217. *Hydrolytic Decomposition of Esters of Nitric Acid. Part I. General Experimental Techniques. Alkaline Hydrolysis and Neutral Solvolysis of Methyl, Ethyl,* iso*Propyl, and* tert.-*Butyl Nitrates in Aqueous Alcohol.*

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Hydrolytic decomposition of organic nitrates, $CH_2R{\cdot}CH_2{\cdot}O{\cdot}NO_2$, involves the possibility of the occurrence of three simultaneous reactions : nucleophilic substitution (S_N) to give the alcohol $CH_2R{\cdot}CH_2{\cdot}OH$ and nitrate, β-hydrogen elimination (E) to give olefin $CHR{:}CH_2$ and nitrate, and α-hydrogen elimination (E_{CO}) to yield a carbonyl compound $CH_2R{\cdot}CHO$ and nitrite.

Hydrolysis of primary and secondary alkyl nitrates occurs at approx. one-fortieth of the rate of that of the corresponding alkyl bromides, thus making glass reaction vessels unsuitable (owing to alkali attack) ; it has been studied by using " Polythene " or " Fluon " vessels.

Kinetic studies of alkaline hydrolysis and neutral solvolysis of methyl, ethyl, *iso*propyl, and *tert.*-butyl nitrates in aqueous alcohol yielded the separate rate constants for each of the three concomitant reactions, at several tempertures. In 90% alcohol, alkaline hydrolysis of methyl nitrate results only in substitution (S_N2), the amount of nitrite formed being only just detectable, but both $E2$ and $E_{CO}2$ reactions occur (~2% each) with ethyl nitrate and become more important (~10% each) in *iso*propyl nitrate, whilst a considerable increase in olefin formation is observed from *tert.*-butyl nitrate, the ratio $100E1/(S_N1 + E1)$ increasing slightly with rise of reaction temperature. For methyl, ethyl, and *iso*propyl nitrates the total reactions ($S_N2 + E2 + E_{CO}2$) are of first order with respect to both $[OH']$ and $[RNO_3]$, and the rates are approximately in the ratios 70 : 7 : 1, the corresponding values of the Arrhenius energies of activation being 18·8, 23·6, and 26·3 kcal./mole, respectively. Hydrolysis of *tert.*-butyl nitrate is very much faster, is of first order, and is not markedly accelerated by hydroxyl ions, particularly in the more highly ionising solvent, 60% alcohol. In this solvent, moreover, the S_N2 reaction accounts for $\not<$99% of the total reaction with *iso*propyl nitrate, which is faster than that of ethyl nitrate.

In neutral solvolysis neither olefin- nor carbonyl-elimination reactions could be detected with methyl, ethyl, or *iso*propyl nitrates, the reaction rates being in the order $Me > Et < Pr^i$, but considerable first-order olefin elimination occurs with *tert.*-butyl nitrate, the ratio $100E1/(S_N1 + E1)$ being larger in alkaline media than in neutral solvolysis, and in 90% than in 60% alcohol.

The rates of alkaline hydrolysis of methyl and ethyl nitrates in 60% alcohol are smaller than in 90% alcohol, but that of *iso*propyl nitrate is greater, and that of *tert.*-butyl nitrate very much greater, in the more highly ionising solvent. Neutral solvolysis of methyl, ethyl, and *iso*propyl nitrates occurs faster, and that of *tert.*-butyl nitrate very much faster, in 60% than in 90% alcohol.

The significance and interpretation of the results are discussed in Part II (following paper).

