218. *Hydrolytic Decomposition of Esters of Nitric Acid. Part II.* The Effects of Structural and Solvent Changes on the Substitution and Elimination Reactions which occur in the Hydrolysis of Primary, Secondary, and Tertiary Alkyl Nitrates.*
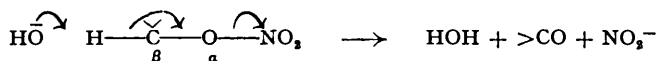
By John W. Baker and (Mrs.) D. M. Easty.

The data recorded in Part I (preceding paper) are used to effect a detailed analysis of the effects of (*a*) structure and (*b*) environmental factors on the rates of each of the three reactions S_N, E, and E_{CO} which occur side-by-side in the hydrolytic decomposition of methyl, ethyl, *iso*propyl, and *tert.*-butyl nitrates, and conclusions regarding mechanism are thus derived.

In the presence of hydroxyl ions in 90% alcohol the velocity sequence $Me > Et > Pr^i \ll Bu^t$ for nucleophilic substitution indicates a bimolecular mechanism for the primary and secondary nitrates and a unimolecular mechanism for the tertiary compound, which are confirmed by the effects of changes in solvent composition on the velocities. In neutral solvolysis the relative rates $Me > Et < Pr^i \ll Bu^t$ show superimposition of some unimolecular mechanism upon a predominantly bimolecular mechanism in the case of the *iso*propyl compound when either the ionising power of the solvent is increased or the nucleophilic power of the attacking reagent is reduced.

Olefin elimination confirms such mechanistic conclusions and is controlled by the electromeric effects of α- and β-substituents. The proportion of olefin is less with the nitrates than with the corresponding bromides.
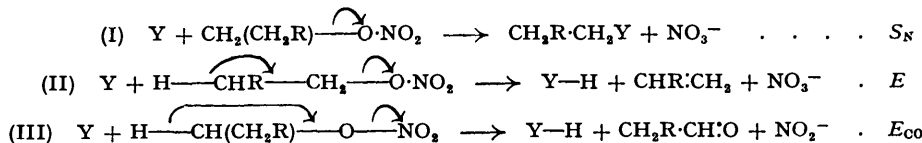
The mechanism for carbonyl elimination is almost certainly bimolecular :

$$\text{HO}^- \quad \text{H} \underset{\beta}{\overset{}{-\!-\!\text{C}\!-\!-}}\underset{\alpha}{\text{O}\!-\!-\!\text{NO}_2} \quad \longrightarrow \quad \text{HOH} + \,{>}\text{CO} + \text{NO}_3^-$$

in which the β-atom of the system, from which the proton is removed, is the α-carbon atom of the nitrate. The *proportion* of carbonyl elimination, $Me \ll Et < Pr^i$, is also controlled by the electromeric effects of alkyl substituents, but the *rates* are in the order $Me \ll Et > Pr^i$ since, with the *iso*propyl compound in the carbonyl elimination the retarding inductive ($+I$) effect of *two* methyl groups acts directly on the β-atom, whereas in olefin elimination only a second-order $+I$ effect of *one* methyl substituent on the α-atom is relayed to the β-position.

The data previously obtained (Baker and Hemming, *J.*, 1942, 191; Baker and Hopkins, *J.*, 1949, 1087) for the values of k_2 in the (reversible) reaction

$$\text{H}\!-\!\text{O}\!-\!\text{C}\!-\!\text{CN} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \text{CO} + \text{HCN}, \text{ make possible a preliminary comparison}$$

with a $1 : 2$ elimination system $\text{H}\!-\!\text{O}\!-\!\text{C}\!-\!\text{X}$, which is complementary to that $\text{X}\!-\!\text{O}\!-\!\text{C}\!-\!\text{H}$ studied in these investigations.

The results recorded in Part I (preceding paper) clearly confirm the correctness of the view there enunciated that the hydrolytic decomposition of organic nitrates may involve the simultaneous occurrence of the reactions (I), (II), and (III) :

$$\text{(I)} \quad Y + CH_2(CH_2R)\!-\!O \cdot NO_2 \quad \longrightarrow \quad CH_2R \cdot CH_2Y + NO_3^- \quad \cdots \quad S_N$$

$$\text{(II)} \quad Y + H\!-\!CHR\!-\!CH_2\!-\!O \cdot NO_2 \quad \longrightarrow \quad Y\!-\!H + CHR{:}CH_2 + NO_3^- \quad \cdot \quad E$$

$$\text{(III)} \quad Y + H\!-\!CH(CH_2R)\!-\!O\!-\!NO_2 \quad \longrightarrow \quad Y\!-\!H + CH_2R \cdot CH{:}O + NO_2^- \quad \cdot \quad E_{CO}$$

All three reactions may occur by uni- or bi-molecular mechanisms depending on the degree of co-operation of the nucleophilic reagent Y in the rate-determining stage of the reaction. Kinetic analyses of such reactions for methyl, ethyl, *iso*propyl, and *tert.*-butyl nitrates,

have made possible a limited general survey of the effects of (1) structural changes in the alkyl group, and (2) environmental factors, on the relative importance and mechanisms of each of these separate reactions. All k values have been corrected for solvent expansion from room temperature ($\sim$20°) to the reaction temperature and are in the usual mole^{-1} l. sec.$^{-1}$ units.

