a reaction which involves distribution of a fixed charge in the transition state, the corresponding value of kS_N2 for phenoxide ion attack is considerably *increased*, in direct opposition to the requirements of this theory:

Solvent: % of H_2O in EtOH	0	40	55
$10^4k^{OH}S_N2$ (l. mole.$^{-1}$ sec.$^{-1}$)	10	—	5·5
$10^3k^{OH}E_{CO}2$ (l. mole.$^{-1}$ sec.$^{-1}$)	13·45	1·98	0·9
$10^4k^{OPh^-}S_N2$ (l. mole.$^{-1}$ sec.$^{-1}$)	7·8	16·0	22·4

The only tentative explanation we can suggest * for these anomalies is that there is some degree of ion association in the sodium aryloxide, a view which has been suggested by various workers (Hardwick, *J.*, 1935, 141; Mitchell, *J.*, 1937, 1792; Woolf, *ibid.*, p. 1172; cf. also Bell, " Advances in Catalysis," Academic Press, New York, 1952, Vol. 4, 154). It must be assumed that whilst the undissociated sodium aryloxide or the ion-pair $Ar\overset{-}{O}\}\overset{+}{N}a$ is as effective as the aryloxide ion for attack on the small exposed hydrogen nucleus (elimination reaction), they are not so effective for attack on the more effectively screened carbon nucleus (substitution reaction). Any such ion association would be expected to increase both with increasing concentration of sodium aryloxide in 100% alcohol (and thus account for the observed drop in kS_N2 with 0·2M-sodium aryloxide) and with decrease in the ionising power of the solvent (thus explaining the much smaller value of $k^{OPh^-}S_N2$ in 100% alcohol). It is, of course, recognised that addition of water to the solvent introduces the new equilibria $HOH + OEt^- \rightleftharpoons EtOH + OH^-$ and $HOH + PhO^- \rightleftharpoons PhOH + OH^-$, both interrelated with equilibrium (I) (which has been the main concern in this communication), thus introducing further complications. It is the data for the carbonyl-elimination reaction which most clearly demonstrate the importance and magnitude of the hitherto largely neglected effect of proton-transfer from the solvent to an attacking nucleophilic ion in kinetic studies.

EXPERIMENTAL

Solvents and Materials.—Dry 100% ethyl alcohol was prepared either by Smith's (*J.*, 1927, 1288; cf. Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1106) or by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210), with rigid precautions to exclude atmospheric moisture and carbon dioxide. It was stored under dry nitrogen in the dark, and had d_{20}^{4} 0·7893 (in agreement with that for 100% ethyl alcohol given in International Critical Tables). The maximum water content, determined by Smith's method (*J.*, 1927, 1284), was 0·04%; the alcohol was free from carbonyl compounds (2 : 4-dinitrophenylhydrazine) and was stable to alkali over long periods at 60°. The rate of solvolyses of benzyl nitrate ($10^6k_1^{60} = 1{\cdot}19$ sec.$^{-1}$) with this solvent remained unchanged after it had been stored for 10 months. Addition of 1% of water to the 100% alcohol decreased the value of $10^2k_2^{60}$ for the alkaline hydrolysis of benzyl nitrate from 1·47 to 1·37 l. mole^{-1} sec.$^{-1}$.

Aqueous-alcohol solvents were prepared by mixing x volumes of this dry alcohol with $(100 - x)$ volumes of water to give " x vol. % " alcohol.

Benzyl Nitrate.—Dry benzyl chloride, b. p. 74·5°/15 mm. (50 g.), in dry ether (50 ml.) was kept with *very* finely powdered silver nitrate (75 g.) at room temperature for 12 hr., and was then refluxed at 70—75° (with exclusion of moisture and carbon dioxide) until free from chloride. Ether was distilled from the dried (calcium nitrate) filtrate from silver residues, and the residue was repeatedly fractionated through a column from powdered silver nitrate and calcium carbonate to give a specimen, b. p. 59·0°/0·4 mm., n_D^{20} 1·5206 (Found: C, 55·2; H, 4·2. Calc. for $C_7H_7O_3N$: C, 54·9; H, 4·6%. Purity by complete hydrolysis, 100%). It was best stored in a brown stoppered bottle in a calcium nitrate desiccator and was repurified whenever any deviation from 100% purity by complete hydrolysis was detected.

p-Methoxyphenol was purified by repeated crystallisation from benzene–ligroin (b. p. 60—80°) at −15° in the absence of oxygen, to give colourless crystals, m. p. 56°. With sodium ethoxide solution prepared from dry alcohol (saturated with nitrogen) and clean sodium, colourless solutions (free from oxidation products) of the sodium salt were obtained.