VERY little systematic work on the mechanism of the hydrolytic decomposition of organic nitrates has been reported. Most of the early work (cf. Beilstein, " Handbuch, etc.," Vol. I, pp. 464, 515; Suppl. Vol. I, p. 273) was concerned with explosives, such as glycerol trinitrate and glycol dinitrate, which, because of their polyfunctional character and consequent kinetic complexity, are very unsuitable for the initial stages of the study of mechanism. The only certain conclusion which can be drawn from this early work is that alkaline hydrolysis of such nitrates involves a much more complex decomposition than simple fission into alcohol and metallic nitrate, the presence of nitrite, carbonyl derivatives, and organic acids having been detected in the products. In a paper which summarises and discusses these early results R. C. Farmer (*J.*, 1920, **117**, 806) claimed to have shown that the primary reaction is a true hydrolysis of the general type $RNO_3 + H_2O \longrightarrow ROH + HNO_3$, followed by subsequent oxidation of the products, such as the alcohol, by nitric acid; he claimed that such secondary reactions could be suppressed either by reducing agents or by "protection" of the glycerol formed (by continuous extraction as its phosphoric ester). It was generally observed that the velocity of alkaline hydrolysis is 480 times greater than that of acid hydrolysis and, moreover, that formation of nitrite and the corresponding alcohol "oxidation" products is more prevalent in such alkaline media ("Organic Chemistry of Nitrogen," Sidgwick, Wilson Baker, and Taylor, 1937, Clarendon Press, Oxford, p. 8). Under such conditions the oxidising agent must, of necessity, be either the nitrate *anion* or the parent nitrate ester. It has now been shown that no oxidation of aqueous ethyl alcohol solutions by potassium nitrate occurs under the conditions of hydrolysis of nitrate esters used by us, although the formation of carbonyl derivatives and nitrite is confirmed. The exceedingly slow solvolytic reactions in aqueous alcohol (which we have also investigated) render oxidation by the nitrate ester very improbable; hence earlier views regarding the mechanism of such secondary reactions can scarcely be valid.

The direct formation of nitrite as a primary reaction product was envisaged in the (now discarded) view of Klason and Carlson (*Ber.*, 1906, **39**, 2752) that the initial reaction resulted in the formation of an alkyl peroxide :

$$RO{\cdot}O{\cdot}NO + KOH \longrightarrow RO{\cdot}OH + KO{\cdot}NO$$

followed, in the presence of a thiol, by the reaction

$$RO{\cdot}OH + 2RSH \longrightarrow ROH + R_2S_2 + H_2O$$

and they were thus able to isolate the alcohols glycerol and cellulose from technical "nitroglycerine" and "nitrocellulose," respectively.

A more recent investigation of the hydrolysis of *tert.*-butyl and benzyl nitrates by Lucas and Hammett (*J. Amer. Chem. Soc.*, 1942, **64**, 1928) revealed the concomitant formation of *iso*butene in the first-order solvolysis of the former :

$$\begin{cases} Bu^tO{\cdot}NO_2 + 2H_2O \longrightarrow Bu^tOH + H_3O^+ + NO_3^- \\ Bu^tO{\cdot}NO_2 + H_2O \longrightarrow C_4H_8 + H_3O^+ + NO_3^- \end{cases}$$

and of benzaldehyde, it was claimed, *both* in the first-order reactions * (*a*) and in the second-order reactions (*b*) in the case of the latter :

$$(a)\ \begin{cases} Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2 + 2H_2O \longrightarrow Ph{\cdot}CH_2{\cdot}OH + H_3O^+ + NO_3^- \\ Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2 \xrightarrow{H_2O} Ph{\cdot}CHO + HNO_2 \end{cases}$$

$$(b)\ \begin{cases} Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2 + OH^- \longrightarrow Ph{\cdot}CH_2{\cdot}OH + NO_3^- \\ Ph{\cdot}CH_2{\cdot}O{\cdot}NO_2 + OH^- \longrightarrow Ph{\cdot}CHO + H_2O + NO_2^- \end{cases}$$

These reactions were followed (in aqueous dioxan) by acid–alkali titration and determination of *iso*butene and benzaldehyde by standard methods.