(I) *The Substitution Reaction* S_N.—Of the various methods which have been devised to diagnose the mechanism of a substitution reaction (cf. Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979, for summary) only three can be applied on the basis of the data at present available for the hydrolysis of organic nitrates. These are the effect on reaction rate of (*a*) structural changes in the nitrate, (*b*) changes in the solvent, and (*c*) changes in the nucleophilic power of the attacking reagent.

(*a*) If the substitution reaction (I) proceeds by a bimolecular mechanism, the most probable effect of increasing the inductive electron-release of the group R in $R{\rightarrow}CH_2{\cdot}O{\cdot}NO_2$ will be to decrease the rate, because the larger induced negative charge on the α-carbon atom will hinder the approach of the attacking nucleophilic reagent (the hydroxyl ion in alkaline hydrolysis). In the least ionising solvent, 90% alcohol, this is found to be the case for methyl, ethyl, and *iso*propyl nitrates, all of which follow the second-order rate law in the presence of hydroxyl ions. The relative rates in this solvent at 60° are :

	Me	Et	Pr^i
Relative rates	9·1 *	1	0·1
Arrhenius E (kcal./mole)	18·8	23·6	27·9

* In 75% alcohol : the value (not obtainable, see Part I) in 90% alcohol would be even higher (cf. Table 2).

The velocity order Me$>$Et$>$Pr^i is confirmed by the corresponding values of E, the Arrhenius energy of activation.

Introduction of a third α-methyl substituent, to give *tert.*-butyl nitrate, causes a marked change, since this nitrate undergoes very rapid hydrolysis, following a first-order rate law. Thus the half-life period for hydrolysis with $\sim$0·09M-potassium hydroxide in 90% alcohol at 30° is 48 *minutes*, compared with a value of $\sim$1876 *hours* for ethyl nitrate under the same conditions. It is evident that, with *tert.*-butyl nitrate, we have passed into the range of predominant, if not exclusive, unimolecular mechanism at least for the substitution reaction. This is confirmed by the observation that, in presence of only one-fifth of a molecular proportion of potassium hydroxide the first-order velocity coefficient remains constant throughout the whole reaction in which the medium, originally alkaline, becomes neutral and finally acid. It will be remembered that similar behaviour in the hydrolysis of *tert.*-butyl halides (Hughes, *J.*, 1935, 255) was the earliest evidence for the occurrence

TABLE 1. *Values of the first-order velocity coefficients* $10^5k(S_N1)$ (sec.$^{-1}$) *for* (a) *alkaline hydrolysis and* (b) *neutral solvolysis of* tert.-*butyl nitrate in aqueous alcohol.*
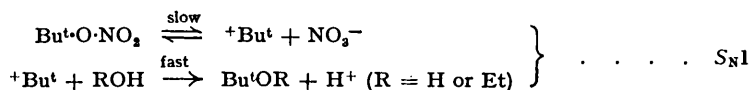
Solvent, aq. EtOH (vol. %)	Temp.	10^5k_1 (a)	10^5k_1 (b)	E (kcal./mole) (a)	E (kcal./mole) (b)
90	30°	18·5	13·9		
,,	20	4·93	3·1	22·3	22·6
,,	0	0·32	0·22		
60	30	(849)	589		
,,	20	236	(170)		
,,	10	(43·7)	43·2	25·0	21·2
,,	8·65	32·6	(38·9)		
,,	0	10·2	12·5		

The values in parentheses are calculated from the best straight-line plot of log k_1 against $1/T$.

of a unimolecular mechanism in substitution reactions. The essential independence of hydroxyl-ion concentration is also clearly demonstrated by a comparison, in Table 1, of the values of $10^5k_1(S_N1)$ for the *substitution* reaction in alkaline media with those for neutral solvolysis in the same solvents.