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* On the basis of other work (Caldin and Long, in the press) Dr. E. F. Caldin privately suggested that the negative charge distribution in the attacking phenoxide might be *greater* than it is in the transition state, where it is more concentrated on the separating nitrate anion, thus leading to *greater localisation* of the charge in the transition state.

m-Nitrophenol was crystallised from benzene and chloroform to constant m. p. 97·5—98°. *p*-Nitrophenol was crystallised from dry toluene to give pale yellow crystals, m. p. 114°, which gradually changed to the reddish β-form (Sidgwick, *J.*, 1915, **107**, 676, 1208). Subsequent crystallisation from water gave the colourless α-form, m. p. 114°, stable to light. It was dried over magnesium perchlorate *in vacuo.*

" AnalaR " phenol, dried *in vacuo* ($MgClO_4$), was used without further purification.

Velocity Determinations.—The general techniques were those previously used (Baker and Easty, *loc. cit.*), refined and modified to suit each particular reagent. Since reaction velocities with benzyl nitrate (deliberately chosen to exclude olefin-elimination reactions) are much greater than those with alkyl nitrates, a sealed glass bulb technique could be employed for both alkaline and solvolytic reactions. Spherical bulbs (2 ml.) were blown from " Monax " glass quill tubing with very small free space, although it was proved that neither considerable variation in the " free-space " volume nor addition of powdered glass had any effect on the values of the velocity coefficients. Bulbs were filled at room temperature from an all-glass apparatus incorporating a gravity-filled pipette suitably connected to a capillary delivery tube, and were all plunged into the thermostat at the same time. Initial concentrations, determined by direct weighing and checked by complete hydrolysis values, were corrected for the amount of reaction which had occurred before temperature equilibrium had been attained (by initial sampling at zero time), for solvent expansion, or for the (small) volume of the liquid ester whenever a known volume of the more concentrated alkali solutions was added directly to the weighed ester. All methods used gave velocity coefficients which agreed to within ±1%. Thermostats were constant to at least ±0·05°. Reaction samples were " frozen " by breaking the bulbs under neutral ether at −10° (when aqueous extracts for nitrate and nitrite determinations were required) or cold acetone (when only acid–alkali titrations were used, bromophenol-blue then being the indicator). The most suitable indicator was determined, by preliminary experiments, for each reagent used. In aqueous extracts acidity was determined by titration with 0·01N-potassium hydroxide, and alkalinity with either 0·01 or 0·02N-sulphuric acid, using methyl-red or methylene-blue screened neutral-red (when large concentrations of nitrite were present), with usual expulsion of carbon dioxide at the end point.

Sodium phenoxide and *p*-methoxyphenoxide were best determined by breaking the sample under carbon dioxide-free distilled water (organic matter being precipitated) and direct titration with acid using screened methyl-red. This avoided complications otherwise encountered due to the presence of nitrous acid. With *m*-nitrophenoxide the very small amount of nitrite formed did not interfere, neither did the indicator property of this reagent, and direct titration of the aqueous extract using acid and screened methyl-red was satisfactory. *p*-Nitrophenoxide was determined by delivery of the sample into an excess of a cold, standard alcoholic solution of hydrochloric acid and back-titration with alkali using bromophenol-blue.

Nitrite determinations were carried out on an aliquot portion of the aqueous extract diluted so that nitrite was in the range 2—10 × 10^{-6}M, by a modification of the Griess–Ilosvay method which involves diazotisation of sulphanilamide and coupling with *N*-1-naphthylethylenediamine dihydrochloride (Shinn, *Ind. Eng. Chem. Anal.*, 1941, **13**, 33; Barnes and Folkard, *Analyst*, 1951, **76**, 55). The colour maximum is rapidly attained and stable for several hours and the optical density was determined with a Hilger 760 Spekker Photoelectric Absorptiometer with an Ilford 604 green filter. The calibration curve (from " AnalaR " sodium nitrite) was linear at least up to an optical density of 0·50, and all determinations were effected below this value. The calibration data are :

$10^6[NO_2^-]$ (mole $l.^{-1}$)	2·425	5·050	7·350	10·10	12·60	14·70
Optical density	0·100	0·210	0·350	0·420	0·520	0·615

Even with low concentrations of nitrite the accuracy of this method is 0·5—1% and hence accurate values for $kE_{CO}2$ could be obtained when the elimination was only ~1% of the total reaction.

Nitrate determinations were also made on the aqueous extracts by Baker and Easty's gravimetric method (*loc. cit.*). When nitrite was also present it was first destroyed by a 50% excess of sulphamic acid. The accuracy (±1%) was tested with both " AnalaR " potassium nitrate and aqueous nitric acid :

		Found :	
	Calc.	(*a*) no nitrite	(*b*) +0·02M-nitrite
Potassium nitrate (M)	0·01092	0·01099	0·01087
Nitric acid (M)	0·01037	0·01026	—

Reaction Products.—Proof that nucleophilic substitution occurs solely at carbon was provided by larger-scale experiments under conditions closely similar to those used in kinetic studies. A solution containing 5 g. of benzyl nitrate in dry ethyl alcohol containing 0·0654M-benzyl nitrate, 0·426M-phenol, and 0·131M-sodium ethoxide gave, after refluxing for 48 hr., 4·95 g. of pure (twice crystallised) benzyl phenyl ether, m. p. 38—39° (Found: C, 84·7; H, 6·1. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·5%). This corresponds to an isolated yield of 82%, and kinetic experiments show that 10% of benzaldehyde is formed by a concurrent carbonyl elimination reaction.