It was therefore decided to commence a systematic kinetic study of the hydrolysis of organic esters of nitric acid, beginning with the simple alkyl mononitrates with which there should be a reasonable prospect of disentangling possibly superimposed modes of decomposition and of elucidating their detailed mechanisms. As a theoretical background there was available the considerable knowledge of the hydrolysis and solvolysis of alkyl halides and the concomitant elimination reactions resulting from the researches of Ingold, Hughes, and their collaborators. In view of the general applicability of such mechanisms to the hydrolytic and solvolytic decomposition of alkyl halides, onium compounds, etc., it seemed *a priori* that the hydrolysis of organic nitrates might partake of the same general

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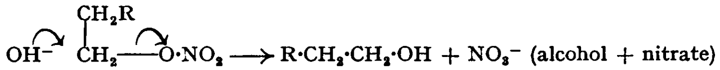
* Investigations at present in hand have revealed that neither nitrite nor benzaldehyde is formed in the first-order *solvolysis* of benzyl nitrate, but the reaction giving rise to such products is important in the second-order *alkaline* hydrolysis of this nitrate.

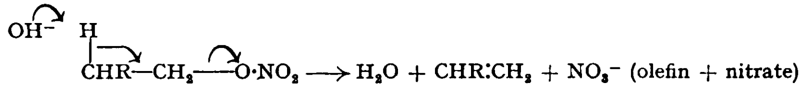
character. In one respect, however, the nitric esters have more in common with carboxylic esters than with alkyl halides, *viz.*, that, just as mechanisms involving both alkyloxy, $\mathrm{CO{\cdot}O{-}\vdots{-}R}$, and acyloxy, $\mathrm{CO{-}\vdots{-}OR}$, types of fission have been shown to function in the hydrolysis of carboxylic esters (Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686), so there is a possibility that both nitrate, $\mathrm{\geqslant C{-}\vdots{-}O{\cdot}NO_2}$, and nitrite, $\mathrm{\geqslant C{\cdot}O{-}\vdots{-}NO_2}$, fission may occur in the hydrolysis of nitric esters. Thus the hypothesis upon which the experimental investigation was planned was that hydrolytic fission of organic nitrates might involve concomitant substitution and elimination reactions with both nitrate and nitrite fission, in all of which duality of mechanism, uni- and bi-molecular, might enter and be controlled by essentially the same kind of structural and environmental factors as have been shown to operate in the corresponding reactions of alkyl halides. Expressed for simplicity only in terms of the bimolecular mechanisms (the corresponding unimolecular mechanisms will be obvious) for hydrolysis with hydroxyl ions * the following three modes of hydrolytic decomposition are expected (Baker and Easty, *Nature*, 1950, **166**, 156):

(I) Nucleophilic substitution (S_N2)



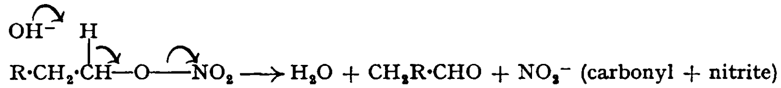
$$\mathrm{OH^- \;\; \overset{CH_2R}{\overset{|}{CH_2}}{-}O{\cdot}NO_2 \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}OH + NO_3^-} \text{ (alcohol + nitrate)}$$

(II) β-Hydrogen elimination, olefin formation ($E2$)



$$\mathrm{OH^- \;\; \overset{H}{\overset{|}{C}}HR{-}CH_2{-}O{\cdot}NO_2 \longrightarrow H_2O + CHR{:}CH_2 + NO_3^-} \text{ (olefin + nitrate)}$$

(III) α-Hydrogen elimination, carbonyl formation ($E_{CO}2$)



$$\mathrm{OH^- \;\; R{\cdot}CH_2{\cdot}\overset{H}{\overset{|}{C}}H{-}O{-}NO_2 \longrightarrow H_2O + CH_2R{\cdot}CHO + NO_2^-} \text{ (carbonyl + nitrite)}$$

Reactions (I) and (II) give nitrate ion, and (III) gives nitrite ion. In order to sort out these three simultaneous reactions the course of the hydrolysis has been followed by independent determinations of the various products formed, *viz.*, (1) acid–alkali titration (for OH^- or H_3O^+) which gives the combined velocity for all three reactions; (2) determination of nitrate ion, which gives the overall velocity of reactions (I) and (II); (3) olefin determination, which permits the apportionment of the velocity coefficient for the reactions (I) + (II), obtained from the nitrate determinations, between the two separate reactions; (4) nitrite ion determination, which gives the velocity coefficient for reaction (III) and could be checked by (5) determination of the carbonyl derivative formed. Thus a check on the concomitant formation of each of the products may be obtained: *e.g.*, when all three reactions are structurally possible the amount of hydroxyl ion removed should be equivalent at every stage of the reaction to that of nitrate + nitrite ions formed, whilst the values for nitrite alone should be equivalent to that obtained for the carbonyl derivative. Reaction (II) is structurally impossible with methyl nitrate, whilst reaction (III) is similarly excluded in the case of *tert.*-butyl nitrate. These features are especially significant since, if experiment confirms expectations, explanations of the formation of carbonyl compounds and nitrite based on secondary oxidation reactions are rendered extremely improbable.