Although there may be some error in the various calculated values of 10^5k_1 (since the E values were determined from observations at only three temperatures and are derived

4 I

from an experimental analysis of the various simultaneous reactions), there can be no doubt that the presence of hydroxyl ions causes no *significant* increase in the velocity of the reaction which, in both media, is proceeding predominantly by a unimolecular mechanism

$$
\begin{aligned}
\text{Bu}^t\cdot\text{O}\cdot\text{NO}_2 &\overset{\text{slow}}{\rightleftharpoons} {}^+\text{Bu}^t + \text{NO}_3{}^- \\
{}^+\text{Bu}^t + \text{ROH} &\overset{\text{fast}}{\longrightarrow} \text{Bu}^t\text{OR} + \text{H}^+ \text{ (R = H or Et)}
\end{aligned}
\Biggr\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad S_N1
$$

The more highly ionising solvent 60% alcohol would be expected to shift the position of change-over from a bimolecular to a unimolecular mechanism more in the direction of smaller electron-release by the alkyl group, and there are clear indications that, in this solvent, there is considerable incursion of the unimolecular mechanism with *iso*propyl nitrate. The values of the second-order velocity coefficients ($10^5 k_2$) at 60° for alkaline hydrolysis in 60% alcohol are Me 22·1, Et 2·35, Pr^i 2·98, *i.e.*, Me>Et<Pr^i.

In the neutral solvolysis the much weaker nucleophilic power of water or alcohol molecules would tend to favour the unimolecular mechanisms. Only very limited data are at present available but they indicate that in both 90% and 60% alcohol there is a velocity minimum at the ethyl compound, the values of $10^5 k_1$ at 60° being

	Me	Et	Pr^i	Bu^t
In 90% alcohol	0·007$_3$	0·003	0·007	(367)
In 60% alcohol	0·0196	0·011	0·048	(14 450)

The order Me>Et<Pr^i≪Bu^t strongly suggests incursion of the unimolecular mechanism with the *iso*propyl compound, and exclusive unimolecular mechanism for the *tert.*-butyl nitrate. The values for the second-order velocity coefficients calculated on the basis of solvent–concentration and recorded in Part I (pp. 1199, 1200) point to the same conclusion. For methyl and ethyl nitrates the velocity for attack by the strongly nucleophilic hydroxyl ion is greater than that for attack by the neutral solvent molecules by a factor of 10^4 to 10^5, whilst this factor for *iso*propyl nitrate is only ~10^3. This point may be further illustrated by the application to our data, of the method used by Bateman, Cooper, Hughes, and Ingold (*J.*, 1940, 931) in the corresponding halide series illustrating the effect of adding a strongly basic reagent (KOH) to the solvent. If the concentration of alkali in the alkaline hydrolysis is regarded as buffered to 1N then the values of the second-order velocity coefficients become essentially first-order velocity coefficients and are thus directly comparable with the first-order constants in the solvolysis reaction, their sum giving a measure of the *total* reaction. In 60% alcohol at 60° the values are

		Me	Et	Pr^i	Bu^t
Solvolysis	$10^5 k_1$	0·0196	0·011	0·048	(14 450)
KOH hydrolysis, buffered to 1N	$10^5 k_1$	22·1	2·35	2·98	—
Total		22·1	2·36	3·03	(14 450)

Thus the reactions of methyl and ethyl nitrates are exclusively second-order, that of *iso*propyl nitrate is predominantly so, with a small incursion of a first-order reaction, whereas with the *tert.*-butyl compound the reaction is exclusively first-order. Thus the general picture in the series of alkyl nitrates is very similar to that for the alkyl halides, the position of change-over from bimolecular to unimolecular mechanism in aqueous-alcoholic solvents being located in the region of the *iso*propyl compound. Attention was called in Part I (p. 1195) to the much slower rate of hydrolysis of the alkyl nitrates than of alkyl bromides but such discrepancy is limited to the bimolecular mechanism: the rate of unimolecular hydrolysis of *tert.*-butyl nitrate is comparable in magnitude with that of *tert.*-butyl bromide. Thus the value $10^5 k_1$ (at 25°) = 37·2 for the bromide in 80% alcohol (Hughes and McNulty, *J.*, 1937, 1285) may be compared with those in 90% and 60% alcohol in Table 1. Examination of molecular models suggests that the reason for this much slower bimolecular hydrolysis of the nitrate is probably not steric in character since a large area of the α-carbon atom would seem to be exposed to nucleophilic attack. Pending further investigation, it seems more probable that it is due to repulsive forces between

the nucleophilic reagent and the negative charge field on the oxygen ends of the dipole in the nitrate group. A similar disparity was observed (Baker and Nathan, *J.*, 1936, 238) between the rate of quaternary salt formation of benzyl bromide and benzyl nitrate with pyridine in dry acetone at 40°, the values of 10^4k_2 being, respectively, 4·82 and 0·023 mole^{-1} l. sec.$^{-1}$. Our data for E for these reactions are not considered sufficiently extensive or accurate to warrant an attempt to analyse the effects of substitution on the A and E factors in the Arrhenius equation. The E values are of the same order as those for the alkyl halides.

