Hydrolytic Decomposition of Esters of Nitric Acid. Part IV. Acid Hydrolysis, and the Effects of Change in the Nucleophilic Reagent on the S_N and E_{CO} Reactions.*

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

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The rates of solvolysis of ethyl, *iso*propyl, *tert.*-butyl, benzyl, and 4-methylbenzyl nitrate in aqueous ethanol are not accelerated by acids and hence neither the uni- nor the bi-molecular mechanisms is subject to acid catalysis. The carbonyl elimination ($E_{CO}2$) reaction never occurs in such solvolytic decompositions, because the solvent molecules are too weakly basic to effect the removal of the α-hydrogen.

By using benzyl nitrate [with which olefin elimination (E) is structurally impossible] it is shown that continuous decrease in the nucleophilic power of the reagent towards carbon results in the familiar decrease in the velocity of the S_N2 reaction until, finally, a change over to the S_N1 mechanism occurs. Such nucleophilic power does not run parallel with the basic strength of the reagent, *i.e.*, its proton affinity, indicated by the speeds of the concurrent $E_{CO}2$ reaction, which can only proceed by a bimolecular mechanism. Hence the velocity decrease in this reaction caused by continuous decrease in the basic strength of the reagent is now followed by its complete suppression. It is shown that earlier observations regarding the supposed suppression of carbonyl " oxidation " products by addition of " reducing " agents such as quinol (H_2Q) or thiophenol are actually due to an ion-exchange of the type $H_2Q + OEt^- \rightleftharpoons HQ^- + HOEt$, which replaces the strongly basic OEt^- by a much more weakly basic ion (HQ^- or PhS^-), unable to effect the elimination of the α-hydrogen required for the $E_{CO}2$ reaction, whilst the great nucleophilic power of the PhS^- ion towards carbon enormously increases the velocity of the S_N2 reaction.

In Parts I and II (*J.*, 1952, 1193, 1208) the theory that the complex products formed by hydrolytic decomposition of organic nitrates are consistently and adequately explained on the basis of three simultaneous reactions, *viz.*, (i) nucleophilic substitution at $C_\alpha(S_N)$,† (ii) olefin elimination at H_β (E), and (iii) carbonyl elimination at H_α (E_{CO}), was established experimentally for hydrolyses in neutral and alkaline media. In this communication attention is focused on two other aspects of the problem, *viz.*, (1) hydrolyses in acid media and (2) the effects of change in the attacking nucleophilic reagent on the substitution and the elimination reactions. Both are related to certain observations in the literature which need re-examination in the light of the mechanism now proposed for the production of nitrite and " oxidised " (carbonyl) products.

(A) *Hydrolyses in acid media.*

Theoretically all three reactions, S_N, E, and E_{CO}, might be subject to acid catalysis. By co-ordination of a proton the nitric ester could afford its conjugate acid which could then undergo substitution and elimination reactions by either uni- or bi-molecular mechanisms in a manner similar to that already established for carboxylic esters (Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686), *e.g.*, for the unimolecular mechanisms :

$$R\cdot CH_2\cdot CH_2\cdot O\cdot NO_2 + H_2OR^+ \rightleftharpoons R\cdot CH_2\cdot CH_2\cdot O\cdot NO_2H^+ + HOR\ (R{=}H \text{ or } Et) \quad . \quad (1)$$

$$R\cdot CH_2\cdot CH_2\overset{\curvearrowleft}{-O}\text{-}NO_2H^+ \xrightarrow{\text{Slow}} R\cdot CH_2\cdot CH_2^+ + HNO_3$$

$$R\cdot CH_2\cdot CH_2^+ + Y \xrightarrow{\text{Fast}} R\cdot CH_2\cdot CH_2\cdot Y \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad S_N1cA$$

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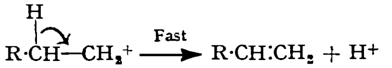
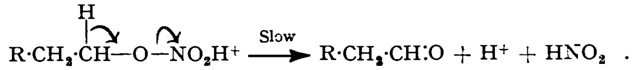
* Part III, *J.*, 1954, 3225.