Preliminary experiments soon revealed that alkaline hydrolysis of primary and secondary alkyl nitrates occurs very much more slowly than does that of the corresponding halides. Thus the value of 10^5k_2, the second-order velocity coefficient for the total reaction in the alkaline hydrolysis of ethyl nitrate in 90% ethyl alcohol (EtOH 90, H_2O 10% by vol.)

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* The problems of acid-catalysed hydrolysis and attack by other nucleophilic reagents are under investigation.

at 59·3° is 4·44, whereas the corresponding value for ethyl bromide in 80% alcohol at 55° is 171 mole^{-1} l. sec.$^{-1}$ (Bateman, Cooper, Hughes and Ingold, *J.*, 1940, 931). The corresponding values of 10^5k_1 (sec.$^{-1}$) for solvolysis are: ethyl nitrate 0·003, ethyl bromide 0·139. This very slow hydrolysis introduced a formidable experimental difficulty. Experiments showed that the long periods over which it thus became necessary to study the reaction, even at relatively high temperatures (~60—100°), made glass reaction vessels unsuitable because of the extensive alkali attack. Attention was therefore first directed to the designing of suitable vessels in which the ordinary sealed glass bulb technique could be satisfactorily simulated. The reaction vessel evolved after much experiment was composed of " Polythene " (or " Fluon ") (see Fig. 1).

The reaction vessel itself consists of a " Polythene " lining vessel accurately turned from 1" rod, and of capacity 5·6 c.c. (to take a 5-c.c. sample of reaction mixture and allow for thermal expansion). The vessel is flanged and fits snugly into the cavity of a thick, cylindrical brass container, the purpose of which is to support the " Polythene " against deformation by pressure and thermal softening. The vessel is closed by an accurately plane-ground " Polythene " cap, a gas-tight joint being obtained by means of a screwed-in brass stopper-cap, in the base of which a second " Polythene " disc is fitted so that the actual pressure is applied between two " Polythene " surfaces and the flange of the reaction vessel. A small cylindrical hole in the base of the brass container permits the insertion of a thin metal rod by means of which the " Polythene " lining vessel can be carefully removed without disturbing its contents, which are then washed out for analysis. The vessel is conveniently suspended in the thermostat by means of a stout wire support which fits round the brass container below the cap flange. A series of such vessels is used for each kinetic experiment, each vessel corresponding to a single sealed bulb. Such " Polythene " vessels were found to be sufficiently resistant to alkali attack and were satisfactory for long periods up to 60°, but at higher temperatures cracking and deformation of the " Polythene " vessels occurred. Subsequently it was found that " Fluon " was an even more suitable polymer to employ for the lining vessels.* In this material the alkaline reaction mixture remains almost colourless (in " Polythene " it becomes somewhat brown) and alkali attack, even after repeated use, is undetectable. The coefficients of expansion of brass and both " Polythene " and " Fluon " are such that, whilst the lining vessel is easily removed after the whole vessel has been cooled in ice, warming to reaction temperatures causes expansion of the polymer relative to the brass and a tight fit is thus attained. The general agreement between the values of the velocity coefficients derived from titration of excess alkali with acid and from the gravimetric determinations of nitrate ion (when no $E_{\mathrm{CO}}2$ reaction occurs) confirms the reliability of the alkali determinations in such vessels.

The techniques for determination of nitrate, nitrite, and olefin are described in the experimental portion.