(b) Evidence derived from the second diagnostic method, *viz.*, the effect of solvent changes, confirms the above conclusions regarding mechanism. Since the bimolecular

mechanism with hydroxyl ions $\overset{-}{HO} + RO\cdot NO_2 \longrightarrow \overset{\delta-}{HO}\text{-}\text{-}R\text{-}\text{-}\overset{\delta-}{O\cdot NO_2} \longrightarrow HOR + \overset{-}{NO_3}$ involves only a dispersal of the charge in the transition state, increase in the water content of the solvent should, on the Hughes–Ingold solvent theory (*J.*, 1935, 244), cause a small decrease in the velocity. This is found to be the case for methyl and ethyl nitrates (Table 2). In contrast, the velocity of hydrolysis of *iso*propyl nitrate is greater,

TABLE 2. *Effect of change of medium on the velocity coefficients* $10^5k_2(S_N2)$ *or* $10^5k_1(S_N1)$
for alkaline hydrolysis of alkyl nitrates.

Nitrate		Vol. % of water in the aqueous alcohol		
		10	25	40
MeNO$_3$	10^5k_2 at 60°	—	40·2	22·1
,, ...	,, at 44·8°	—	10·1	5·2
EtNO$_3$	10^5k_2 at 60°	4·1	—	2·35
,, ...	,, at 44·8°	0·98 *	—	0·47 *
Pr^{i}NO$_3$	10^5k_2 at 60°	0·46	—	2·98
Bu^{t}NO$_3$	10^5k_1 at 20°	4·93	—	236
,, ...	,, at 0°	0·32	—	10·2

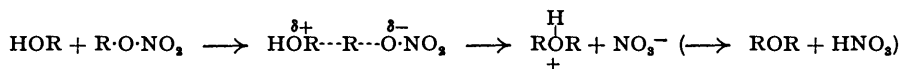* Total reaction ($S_N2 + E2 + E_{\text{co}}2$).

and that of *tert.*-butyl nitrate very much greater, in the more highly ionising solvent. This is in harmony with the requirements of a unimolecular mechanism in which the transition state $\overset{\delta+}{R}\text{-}\text{-}\overset{\delta-}{O\cdot NO_2}$ involves an increase in the magnitude of the charge, the hydrolxyl ion not being involved in the rate-determining stage of the reaction.

(c) In neutral solvolysis, the same large velocity increase in the more highly ionising solvent is observed (Table 3) in the case of the tertiary nitrate (in agreement with the

TABLE 3. *Effect of change of medium on the velocity coefficients* $10^5k_1(S_N)$ *for*
neutral solvolysis of alkyl nitrates.

			Vol. % of water in the aqueous alcohol	
			10	40
MeNO$_3$	at	60°	0·0073	0·0196
,,	,,	~97°	0·28	0·87
EtNO$_3$	,,	60°	0·003	0·011
Pr^{i}NO$_3$	,,	60°	0·007	0·05
Bu^{t}NO$_3$	,,	30°	13·9	589
,,	,,	0°	0·22	12·5

requirements of the unimolecular mechanism) but the velocity of neutral solvolysis of methyl and ethyl nitrates, unlike those of the alkaline hydrolysis, is also higher in 60% than in 90% alcohol. This is expected since the bimolecular mechanism

$$HOR + R\cdot O\cdot NO_2 \longrightarrow \overset{\delta+}{HOR}\text{-}\text{-}R\text{-}\text{-}\overset{\delta-}{O\cdot NO_2} \longrightarrow \overset{H}{\underset{+}{ROR}} + NO_3^- (\longrightarrow ROR + HNO_3)$$

involves an increase in the magnitude of the charge in the transition state, although the magnitude of the observed velocity increase is smaller than might have been expected.

*iso*Propyl nitrate also undergoes solvolysis more rapidly in the more aqueous solvent but the order of magnitude of the increase resembles those for methyl and ethyl nitrates

more closely than the large increases observed with the tertiary nitrate, for which all evidence supports a unimolecular mechanism.