† *Note added*, 19.1.55: In primary *alkyl* nitrates some attack at the nitrogen atom is now known to occur (Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603).



$$\mathrm{R{\cdot}CH{-}CH_2^+ \xrightarrow{\text{Fast}} R{\cdot}CH{:}CH_2 + H^+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad E\mathrm{1cA}$$



$$\mathrm{R{\cdot}CH_2{\cdot}CH{-}O{-}NO_2H^+ \xrightarrow{\text{Slow}} R{\cdot}CH_2{\cdot}CH{:}O + H^+ + HNO_2} \quad . \; . \; . \; . \quad E\mathrm{co1cA}$$

Formulation of the corresponding bimolecular mechanisms is obvious. For nitrates which exhibit borderline S_N2–S_N1 characteristics such acid catalysis, by greatly increasing the electron-attracting power of the separating group, might, if it occurs, cause a change over from bi- to the uni-molecular mechanism. The formation of carbonyl compounds and nitrite under acid conditions has been recorded by R. C. Farmer (*J.*, 1920, **117**, 810) and by Lucas and Hammett (*J. Amer. Chem. Soc.*, 1942, **64**, 1928), whilst autocatalysis was reported by Silberrad and R. C. Farmer in the hydrolysis of nitrocellulose (*J.*, 1906, **69**, 1759) and by Biron in the case of ethyl nitrate in aqueous solution (*Chem. Zentr.*, 1901, **1**, 365).

We have examined the effect of both liberated and initially added acid on the rates of hydrolysis of various organic nitrates typical of different mechanistic ranges, *viz.*, ethyl (S_N2), *iso*propyl, benzyl, and 4-methylbenzyl (S_N2–S_N1 borderline), and *tert.*-butyl (S_N1), in aqueous ethanol. In such solvents reaction of liberated nitric acid with the solvent introduces complications when the alcohol content is high and the rate of solvolysis of the nitrate is very slow. A blank experiment with 0·01M-nitric acid in 90-vol. % aqueous ethanol at 60° showed negligible reduction in acidity up to 400 hours, but thereafter acidity was removed at an increasing rate. Initial attack appears to be pure esterification (no nitrite produced), followed by increasing attack involving oxidation of the solvent with production of nitrite. Addition of 0·036M-*iso*propyl alcohol had no effect on the acid removal, indicating that the solvolysis reaction (of *iso*propyl nitrate) is not appreciably reversible under the conditions used. With solvents of lower alcohol content no attack of nitric acid on the solvent occurs for long periods; *e.g.*, in 60% aqueous-ethanolic solution initially containing 0·02M-nitric acid, 0·015M-*iso*propyl alcohol at 60° showed no appreciable drop in acidity until ~1000 hours. Hence, in every case, blank experiments have enabled conditions to be chosen so that accurate determination of the rate of solvolysis was achieved before any appreciable attack on the solvent by nitric acid occurred. With the more rapid reactions with *tert.*-butyl and benzyl nitrate this was possible even in 90% and 100% alcohol. The results obtained with all the nitrates investigated are given in Table 1, where the values of k_1 are the mean of at least ten concordant observations. All velocity coefficients in this paper are in terms of moles, litres, and seconds.

TABLE 1. *Acid solvolysis of* $\mathrm{R{\cdot}O{\cdot}NO_2}$ *in* x% *aqueous ethanol.*

R	Solvent, x%	Temp.	Initial [HNO_3]	Initial [HCl]	Final [HNO_3]	10^5k_1, sec.$^{-1}$
Et	45	60°	—	—	0·0171	0·0158 ± 0·0001
Pr^i	60	60·2	—	—	0·0225	0·0497 ± 0·0009 * 0·0487 ± 0·0005 †
,, ...	,,	,,	(CaCO$_3$ added)	—	—	0·0492
Bu^t	90	60·2	0·0100	—	0·0340	3·95 ± 0·04
,, ...	,,	,,	0·0592	—	0·0798	4·11 ± 0·03
,, ...	90, +0·5M-NMe$_4$}NO$_3$	,,	0·0120	—	0·0480	3·90 ± 0·01
CH$_2$Ph	45	,,	—	—	0·0200$_4$	4·28 ± 0·08
,, ...	,,	,,	0·0561	—	0·0770	4·30 ± 0·10
,, ...	45, +0·5M-KNO$_3$	,,	—	—	0·0208	4·26 ± 0·02
,, ...	60	,,	—	—	0·0418	1·71 ± 0·01
,, ...	,,	,,	—	0·1035	0·0492	1·83 ± 0·02
,, ...	100	,,	—	—	0·0123	1·19 ± 0·01
p-Me·C$_6$H$_4$·CH$_2$	90	60·5	—	—	0·0415	1·95 ± 0·01
,,	,,	,,	—	0·1019	0·0396	1·94 ± 0·03

* H_3O^+ determination. † NO_3^- determination.