No suitable method for the direct determination of the very small amounts of carbonyl derivatives formed in the hydrolysis of simple alkyl nitrates has yet been found. The 2 : 4-dinitrophenylhydrazones, although suitable for qualitative detection, are too soluble to be employed for gravimetric determination. In (unpublished) experiments with benzyl nitrates, however, this method (Eitel and Lock, *Monatsh.*, 1939, **72**, 385) is suitable and accurate for the determination of substituted benzaldehydes and the good agreement between the values for such aldehyde determinations and those of concomitantly formed nitrite ion justify the use of the latter determinations in order to evaluate the proportion of $E_{\mathrm{CO}}2$ reaction in the aliphatic series.

In solvolysis experiments the reaction was carried out in sealed glass bulbs in the presence of accurately weighed amounts of pure calcium carbonate, such that there was always a slight excess over the amount of acid formed at various time intervals. By this means it was hoped to eliminate, or at least minimise, any possible autocatalysis by free nitric acid.

Since one criterion of mechanism is the effect on reaction rate of change in the ionising power of the solvent by application of the Hughes–Ingold theory (*J.*, 1935, 244), a solvent

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* The difficulty in supply of suitable " Fluon " rod long prevented the general replacement of the " Polythene " vessels by this material, only a single sample vessel being available. Hence most of the investigations described in this paper were carried out in " Polythene," but " Fluon " is being used in our later work.

miscible with water was desirable. Initially aqueous dioxan, the solvent used by Lucas and Hammett (*loc. cit.*), was examined, but it was found that dioxan interfered with the accuracy of the gravimetric nitrate determinations with nitron. Since preliminary trials had shown that potassium nitrate, with or without addition of potassium hydroxide, had no action on aqueous ethyl alcohol under any of the conditions likely to be used in the kinetic experiments, it was decided to use this solvent. This makes possible direct comparison of our results with those for alkyl halides, which were obtained in the same type of solvent. It was also proved that when the standard ether-extraction technique is used for removal of unchanged alkyl nitrate, no interference with the gravimetric determination of nitrate ion in the aqueous solution is encountered. A further advantage is that, since preliminary examination suggested that even free nitric acid (~0·03M) has no detectable reaction with aqueous alcohol for periods up to ~168 hours at 60°, it should be possible to obtain at least initial rates in the same solvent when acid catalysis of hydrolysis is investigated.

This communication describes the results of investigations with methyl, ethyl, *iso*-propyl, and *tert.*-butyl nitrates, aimed at providing a general picture of the field into which the finer details, such as salt effects, etc., can later be fitted. A general discussion of the results is given in Part II (following paper).

FIG. 1.

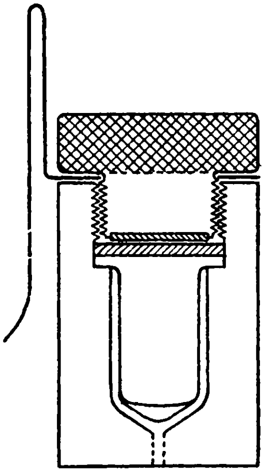


FIG. 2.

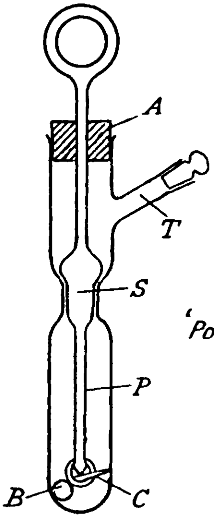
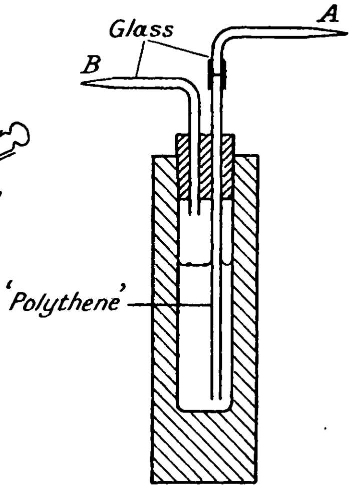


FIG. 3.