(II) *Olefin Elimination* E.—With ethyl and *iso*propyl nitrates significant olefin elimination only occurs in the alkaline hydrolysis and has not been detected in the neutral solvolysis of these compounds. This is in accord with a bimolecular elimination reaction for these two esters since a reagent of low nucleophilic power retains its capacity for attack at carbon long after it has ceased to be able to attack hydrogen. As would be expected from the unimolecular mechanism valid for *tert.*-butyl nitrate which, in both media, involves the formation of a *tert.*-butyl cation as the rate-determining stage, *iso*butene is formed in both alkaline hydrolysis and neutral solvolysis. In the halide series it is known that second-order eliminations of alkyl halides obey the Saytzeff rule and are controlled by the electromeric effect (Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2114). The major factor which determines that the hyperconjugative effect shall be predominantly in control, is the neutral character of the group subsequently eliminated as an anion. It would therefore be expected that the nitrates, in which the group $-O \cdot NO_2$, although containing a dipole, is formally neutral, would follow the same rule. If this is so, introduction of an α- or a β-methyl substituent should increase the rate and proportion of olefin elimination and hence, for the series studied, these should increase in the order $Et < Pr^i < Bu^t$. The *tert.*-butyl nitrate, however, undergoes unimolecular elimination which is also governed

TABLE 4. *Rate constants and proportions of olefin formed in the hydrolysis of*
$CH_3 \cdot CR_2 \cdot O \cdot NO_2$ *with* $\sim 0 \cdot 1M$-KOH *in* 90% EtOH.

α-Substituents (R_2)	Temp.	$100E_2/(S_N2 + E2 + E_{co}2)$	$10^5k(E2)$	$10^5k(E1)$
H, H	59·3°	2	0·08	—
,,	30	4	0·006	—
H, Me	59·3	14·5	0·09	—
,,	79·7	11·1	0·72	—
Me, Me	59·3	~50 *	—	246 *
,,	30	23	—	5·5

* Calc. from the plots of $1/T$ against log $k(S_N1)$ and $k(E1)$.

by the Saytzeff rule so that, in spite of the change of mechanism, the given order should be maintained. Data in Table 4 clearly establish that, as α-methyl substituents are successively introduced into the molecule, the proportion of olefin formed does increase. This is ascribed to the resulting increased stabilisation due to hyperconjugation with the forming double bond in the transition stage (cf. Dhar *et al.*, *loc. cit.*, p. 2107) :
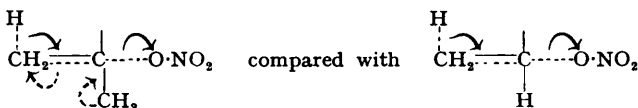
The only data yet available regarding the effect of change of solvent on the olefin elimination reaction are those for *tert.*-butyl nitrate. The rate-determining stage in this unimolecular mechanism is the same for both the substitution and elimination reactions and involves the transition state

$$Bu^tO \cdot NO_2 \longrightarrow \overset{\delta+}{Bu^t} \cdots \overset{\delta-}{O \cdot NO_2} \longrightarrow \overset{+}{Bu^t} + \overset{-}{O \cdot NO_2}$$
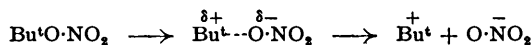
in which the magnitude of the charge is increased. In accordance with the theory of solvent effect enunciated by Cooper, Dhar, Hughes, Ingold, MacNulty, and Woolf (*J.*, 1948, 2045) the value of 10^5k_1 for the total reaction ($S_N1 + E1$) should greatly increase as the proportion of water in the aqueous-alcoholic solvent is increased. This is found to be the case for reaction in both alkaline and neutral media. The data are in Table 5.

In the alkaline media $E1/S_N1$ depends on the relative effects of the ionising medium on the transition states in the *fast* reaction, $HO^- + \overset{+}{Bu^t} \longrightarrow \overset{\delta-}{HO} \cdots \overset{\delta+}{Bu^t} \longrightarrow Bu^tOH$

for S_N1, and $\overset{\delta-}{HO} \cdots H \cdots \overset{\delta+}{CH_2} = CMe_2 \longrightarrow H \cdot OH + CH_2:CMe_2$ for $E1$, in *both* of which there is a reduction of charge so that no prediction regarding the effect of change

in medium on the *proportion* of olefin elimination is possible. Experimentally it is found (Table 6) that there is less olefin formation in the more highly ionising solvent. In neutral solvolysis, the transition states of both the fast reactions, *viz.*, $ROH \overset{\delta+}{-\!\!-\!\!-} \overset{\delta+}{Bu^t} \longrightarrow$ $\overset{+}{Bu^t}\overset{\delta+}{ORH}$ for S_N1 and $ROH \overset{\delta+}{\cdots}H\cdots CH_2 \overset{\delta+}{=\!=\!=} CMe_2$ for $E1$, are formed with dispersal of a given charge, which, however, is more extensive in the elimination reaction. It would thus be expected that, in the more aqueous alcohol, there would be a small decrease in the proportion of olefin formed by neutral solvolysis. Data in Table 6 confirm this.

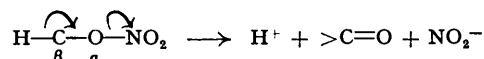TABLE 5. *Solvent effects on the values of* $10^5k_1(S_N1 + E1)$ *for* Bu^tNO_3 *in aqueous* EtOH.