Neither nitrite nor carbonyl formation has been detected in the *solvolytic* reaction in aqueous alcohol of any of the large number of mononitrate esters which have now been examined in this laboratory.* At every stage in the solvolytic reaction the concentration of nitrate ion produced is identical with that of the acidity developed. Thus the E_{CO} reaction does not occur in solvolyses in aqueous-alcoholic solvents; substitution at C_α (with liberation of nitric acid) is the sole reaction except when, in a structurally suitable ester undergoing solvolysis by the unimolecular mechanism, elimination of a proton from the carbonium ion first produced gives rise to concomitant olefin formation ($E1$). All the evidence, as Lucas and Hammett themselves recognized (*loc. cit.*), indicates that the production of benzaldehyde which they observed in the solvolysis of benzyl nitrate in 60% aqueous dioxan arises from a distinct oxidation reaction which is most probably a peroxide-catalysed, free-radical reaction involving homolytic and not heterolytic fission. We have used their observation as a control experiment for the negative results obtained in aqueous-alcoholic solution. Parallel experiments, with the same sample of benzyl nitrate, were set up, one in aged 60% aqueous dioxan and the other in 60% aqueous alcohol. Nitrite and benzaldehyde production were readily detected in the former but were completely absent in the latter.

As the results in Table 1 show, no evidence of acid catalysis was obtained. In any one run the first-order velocity coefficient remained constant throughout, showing no upward drift as the medium became increasingly acid, and its value was unchanged when neutrality was maintained throughout by the presence of calcium carbonate. Initial addition of nitric or hydrochloric acid in concentrations up to 0·1N caused no significant increase in the rate constant, and the absence of appreciable salt effects was indicated by the observation that addition of similar concentrations of potassium or tetramethylammonium nitrate also caused no detectable change in rate.

We are thus unable to confirm (at least for the solvolysis of simple *mono*-nitrate esters in aqueous-alcohol) earlier observations either of acid catalysis or of the production of nitrite and " oxidised " products in such solvolytic reactions.

This absence of acid catalysis is in harmony with the general observation (Olivier and Berger, *Rec. Trav. chim.*, 1922, **41**, 637) that esters of strong acids, unlike carboxylic esters, are not subject to acid-accelerated hydrolyses in aqueous media. This means that although the equilibrium

$$R'\cdot CO\cdot OR + H_3O^+ \rightleftharpoons R'\cdot CO\cdot OHR^+ + H_2O$$

affords a sufficiently high concentration of the conjugate acid $R'\cdot CO\cdot OHR^+$ to cause a rapid, acid-accelerated fission, the equilibrium (1) (p. 608) must be displaced essentially to the left. The difference between the two types $RO\cdot COR'$ and $RO\cdot NO_2$ probably arises from the much greater loss of resonance stabilisation which would result from proton-addition to the nitric ester. The loss of resonance energy consequent on the formation of the conjugate acid, $(\overset{-}{O}{-}\underset{|}{\overset{+}{N}}{=}O \longleftrightarrow O{=}\underset{|}{\overset{+}{N}}{-}\overset{-}{O}) \longrightarrow HO{-}\overset{+}{N}{=}O$, would be greater than in $(>C{=}O \longleftrightarrow >\overset{+}{C}{-}\overset{-}{O}) \longrightarrow >\overset{+}{C}{-}OH$, and this difference in basicities of nitro- and carbonyl compounds is confirmed by the fact that simple ketones behave as fully ionised bases in 100% sulphuric acid whereas mononitro-compounds are weak bases even in this medium, nitromethane, for example, being only 20% ionised (Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 58, 60). Proton addition to the alkyl-oxygen atom should cause considerable loss of resonance stabilisation in both systems, $RO\cdot\underset{|}{C}{=}O \longleftrightarrow R\overset{+}{O}{=}\underset{|}{C}{-}\overset{-}{O}$ and $RO{-}\underset{O^-}{\overset{+}{N}}{=}O \longleftrightarrow R\overset{+}{O}{=}\underset{O^-}{\overset{+}{N}}{-}\overset{-}{O}$ but Cowley and Partington (*J.*, 1933, 312, 1252), from a comparative study of the dipole moments of nitro-compounds $R\cdot NO_2$ and nitric esters $RO\cdot NO_2$ conclude that inductive relay of the $-I$ effect of the nitro-group is effectively damped out in the ester by the interposed, unsaturated oxygen atom. This, then, because of its positive character, would be unlikely to behave as a basic centre for attachment of a proton. That the difference in behaviour of the two ester types ·O·COR and

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* The trace of nitrite, equivalent to $<0\cdot3\%$ of E_{CO} reaction, detected in the solvolysis of 4-nitrobenzyl nitrate in 90% ethanol at 75° (Baker and Heggs, following paper) is the only exception and is of doubtful significance since it may arise from oxidation of the solvent.