Methyl and Ethyl Nitrates.—Examination of methyl nitrate presented some unexpected difficulties. 90% Alcohol which was as little as 0·03M with respect to both nitrate and potassium hydroxide immediately became turbid, the separated droplets being essentially a concentrated aqueous solution of potassium hydroxide. The reason for such non-homogeneity, which does not occur with any of the other alkyl nitrates studied, is not known. To overcome this difficulty kinetic investigations with this nitrate were conducted in 75% and 60% alcohol, in both of which solvents homogeneity could be maintained.

Since the parallel and equivalent formation of nitrate ions with the loss of hydroxyl ion (nitrite formation is negligible with methyl nitrate) is an essential feature of the postulated mechanisms, typical data which unequivocally demonstrate such equivalence are recorded in Table 1. Incidentally, the great improvement in individual consistency which is obtained in " Fluon " vessels relative to the " Polythene " vessels first employed is apparent. With the gradual replacement of " Polythene " by " Fluon " it thus became unnecessary to determine hydroxyl ion, nitrate, and nitrite for every individual sample.

In all Tables x is the amount of reaction which has occurred at time t.

TABLE 1. (i) *Neutral solvolysis of methyl nitrate in* 60% EtOH *at* 60·2° (" *Monax* " *glass bulbs*).

Initial [CH_3NO_3] = 0·0301M.

Time (hours)	10^2x (mole l.$^{-1}$)		10^7k_1 (sec.$^{-1}$) *	
	H_3O^+	NO_3^-	H_3O^+	NO_3^-
336	—	0·65	—	2·03
450	—	0·83	—	2·00
617	0·972	—	1·75	—
953	1·42	1·49	1·86	1·99
1698	2·02	2·08	1·82	1·92
		Mean	1·81 ± 0·04	1·99 ± 0·03

(ii) *Alkaline hydrolysis of* $EtNO_3$.

(a) *In* 90% EtOH *at* 59·3° (" *Polythene* ").

Initial [$EtNO_3$] = 0·0307; [KOH] = 0·0999M.

Time (hours)	10^2x (mole l.$^{-1}$)			10^5k_2 (mole^{-1} l. sec.$^{-1}$) *	
	OH^-	NO_3^-	NO_2^-	OH^-	NO_3^-
4	0·172	0·196	—	4·05	4·60
18	0·709$_5$	0·723$_5$	—	4·21	4·31
24	0·858	0·898	—	3·97	4·15
30·42	1·035	1·063	—	3·98	4·10
44	1·428	1·328	—	4·30	4·00
∞ (816)	2·984	2·790	0·148	—	—
		$\underbrace{2{\cdot}790 \quad 0{\cdot}148}_{2{\cdot}938}$		Mean 4·11 ± 0·1	4·2 ± 0·2

(b) *In* 60% EtOH *at* 44·8° (" *Fluon* ").

Initial [$EtNO_3$] = 0·309; [KOH] = 0·0909M.

Time (hours)	10^2x (mole l.$^{-1}$)			10^5k_2 (mole^{-1} l. sec.$^{-1}$) *	
	OH^-	NO_3^-	NO_2^-	OH^-	NO_3^-
43·5	0·189	0·200	—	0·451	0·475
94·0	0·403	0·410	—	0·460	0·474
162·0	0·692	0·658	—	0·497	0·471
233·6	0·864	0·888	—	0·450	0·469
329·7	1·17	1·13	—	0·475	0·453
425·9	—	—	0·012	—	—
427·4	1·32	1·38	—	0·434	0·463
			Mean	0·46 ± 0·02	0·47 ± 0·01

* Values of k_1 and k_2 are uncorrected for expansion.

In the alkaline hydrolysis of methyl nitrate, contrary to statements in the literature, the reaction is essentially bimolecular *substitution* (S_N2) only, since nitrite produced was barely detectable (<0·1% of the total reaction). The results obtained are given in Table 2. In all such summarised results the values of the velocity coefficients have been corrected for solvent expansion from room temperature to the temperature of the experiment. The mean deviations from the mean value are recorded in each case.

TABLE 2. *Values of the second-order velocity coefficients for the alkaline hydrolysis* (S_N2) *of methyl nitrate in* 75% *and* 60% EtOH.