Calculation of Velocity Coefficients.—In solvolyses the pseudo first-order rate coefficient was calculated from the usual equation using the "long interval" method (Weissberger, "Technique of Organic Chemistry," Vol. VIII, Interscience Publ. Inc., New York, 1953, p. 187). At least ten individual samples were taken in each run, reactions being followed to ~80% completion. In agreement with Winstein (*J. Amer. Chem. Soc.*, 1951, **73**, 2702) rate coefficients, even in mixed solvents, were strictly reproducible to at least 2—3%.

In reactions with anions the experimental second-order coefficient k_2 was determined from the usual equation. Correction for first-order solvolysis was made by using the equation $\bar{k}_2 + t\mathrm{d}\bar{k}_2/\mathrm{d}t = k_2^{\mathrm{corr.}} + k_1/(b - x)$ (Hughes, Ingold, and Shapiro, *J.*, 1936, 225) where $k_2^{\mathrm{corr.}}$ is the true second-order coefficient (substitution + elimination), k_1 = the first-order solvolysis constant, and x is the total reaction at time t. In our experiments $t\mathrm{d}\bar{k}_2/\mathrm{d}t$ was neglible. The percentage of solvolysis (A) is given by

$$A = \frac{100k_1}{k_2^{\mathrm{corr.}}x} \ln\left\{\frac{(k_1/k^{\mathrm{corr.}}) + b}{(k_1/k_2^{\mathrm{corr.}}) + (b - x)}\right\}$$

(Hughes *et al.*, *loc. cit.*). Nitrite determinations permit determination of the percentage of carbonyl elimination (B) whence the percentage of substitution is (100-A-B). Hence the true values of kS_N2 and $kE_{CO}2$ were determined. Application of this method is given in Table 2.

TABLE 2. *Sodium* m-*nitrophenoxide and benzyl nitrate in* 100% EtOH *at* 60°.

Initially, $[NaO{\cdot}C_6H_4(NO_2)] = 0{\cdot}08894$M; $[Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2] = 0{\cdot}05357$M.

$10^4\bar{k}_2$ l. mole⁻¹ sec.⁻¹	$10^4k_1/(b - x)$ l. mole⁻¹ sec.⁻¹	$10^4k_2^{\mathrm{corr.}}$ l. mole⁻¹ sec.⁻¹	Solvolysis (%) calc. (A)	E_{CO} (%) obs. (B)	S_N2 (%) 100-A-B	10^4kS_N2 l. mole⁻¹ sec.⁻¹	$10^4kE_{CO}2$ l. mole⁻¹ sec.⁻¹	$10^4\bar{k}E_{CO}2$ [% $E_{CO} \times \bar{k}_2$] l. mole⁻¹ sec.⁻¹
2·982	0·151	2·831	4·95	—	—	—	—	—
2·972	0·157	2·815	5·03	7·93	87·04	2·580	0·235	0·236
2·885	0·163	2·722	5·13	7·57	87·30	2·505	0·217	0·218
2·890	0·169	2·721	5·22	7·15	87·63	2·516	0·205	0·207
2·882	0·175	2·707	5·29	7·21	87·50	2·501	0·206	0·208
2·970	0·184	2·786	5·41	6·87	87·72	2·583	0·203	0·204
2·936	0·190	2·746	5·49	6·58	87·93	2·554	0·192	0·193
2·852	0·195	2·657	—	—	—	—	—	—
2·915	0·206	2·709	5·69	6·04	88·27	2·535	0·174	0·176
2·925	0·213	2·712	5·77	5·98	88·25	2·539	0·173	0·175
2·923	0·221	2·702	5·87	5·77	88·36	2·536	0·166	0·168
2·932	0·231	2·701	5·97	5·63	88·40	2·539	0·162	0·165
2·975	0·238	2·737	6·05	5·56	88·39	2·575	0·162	0·165
2·912	0·243	2·672	6·10	5·44	88·46	2·517	0·155	0·158

In practice this method is tedious, and the following simpler method was subsequently used. The percentage of the *total* reaction (including solvolysis) proceeding by the elimination route is known from nitrite determinations, whence $\bar{k}E_{CO}2 = \%E_{CO} \times \bar{k}_2$. In practice $\bar{k}E_{CO}2$ was identical with $kE_{CO}2$ calculated by the rigorous method. This is illustrated in the last column of Table 2 and was checked by sample calculations using the rigorous method in other cases. The value of kS_N2 then equals $k_2^{\mathrm{corr.}} - kE_{CO}2$, as above. Not less than ten samples from each run, followed to ~70% completion, were taken; the estimated accuracy of the *separated* rate constants is at least 5%.

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DEPARTMENT OF ORGANIC CHEMISTRY,
THE UNIVERSITY, LEEDS.

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