$\cdot\mathrm{O\cdot NO_2}$ does arise from such differences in basic strength is confirmed by the knowledge that, in 100% sulphuric acid, proton-transfer can occur not only to carboxylic esters but also to organic nitrates, with consequent acid-accelerated fission; *e.g.*, $\mathrm{EtO\cdot NO_2 + 3H_2SO_4 \longrightarrow EtO\cdot SO_3H + NO_2^+ + H_3O^+ + 2HSO_4^-}$ (Kuhn, *J. Amer. Chem. Soc.*, 1947, **69**, 1974) These products suggest that in such strongly acid media proton addition occurs at the alkoxy-oxygen atom to give an initial fission $\mathrm{Et\underset{H}{\overset{+}{O}}{-}NO_2 \longrightarrow EtOH + NO_2^+}$. Preliminary examination of the behaviour of other simple alkyl nitrates in 100% sulphuric acid, however, revealed that more complicated reactions often occur. Thus one of us (J. W. B.) with Dr. Easty found that the solvolysis of *iso*propyl nitrate with 100% sulphuric acid gives much nitrous acid, carbonyl derivatives, and pseudo-acidic products of the nitroparaffin type.

The observation that, in contrast with the nitrates, the hydrolysis of organic nitrites is acid-catalysed (Allen, *J.*, 1954, 1968) is also in harmony with these views. The more strongly basic character of the nitrous esters is doubtless to be associated with the smaller loss in resonance energy which would result from the conversion of the neutral ester $\mathrm{RO{-}N{=}O \longleftrightarrow R\overset{+}{O}{=}N{-}\overset{-}{O}}$ into its conjugate acid.

(B) *Changes in the nucleophilic reagent.*

Since the two elimination reactions, E and E_{CO}, have specific structural requirements, it is possible to exclude one or other and so make a direct study of the relative effects of changing the nucleophilic reagent on the substitution and on one particular elimination reaction. By using benzyl nitrate, olefin formation is excluded, and we have thus studied the comparative effects of decreasing nucleophilic power upon the S_N reaction, in which the attack is at C_α (cf. p. 613), and on the E_{CO} reaction, in which it is at H_α.

The complete absence of the E_{CO} reaction in solvolytic reactions in aqueous alcohol with all the organic nitrates we have investigated is in harmony with the view (Part III, *loc. cit.*) that this reaction occurs only by the bimolecular mechanism, and that neither water nor alcohol molecules are sufficiently basic to effect the removal of the α-hydrogen atom. This interpretation is confirmed by the observation that when the more strongly basic solvent triethylamine is used the production of both nitrite and benzaldehyde is readily demonstrated.

In a good ionising solvent but with a reagent of high nucleophilic activity both the S_N and E_{CO} reactions may proceed by a bimolecular mechanism. Gradual reduction in the nucleophilic power of the reagent will first cause a decrease in the velocity of both reactions. Ultimately, when the reagent is too weakly necleophilic to take part in a S_N2 mechanism, there may be a change over to the unimolecular S_N1 mechanism and the rate will now be constant and independent of the reagent (cf. Gleave, Hughes, and Ingold, *J.*, 1935, 238, Fig. 2). No such alternative is, however, available to the $E_{\mathrm{CO}}2$ reaction and hence, when the reagent is too weakly basic to assist in the removal of the α-hydrogen, the E_{CO} reaction will be completely suppressed. Such changes are illustrated by the following results of the action of various nucleophilic reagents, Y, on benzyl nitrate in 45% aqueous alcohol at 60°.

	(*a*)				(*b*)		
Y =	PhO^-	OH^-	$p\text{-}NO_2\cdot C_6H_4\cdot O^-$	$CO_3^=$	$H\cdot CO_2^-$	Cl^-	EtOH
10^5k (S_N2)	220	50	(30) *	(14)	—	—	—
10^5k (S_N1)	—	—	—	—	4·30	4·30	4·30
10^5k ($E_{\mathrm{CO}}2$)	(9)	106	(~0·2)	(7)	← no reaction →		

* Downward drift 40 → 20 observed.