	Vol. % of H_2O in aq. EtOH	
	10	40
~0·09M-KOH at 20°	6·47	265
,, ,, 0°	0·38	11·3
Solvent only ,, 30°	16·3	641
,, ,, 0°	0·25	13·3

TABLE 6. *Solvent effects on the ratio* $100E1/(S_N1 + E1)$ *in the hydrolysis of* Bu^tNO_3.

	Vol. % of H_2O in the aq. EtOH	
	10	40
~0·09M-KOH at 20°	23·8	11·1
,, ,, 0°	15·6	9·8
Solvent only ,, 30°	14·6	8·1
,, ,, 0°	12·8	6·0

Thus, from the admittedly limited data available it would appear that olefin elimination from ethyl and *iso*propyl nitrates occurs by a bimolecular mechanism but that from *tert.*-butyl nitrate is mainly, if not exclusively, unimolecular. All such eliminations are controlled predominantly by the electromeric effect of α- and β-alkyl substituents which, by hyperconjugation with the forming double bonds, lower the energy of the transition state and so increase the proportion of the olefin formed in the series $Et < Pr^i < Bu^t$.

(III) *Carbonyl Elimination*, E_{CO}.—The reaction (III), which is specific to alkyl esters of oxyacids such as nitric, involves the removal, as a proton, of the hydrogen attached to the α-carbon atom of the nitrate which is, of course, a β-hydrogen atom in the generalised scheme of 1 : 2-elimination reactions $H\overset{\frown}{\underset{\beta}{-a}}\overset{\frown}{\underset{\alpha}{-b}}X \longrightarrow a{=}b + HX$, the α-atom being oxygen :

$$H\overset{\frown}{\underset{\beta}{-C}}\overset{\frown}{-O}\underset{\alpha}{-NO_2} \longrightarrow H^+ + {>}C{=}O + NO_2^-$$

The question whether inductive or electromeric effects control such elimination is interesting. Since, in neutral solvolysis, at the most only a minute trace of nitrite is formed and the reaction is structurally impossible with *tert.*-butyl nitrate, we need only consider a bimolecular mechanism. It is in this mechanism that predominant control by either the inductive or the electromeric effect is determined essentially by the nature of the group X, whether it is initially positively charged or neutral, respectively (Dhar *et al.*, *loc. cit.*). In the case of the carbonyl elimination reaction this group X is $-\overset{+}{N}\overset{O^-}{\underset{O}{\diagdown}}$ which, although formally neutral, carries an integral positive charge on the atom which is directly attached to the α-atom of the system. It has been suggested that the reason why bimolecular eliminations from alkyl-substituted 'onium compounds are controlled predominantly by the inductive effect (Hofmann rule) is because the strong electron attraction $(-I)$ of the positive charge of the 'onium group, relayed through the α-carbon atom, stimulates the maximum operation of the $+I$ effect of any β-alkyl substituent. In the organic nitrates such relay of the $-I$ effect of the nitro-group occurs through an intervening unsaturated atom, bivalent oxygen, and it would thus be expected that its effect on C_β would be largely damped out. Hence we might expect that bimolecular carbonyl elimination from organic

nitrates would be controlled predominantly by the electromeric effect, as is the case in the alkyl halides. This would require that, in the alkaline hydrolysis of $RO \cdot NO_2$, the proportion of $E_{CO}2$ reaction should run parallel to olefin formation and increase in the order, $R = Me < Et < Pr^i$. The data in Table 7 show that this is confirmed. With methyl nitrate, nitrite formation is barely detectable, with ethyl nitrate it is measurable, whilst with *iso*propyl nitrate it is comparable in importance to the olefin-elimination reaction.

TABLE 7. *Proportion and values of* $10^5k(E_{CO}2)$ *for the carbonyl elimination reaction of* $RO \cdot NO_2$ *with* ~ 0.09M-KOH *in* 90% EtOH.

Nitrate	Temp.	$100E_{CO}2/(S_N2 + E2 + E_{CO}2)$	$10^5k(E_{CO}2)$
MeO·NO₂ *	44·8°	~0·1	negligible
,, *	60·2	~0·1	,,
EtO·NO₂	30	2·0	0·003
,,	59·3	4·8	0·2
Pr¹O·NO₂	59·3	13·7	0·09
	79·7	8·5	0·55

* In 75% EtOH.