Initial [$MeNO_3$] ~0·03; [KOH] ~0·09M.

Solvent, Aq. EtOH (vol. %)	Temp.	10^5k_2 (mole^{-1} l. sec.$^{-1}$)			E (kcal./mole)
		(OH^-)	(NO_3^-)	Mean	
75	60·2°	41·2 ± 1·6	39·2 ± 1·5	40·2 ± 1·5	18·8
,,	44·8	10·3 ± 0·25	9·92 ± 0·6	10·1 ± 0·4	
60	60·2	22·0 ± 0·5	22·3 ± 0·8	22·1 ± 0·7	19·7
,,	44·8	5·2 ± 0·2	5·2 ± 0·2	5·2 ± 0·2	

The slower alkaline hydrolysis of ethyl nitrate was more difficult to follow since, with this nitrate, the proportions of the two elimination reactions ($E2$ and $E_{CO}2$), although small, are significant, as the following analysis shows :

Solvent	Temp.	$100X/(S_N2 + E2 + E_{CO}2)$		
		$X = S_N2$	$E2$	$E_{CO}2$
90% EtOH	80°	94	4	2
,,	60	93·2	2	4·8
60% EtOH	60	98·8	0·2	1

Such olefin and nitrite determinations were therefore subject to rather large errors and are only approximate; for this reason no separate values of the Arrhenius energies of activation for $E2$ and $E_{\rm CO}2$ are recorded but only those for the total reaction, for which a plot of log k_2 and $1/T$ gave a good straight line. The results are in Table 3.

TABLE 3. *Alkaline hydrolysis of ethyl nitrate under various conditions in aqueous alcohol.*

Initial [$EtNO_3$] ~0·03; [KOH] ~0·09M.

Solvent, Aq. EtOH (vol. %)	Temp.	10^5k_2 (mole^{-1} l. sec.$^{-1}$)				E (total reaction) (kcal./mole)
		$S_{\rm N}2$	$E2$	$E_{\rm CO}2$	Total	
90	59·3°	4·13	0·08	0·21	4·44 ± 0·04	23·6
90	45·0		(not determined)		0·98 ± 0·1	
90	30·0	0·131	0·006	0·003	0·14 ± 0·017	
60	~84		(not determined)		~5·8	21·9
60	60·2	2·34	0·004	0·024	2·37 ± 0·11	
60	44·8	0·47	—	(0·004)	0·47 ± 0·012	

At this stage it may be noted that, for both methyl and ethyl nitrates, the velocity of alkaline hydrolysis is slower in the more highly ionising solvent, 60% alcohol. There is an indication that the incursion of the two elimination reactions (always small) is also less in this solvent than it is in 90% alcohol.

In view of the very much smaller nucleophilic power of the water or alcohol molecule compared with that of the hydroxyl ion it is not surprising that the neutral solvolyses of both ethyl and methyl nitrates are extremely slow reactions: the half-life period for ethyl nitrate in 90% alcohol at 60° is ~250 days. In these solvolytic reactions, substitution ($S_{\rm N}2$) is the sole reaction and no elimimation reactions could be detected. The values of the velocity coefficients for neutral solvolysis of methyl and ethyl nitrates are given in Table 4.

TABLE 4. *Values of the first-order velocity coefficients for neutral solvolysis of* RNO_3 *in aqueous aocohol.*

Initial [RNO_3] ~0·03M.

R	Solvent, Aq. EtOH (vol. %)	Temp.	Mean 10^5k_1 (sec.$^{-1}$)	E (kcal./mole)
CH_3	90	96·2°	0·28 ± $0{\cdot}01_5$	24·8
,,	,,	60·2	0·0073 ± 0·0007	
,,	60	97·7	0·87 ± 0·06	24·8
,,	,,	60·2	$0{\cdot}019_6$ ± 0·001	
C_2H_5	90	59·3	0·003 ± 0·0003	
,,	60	60·2	0·011 ± 0·0008	