The two *groups* of reagents (*a*) of higher nucleophilic power and (*b*) of very weak nucleophilic character show the deductions made above to be verified. Assignment of the actual order of decreasing nucleophilic power within these groups is much more difficult. Various attempts to assign numerical values to nucleophilic power (*e.g.*, Swain and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141; Edwards, *ibid.*, 1954, **76**, 1540) make it clear that, contrary to the earlier simple assumption, nucleophilic power does not run parallel with proton-acceptor power, *i.e.*, with basicity, and, moreover, varies with the substrate. It is thus not possible to say just where, in a series of reagents of varying nucleophilic power, is the position of the solvent, and this makes it impossible to say with certainty whether, in group (*b*), an actual change over to the unimolecular mechanism has occurred. The same results would be obtained if the other reagents in this group, *viz.*, HCO_3^- and Cl^-, were much more weakly nucleophilic than the solvent molecules. This ambiguity seems to be present in any application of this test for the unimolecular mechanism unless (as, at present, seems difficult) the reagents can be placed in a *correct* order of decreasing nucleophilic power in which the solvent is the weakest. The complications which arise from proton transfer between the solvent and the reagent Y have been examined in Part III (*loc. cit.*), where an attempt was made to eliminate such complications in 100% ethanol, but in mixed aqueous-alcoholic solvents, where three inter-related equilibria are involved, this is more difficult. For this reason the actual values of k ($E_{CO}2$) for PhO^- and $CO_3^=$ have little significance since at least some of the elimination will be due to OH^- and OEt^- ions. The lyate-ion effect (Benfey, Hughes, and Ingold, *J.*, 1952, 2488) with OH^- in a highly aqueous solvent greatly decreases the apparent nucleophilic power of this anion towards carbon, giving the order $PhO^- > OH^-$, for the S_N2 reaction, but leaves its ability to attack hydrogen unimpaired, so that the more usual order $OH^- > OPh^-$ is followed in the $E_{CO}2$ reaction. The reaction course with only a slight excess of sodium carbonate as the reagent is instructive. Initially, the value of a calculated first-order constant for total reaction falls (indicating the superimposition of some second-order reaction) and the concentration of nitrite ion produced increases, both regularly, until, at ~50% reaction, the liberated nitric acid has converted all the original $CO_3^=$ ion into the much more weakly nucleophilic HCO_3^- ion. For the remainder of the run the nitrite concentration then remains unchanged, showing that the E_{CO} reaction has how been suppressed, whilst the value of the first-order velocity coefficient becomes identical with that for the solvolysis reaction (cf. p. 615). With a higher initial $[Na_2CO_3]$, corresponding to approximately a four-fold excess, complete conversion into bicarbonate cannot occur and, in this case, nitrite production continues throughout the whole run but the values of k ($E_{CO}2$) and, to a smaller extent, of k (S_N2), fall continuously as the reaction progresses. The conversion $CO_3^= + H^+ \longrightarrow HCO_3^-$ begins as soon as any nitric acid has been liberated, and hence the recorded values of k ($E_{CO}2$) and k (S_N2) are those obtained by extrapolation to zero reaction in this experiment.

TABLE 2. *Values of* k (S_N2) *and* k ($E_{CO}2$) *in l. mole*$^{-1}$ *sec.*$^{-1}$ *for the reaction of various nucleophilic reagents* Y *on* $CH_2Ph{\cdot}O{\cdot}NO_2$ *in* 100% EtOH *at* 60°.

Y	$pK_a^{25°}$ † in water	10^5k (S_N2)	10^5k ($E_{CO}2$)	$100k$ ($E_{CO}2$)/[k (S_N2) + k ($E_{CO}2$)]
PhS^-	—	21,000 ‡	—	0
EtO^-	—	100	1345	93
p-$MeO{\cdot}C_6H_4{\cdot}O^-$	10·16	110	5·63	4·9
PhO^-	9·95	60	3·8	5·9
m-$NO_2{\cdot}C_6H_4{\cdot}O^-$	8·35	13·7	0·217	1·6
p-$NO_2{\cdot}C_6H_4{\cdot}O^-$	7·14	5·0	0·085	1·7
C_5H_5N	5·13	4·0	(Nil)	0
EtOH	—	0·007 *	(Nil)	0

* k (S_N2) = k_1/[EtOH] = {0·119 ÷ 17·2} × 10^{-5}.

† Judson and Kilpatrick, *J. Amer. Chem. Soc.*, 1949, **71**, 3110.

‡ Extrapolated from values at 20° and 30°.

In a solvent of low ionising power, such as 100% alcohol, transition to the unimolecular mechanism is less likely. In such a case decrease in the nucleophilic power of the reagent should cause a continuous decrease in the velocity of the S_N2 reaction. Since nucleophilic activity towards hydrogen diminishes much more rapidly than that towards carbon, the accompanying $E_{CO}2$ reaction should exhibit a more rapid fall in velocity until, when the reagent is devoid of nucleophilic activity towards hydrogen, it is completely suppressed. These conclusions are verified by the results in Table 2, where the values for both k (S_N2) and k ($E_{CO}2$) for the aryloxides are the true values (determined by suppression of proton exchange) obtained in Part III (*loc. cit.*). A strong lyate-ion effect, now with ethoxide in dry ethyl alcohol, is apparent in the substitution reaction, this reagent being less effective than the *p*-methoxyphenoxide ion. The satisfactory straight-line Brönsted plots between pK_a with either k ($E_{CO}2$) or k (S_N2) were noted in Part III; the value for EtO^- falls satisfactorily on the k ($E_{CO}2$)-pK_a curve, but is some 80 times too low to fit on the k (S_N2) plot. The enormously greater nucleophilic activity towards carbon of the more weakly basic thiophenoxide ion compared with that of phenoxide is reflected in both the energy and entropy factors in the Arrhenius equation :