In any comparison of the velocities, $10^5k(E_{CO}2)$, there is, however, another factor to be considered. In the carbonyl-elimination reaction the hydrogen removed as a proton is attached to C_α and the inductive ($+I$) effects of α-alkyl substituents, directly attached to the carbon from which proton elimination occurs, would exert a strong, first-order retarding effect on such ionisation. Such modifying influences of inductive effects on predominant control by the electromeric effect were noted by Dhar, Hughes, Ingold, *et al.* (*loc. cit.*) in elimination reactions of alkyl halides and sulphonium compounds. In our data they are revealed in the observation that, whilst the *proportion* of the $E_{CO}2$ reaction is much higher with *iso*propyl than with ethyl nitrate (as required by electromeric control), the value of $10^5k(E_{CO}2)$ is lower for the former compound (0·09 at 59·3°) than for the latter (0·2 at 59·3°). Thus the inductive effect ($+I$) of the two α-methyl substituents in *iso*-propyl nitrate greatly decreases the velocity of total reaction with hydroxyl ions ($S_N2 + E2 + E_{CO}2$), whilst the hyperconjugation effect with the forming double bond in the transition states of both olefin (*a*) and carbonyl (*b*) elimination reactions increases the
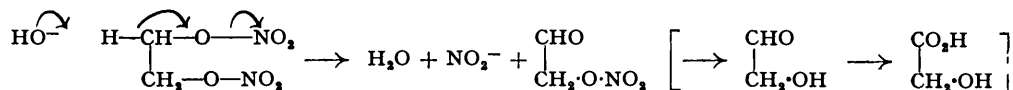

(*a*) $\overset{\delta-}{HO}$---H--$CH_2$$\overset{}{=}$CH···$\overset{\delta-}{ONO_2}$

(*b*) $\overset{\delta-}{HO}$---H--C$\overset{}{=}$O---$\overset{\delta-}{NO_2}$

proportion of these reactions in both cases by the relative lowering of the energy levels of the two transition states. With *iso*propyl nitrate, however, whereas in olefin elimination (*a*) the retarding inductive ($+I$) effect of *one* α-methyl substituent is relayed only in second-order magnitude to C_β (from which proton separation occurs) and so does not greatly affect the value of $k(E2)$, in the carbonyl reaction (*b*), the retarding inductive effects of *two* methyl substituents are operating *directly* on the β-atom of the system, *i.e.*, on the atom from which the proton separates, and hence greatly reduce the velocity of the $E_{CO}2$ reaction to a value lower than that for the corresponding reaction of ethyl nitrate, which carries only one such methyl substituent.
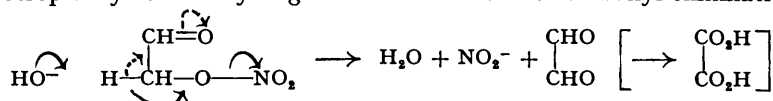
The overall picture of the mechanism of hydrolytic decomposition of simple alkyl nitrates is thus seen to fit in well to the general pattern of the theories of substitution and elimination reactions which have been established in such detail for the system H—C—C—X by the research school at University College, London, theories which are now shown to be capable of logical extension to 1 : 2-elimination from a system of the type H—C—O—X $\longrightarrow$ C=O + HX (X = NO₂).

The simultaneous occurrence of the three reactions, S_N2, $E2$, and $E_{CO}2$ also indicates the lines along which data in the early literature regarding the alkaline hydrolysis of poly-nitrates such as glycol dinitrate or glycerol trinitrate may be explained. The observed formation of nitrate, nitrite, glycollic acid, aldehyde resins, etc., might well follow from

oxidation of products initially formed by an $E_{CO}2$ type of reaction in accordance with schemes of the type :

$$HO^- \quad H-CH-O-NO_2 \longrightarrow H_2O + NO_2^- + \begin{array}{c} CHO \\ | \\ CH_2 \cdot O \cdot NO_2 \end{array} \left[\longrightarrow \begin{array}{c} CHO \\ | \\ CH_2 \cdot OH \end{array} \longrightarrow \begin{array}{c} CO_2H \\ | \\ CH_2 \cdot OH \end{array} \right]$$

The electron-attracting CHO group thus formed would then greatly facilitate the ionisation of the prototropically related hydrogen to favour a further carbonyl-elimination reaction,

$$HO^- \quad H-CH-O-NO_2 \longrightarrow H_2O + NO_2^- + \begin{array}{c} CHO \\ | \\ CHO \end{array} \left[\longrightarrow \begin{array}{c} CO_2H \\ | \\ CO_2H \end{array} \right]$$
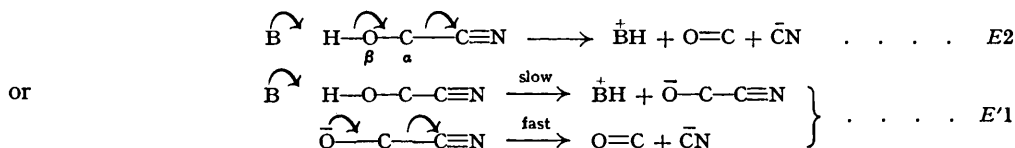
Such reactions would, of course, be superimposed on the ordinary substitution reaction giving nitrate ion and alcohol. Accurate kinetic examination of the decomposition of such polynitric esters must await the increase in our understanding of such reactions which should accrue from further studies of the effects of structural and environmental factors on the hydrolytic decomposition of simple mononitrates such as are already in hand.