	E, kcal. mole^{-1}	$\log_{10} A$		E, kcal. mole^{-1}	$\log_{10} A$
PhO^-	19·3	9·5	PhS^-	17·5	10·7

Such high nucleophilic activity of the thiophenoxide ion towards carbon (a first-period element) is well known but not completely understood, and it is perhaps significant that it does not seem to be observed when the nucleophilic attack is at a second-period element, since Dostrovsky and Halmann (*J.*, 1953, 508) found that, for attack on phosphorus, the order of activity in ethanol solution was $PhO^- > EtOH > PhS^-$, the thiophenoxide ion causing no increase in the observed rate of solvolysis. The specific implications of the high nucleophilic activity of thiophenoxide towards carbon, coupled with its lack of reaction with hydrogen, are discussed below.

To complete our verification of expected velocity relationships we have examined the effect of various reagents on the decomposition of *tert.*-butyl nitrate in 90% aqueous alcohol. Here carbonyl elimination is structurally excluded and the unimolecular mechanism ($S_N1 + E1$) has previously been established. The results are in Table 3.

TABLE 3. *Hydrolytic decomposition of* $Bu^t{\cdot}O{\cdot}NO_2$ *in* 90% *aqueous* EtOH *at* 20° *in the presence of* 0·05M-Y.

Y	OR^- *	N_3^-	Cl^-	NO_3^-	EtOH
10^5k_1	4·51	4·60	4·40	3·90	3·99

* R = Et, H due to $HO^- + EtOH \rightleftharpoons EtO^- + H_2O$.

Evidently the total reaction ($S_N + E$) is following the unimolecular mechanism and is independent of the nature and concentration of any added reagent. The small increase in velocity observed in the presence of 0·05M-OR^-, -N_3^-, and -Cl^- ions is almost certainly due to an ionic-strength salt effect which, in the case of the same concentration of NO_3^-, is nullified by a common-ion, mass-law effect on the reversible ionisation $Bu^tNO_3 \rightleftharpoons Bu^{t+} + NO_3^-$. The new value for k_1 ($S_N + E$) is ~8% higher than that of Baker and Easty (*J.*, 1951, 1201), owing probably to a slight difference in solvent composition and improvements in technique which have been developed. The velocity increase caused by addition of ~0·05M-hydroxide ion is, however, smaller than that previously observed (*idem, ibid.*) when a larger $[OH^-]$ was added.

The observed suppression of the E_{CO} reaction with weakly nucleophilic reagents provides a satisfactory explanation of the recorded effects of " reducing " agents in preventing the formation of " oxidation " products in the hydrolytic decomposition of organic nitrates. Thus the suppression of " oxidised " products in the alkaline hydrolysis of the polynitrates of glycerol and cellulose by addition of thiophenol (Klason and Carlson, *Ber.*, 1907, **40**, 4183) we regard as due to the replacement of the strongly basic hydroxide ion by the thiophenoxide ion, $HO^- + PhSH \rightleftharpoons PhS^- + H_2O$, which, as our results show, is unable to effect the carbonyl-elimination reaction. Their reported formation of free glycerol and cellulose (rather than their phenylthio-derivatives) is less easily explained, especially in view of Carlson's observation (*ibid.*, p. 4191), which we have confirmed, that a quantitative yield (we obtained 96%) of benzyl phenyl sulphide can be isolated from the action of sodium thiophenoxide on benzyl nitrate. In the kinetic examination, the disappearance of PhS^- is accompanied by the equivalent formation of NO_3^- showing that the reaction is entirely a nucleophilic substitution at carbon. Recently, however, Morrow, Cristol, and van Dolah (*J. Amer. Chem. Soc.*, 1953, **75**, 4259) obtained only *n*-butyl alcohol from the reaction of *n*-butyl nitrate with sodium hydrogen sulphide in aqueous alcohol, no trace of *n*-butanethiol being detected. They formulated the reaction as the attack of the polysulphide ion on either oxygen or nitrogen, but in our investigations we have found no evidence that, in the substitution reaction, nucleophilic attack ever occurs anywhere other than at carbon (but cf. footnote, p. 608).

Ion exchange doubtless explains the suppression of benzaldehyde formation by added quinol (H_2Q) observed by Lucas and Hammett (*loc. cit.*) in the hydrolytic decomposition of benzyl nitrate in 60% aqueous dioxan. In this case, however, the problem is not quite so straightforward. We have already given reasons why we believe that the ***whole*** of the observed benzaldehyde formation in the *solvolysis* of benzyl nitrate in 60% aqueous dioxan arises from a peroxide-catalysed, chain reaction, and its complete suppression by the antioxidant, quinol, observed by Lucas and Hammett, would thus be expected. These authors, however, also record the complete suppression of benzaldehyde formation in the *alkaline* hydrolysis of benzyl nitrate by addition of quinol in concentration $< [OH^-]/2$. In alkaline media there will certainly be some $E_{\mathrm{CC}}2$ reaction, and our interpretation of the effect of added quinol is that, because of the equilibrium $OH^- + H_2Q \rightleftharpoons HQ^- + H_2O$, the strongly basic hydroxyl ion is replaced by the much more weakly basic *p*-hydroxyphenoxide ion which is unable to effect carbonyl elimination. For complete suppression of the $E_{\mathrm{CO}}2$ reaction the concentration of added quinol would need to be sufficiently high to displace the equilibrium completely over to the right so that $[OH^-]$ becomes effectively zero. In agreement with this view, our results (Table 4) show that, in 60% alcohol, the reduction in the proportion of nitrite (benzaldehyde) formation is greater the larger is the concentration of added quinol, but it is certainly not completely suppressed until $[H_2Q] \gg [OH^-]$. The uncertainty whether, with sufficiently high $[H_2Q]$ complete suppression of benzaldehyde formation occurs, arises from our observation than high concentrations of quinol interfere with the determination of nitrite, whilst the unavoidable presence of some benzoquinone gives unreliably high values for the determination of benzaldehyde as its 2 : 4-dinitrophenylhydrazone.

TABLE 4. *Effect of added quinol* (H_2Q) *on the hydrolysis of* 0·0320M-$CH_2Ph{\cdot}O{\cdot}NO_2$ *with* 0·0371N-KOH *in* 60% *aqueous ethanol.*

	$[NO_2^-]$ or [Ph·CHO]			
Time (min.)	No H_2Q	0·001M-H_2Q	0·02M-H_2Q	0·06M-H_2Q
0	0·00084	0·000785	0·00059	—
45	0·00577	0·00546	0·00273	—
125	0·01030	0·00942	0·00702	0·000904
300	0·01403	0·01341	—	—

—— Progressive reduction in E_{CO} reaction ——▶

Lucas and Hammett observed that the suppression of benzaldehyde formation in alkaline media by quinol was accompanied by an increase in the overall rate of hydrolysis of benzyl nitrate. In the light of our values of k (S_N2) for the *p*-methoxyphenoxide ion compared with ethoxide in 100% alcohol (Table 2), and for phenoxide and hydroxide in 45% alcohol (p. 611), their observed increase might well be accounted for by the increased velocity of the substitution reaction by the HQ^- ion. The superimposition of both heterolytic and homolytic reactions of benzyl nitrate under the experimental conditions used by Lucas and Hammett, however, makes the interpretation of their results complicated. In aqueous-alcohol solvents, in which only heterolytic fissions occur, we have found that the change in the nucleophilic power of the attacking reagent as it affects the S_N2 and $E_{\mathrm{CO}}2$ reactions provides an adequate explanation of the effects of added thiophenol or quinol and that our new experimental results amply confirm the view regarding the mechanism of the hydrolytic decomposition of organic nitrates put forward in Part I of this series.

EXPERIMENTAL

Preparation of Solvents and Materials.—Details relating to the solvent and the phenolic reagents used were given in Part III (*loc. cit.*); x% aqueous-ethanolic solutions containing free nitric or hydrochloric acid were prepared by adding $(100 - x)$ volumes of aqueous solutions containing the required amount of acid to x volumes of dry ethanol. Other reagent solutions were prepared by direct dissolution of the required weight of the pure reagent in the x% ethanol, with exclusion of moisture and carbon dioxide throughout. Ethyl, *iso*propyl, and *tert.*-butyl nitrate were prepared and purified as described in Part I (*loc. cit.*), and benzyl nitrate as in Part III (*loc. cit.*).

Tetramethylammonium nitrate was prepared from the iodide and "AnalaR" aqueous silver nitrate and was crystallised from aqueous alcohol. Purity by gravimetric determination of $NO_3^- = 99·7\%$.

Velocity Determinations.—The techniques were those described in Part III. Appropriate titrimetric techniques and indicators were chosen for each reagent. The following are not recorded in Part III.