In conclusion, there is an interesting comparison between the mechanism of E_{OO} elimination in the systems $H-\overset{|}{\underset{|}{C}}-O-X$, discussed in this paper, and that of the complementary system $H-O-\overset{|}{\underset{|}{C}}-X \longrightarrow O{=}C + HX$, data for which are provided by the values of k_2 in the reversible reaction $R \cdot C_6H_4 \cdot CHO + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \cdot C_6H_4 \cdot CH(OH) \cdot CN$ (Baker and Hemming, *loc. cit.*; Baker and Hopkins, *loc. cit.*) which are as follows :

R =	p-	But	Pri	Et	Me	H	F	Cl	Br	I	NO₂
$10^{10}k_2$ at 20° (sec.⁻¹)		0·57	0·57	0·68	0·74	0·74	2·26	2·67	2·98	2·94	12·6
R =	m-						F	Cl	Br	I	NO₂
$10^{10}k_2$ at 20° (sec.⁻¹)							2·18	2·45	2·69	2·92	12·3

As was pointed out by Baker and Hopkins (*loc. cit.*) the dissociation of the cyanohydrin is retarded by electron release towards the carbon atom of the elimination system and facilitated by electron attraction from this carbon atom. Hence the rate-determining step can hardly be the anionisation of a cyanide ion from the cyanohydrin. Since the reaction is base-catalysed, two mechanisms can be considered :

$$B \quad H-O-C-C{\equiv}N \longrightarrow \overset{+}{B}H + O{=}C + \overset{-}{C}N \quad \ldots \ldots \quad E2$$
$$\text{or} \quad B \quad H-O-C-C{\equiv}N \overset{slow}{\longrightarrow} \overset{+}{B}H + \overset{-}{O}-C-C{\equiv}N \left. \begin{array}{c} \\ \overset{-}{O}-C-C{\equiv}N \overset{fast}{\longrightarrow} O{=}C + \overset{-}{C}N \end{array} \right\} \quad \ldots \ldots \quad E'1$$

The first is an ordinary bimolecular elimination mechanism. Since the group (CN) which ultimately separates with its bonding electrons is originally neutral it might be expected that, in this mechanism, as in the elimination of hydrogen halide from alkyl halides, substituents on the α-carbon atom would control the rate of elimination essentially by their electromeric effect, *i.e.*, their capacity to conjugate with the forming carbonyl double bond in the transition state. So far as the limited data available * show, there is no support for this view, since the effect of a nitro-group, in the common phenyl substituent, differs little whether it is in the *meta*- or the *para*-position. The values of k_2 for whole series of substituents clearly suggest that the controlling feature is the *inductive* effect of the substituent R. Bearing in mind Baker and Hopkins's conclusion (*loc. cit.*) that the superimposition of the $+M$ and the $-I$ effect of the halogen substituents satisfactorily accounts for an order of overall electron *attraction* F<Cl<Br∼I, we have a continuous velocity increase as R changes from electron-releasing alkyl groups, through H, to groups with increasing $-I$ effects. Even with the alkyl substituents the small *retarding* effect decreases in the order R = (But ∼Pri)>Et>Me which is essentially the order of

* *Velocity* data are not yet available for the various aliphatic ketone- and aldehyde-cyanohydrin equilibria studied by Lapworth and Manske (*J.*, 1930, 1978).

their decreasing $+I$ effects. It is for such reasons that, pending more diagnostic evidence regarding mechanism, the second mechanism $E'1$ is regarded as more probable. This is a unimolecular mechanism, but it differs from the usual $E1$ mechanism in that the rate-determining stage is the removal of a proton to give an *anion*, in contrast to the usual anionisation of the group X leaving a carbonium ion. This difference in the mechanism of 1 : 2-elimination from the systems H—C—O—X and H—O—C—X is almost certainly related to the much greater ease of fission of a H–O than of a H–C or C–X bond. Electron attraction at the carbon atom, by increasing its positive character, will increase the

strength of the cyanohydrin as an acid $H \rightarrow O \rightarrow \overset{\delta+}{\underset{\underset{R}{\downarrow}}{C}} —X$ and so increase k_2. It is

intended to make a more extensive kinetic study of this system so that more effective comparisons may be possible.