Thiophenoxide.—The minute amount of nitrite produced with this reagent was too small to interfere, and permitted determination of thiophenoxide by arresting the reaction by delivery into a known excess of alcoholic hydrochloric acid and titration of the excess acid with 0·02N-sodium hydroxide, bromophenol-blue being the indicator.

Carbonate and Bicarbonate.—Carbonate and bicarbonate were determined in the aqueous solution, after ether-extraction, by direct titration with 0·01N-sulphuric acid (methyl-red indicator) and boiling to expel carbon dioxide.

Pyridine.—Since this reagent is retained by ether its determination must be effected in the presence of unchanged benzyl nitrate. This prevented its titration with acid and screened methyl-yellow because the indicator was removed from the aqueous phase by the ester. The reaction was followed by gravimetric determination of nitrate on the aqueous extract (Baker and Easty, *loc. cit.*).

Reactions with azide and chloride ions were followed by direct titration with 0·01N-sodium hydroxide, checked, in the case of the former reagent, by gravimetric determination of the nitrate ion produced.

The separate velocity coefficients were calculated by the methods described in Part III. The following are typical runs.

(1) *Acid hydrolysis.* Initial $[Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2] = 0·0280$M; $[HNO_3] = 0·0561$M in 45% ethanol at 60·2°.

Time (min.)	0	45	130	165	225	285	315	345	375	476	525
$10^3[HNO_3]$, mole $l.^{-1}$	57·5	60·4	65·2	66·8	69·2	71·3	72·4	73·1	73·9	76·3	77·0
10^5k_1, $sec.^{-1}$	—	4·24	4·39	4·34	4·27	4·29	4·34	4·27	4·26	4·28	4·18

(2) *Action of sodium carbonate in* 45% *ethanol* (*mole/l.*) *on benzyl nitrate* (0·02856M) *at* 60°.

Time (min.)	0	30	70	110	151	190	230	270	320	380	440	514	580	630
$10^2[Na_2CO_3]$ *	3·835	3·57	3·275	3·03	2·82	2·64	2·48	2·35	2·20	1·995	1·85	1·71	1·64	1·52
10^5k_1	—	5·43	5·18	5·03	4·82	4·74	4·63	4·53	4·44	4·53	4·49	4·41	4·21	4·39
$10^3[NO_2^-]$	0·054	0·229	0·451	0·551	0·600	0·630	0·643	0·643	0·643	0·643	0·643	0·630	0·630	0·630

* Initially Na_2CO_3, subsequently $NaHCO_3$.

(3) *Action of* NaOEt *on* $Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2$ *in* 100% EtOH *at* 60° (*corrected for reaction before zero time*).
Initially [NaOEt] = 0·03664M, $[Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2] = 0·03007$M.

Time (min.)	0	20	40	50	60	70	80	90	105	130	150
10^2[NaOEt]	3·367	2·331	1·833	1·627	1·527	1·428	1·347	1·259	1·196	1·078	0·991
10^2k_2	—	1·45	1·44	1·52	1·46	1·45	1·44	1·47	1·40	1·41	1·48
$10^2[NO_2^-]$	—	0·999	1·431	1·581	1·717	1·801	1·1884	1·953	2·028	2·157	2·195
E_{CO}, %	—	96·4	93·3	90·1	93·3	93·8	93·3	92·6	93·4	93·2	92·7

Equivalence of $[NO_3^-] + [NO_2^-]$ *and* [*Acid*] ≡ $[OEt^-]$ *removed.*

Time (min.)	50	70	90	120	150	160	195
(*a*) $10^2[NO_2^-]$	1·754	1·974	2·126	2·271	2·368	2·386	2·440
(*b*) $10^2[NO_3^-]$	0·250	0·278	0·290	0·305	0·333	0·326	0·348
10^2 [(*a*) + (*b*)]	2·004	2·252	2·416	2·576	2·701	2·712	2·788
10^2 [Acid]	2·038	2·237	2·406	2·550	2·674	2·711	2·763

Equivalence of $[NO_2^-]$ *and* $[Ph{\cdot}CHO]$.

Time (min.)	20	160	1 week
$10^2[Ph{\cdot}CHO]$	1·161	2·391	2·610
$10^2[NO_2^-]$	1·172	2·386	2·619

Effect of concentration changes.

[NaOEt]	$[Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2]$	10^2k_2 (total)	10^2k ($E_{CO}2$)	10^2k (S_N2)
0·034	0·027	1·45	1·35	0·10
0·060	0·04	1·47	1·37	0·10
0·100	0·04	1·48	1·34	0·14

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DEPARTMENT OF ORGANIC CHEMISTRY,
LEEDS UNIVERSITY.

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