Attention may be called to two points. First, unlike the alkaline hydrolyses, the solvolytic reaction is *faster* in the more highly ionising solvent, the 60% alcohol. The velocity coefficient is, of course, of pseudo-first-order for a *bimolecular* reaction in which the solvent concentration is maintained effectively constant. It being assumed that both water and alcohol molecules are equally effective, the approximate total solvent concentration can be calculated to be 20·8 and 32·2 moles per l. respectively for 90 and 60% alcohol. On this basis the values for the second-order velocity coefficients for the solvolytic reaction at 60° are approximately as follows:

EtOH:	90%	60%	
$MeNO_3$	~3×10^{-9}	~6×10^{-9}	mole^{-1} l. sec.$^{-1}$
$EtNO_3$	~$1{\cdot}4 \times 10^{-9}$	~3×10^{-9}	,, ,,

Comparison with the corresponding values for hydrolysis by hydroxyl ion (Tables 2 and 3, using the value in 75% aqueous alcohol, the only one available, for comparison in the case of methyl nitrate) shows that the velocities with the much more strongly nucleophilic hydroxyl ion are greater by the order of 10^4 to 10^5.

iso*Propyl and* tert.-*Butyl Nitrates*.—Experimentally *iso*propyl nitrate was the most difficult of the nitrates to investigate since, in the less ionising solvent, its velocity of decomposition by alkali is much slower even than that of ethyl nitrate and, moreover, all three reactions, $S_{\rm N}2$, $E2$, and $E_{\rm CO}2$ occur in significant proportions. Hence simultaneous determinations of hydroxyl ion, nitrate, nitrite, and olefin are essential. Because of these complications it has, so far, been studied only at two temperatures in 90% alcohol and at a single temperature in 60% alcohol. Most of the work was carried out in "Polythene" vessels and in these the values obtained from determinations of hydroxyl ion used were always rather higher (~10%) than those derived from determinations of nitrate + nitrite ions formed, and the infinity value somewhat exceeded that theoretically required for 100% hydrolysis. As "Fluon" vessels were introduced this disparity was greatly reduced or eliminated, and it may therefore be most probably ascribed to slight alkali attack on the "Polythene" vessels during the prolonged contact necessary to follow the reaction to completion. For this reason results have been calculated on the nitrate and nitrite values, which are regarded as the more reliable.

A summary of the results for the second-order velocity coefficients in alkaline, and for first-order velocity coefficients in neutral, hydrolysis is given in Table 5, all values being corrected for solvent expansion where necessary.

TABLE 5. *Hydrolysis of* iso*propyl nitrate in aqueous ethyl alcohol.*

Initial [Pr^iNO_3] ~0·03; [KOH] ~0·09M.

Solvent, Aq. EtOH (vol. %)	Temp.	(*a*) Alkaline hydrolysis 10^5k_2 (mole^{-1} l. sec.$^{-1}$)				(*b*) Neutral solvolysis 10^5k_1 (sec.$^{-1}$)			Reaction proportions, %		
		S_N2	$E2$	$E_{CO}2$	Total	S_N	E_{CO}	Total	S_N2	$E2$	$E_{CO}2$
90	79·7°	5·3	0·72	0·55	6·52 (*a*)	—	—	—	80·4	11·1	8·5
,,	59·3	0·46	0·09	0·09	0·65	—	—	—	71·8	14·5	13·7
,,	75	—	—	—	—	0·038	*ca.* 0·0003	0·038	>99	0	<1
,,	60	—	—	—	—	0·007	0	0·007	100	0	0
60	60·2	2·98	0	0·03	3·01	—	—	—	99	0	1
,,	60·2	—	—	—	—	0·048	0	0·048	100	—	0

(*a*) These values give E for S_N2 = 27·9 and for total reaction = 26·3 kcals./mole.

The determinations of olefin and nitrite are again not regarded as sufficiently accurate to warrant separate evaluation of the values of the Arrhenius E values for the $E2$ and $E_{CO}2$ reactions. They are of the order of 20—23 kcal./mole. The formation of a carbonyl compound was qualitatively confirmed although it could not be determined quantitatively.

Attention may be directed to the points: (1) the proportion of total elimination reactions ($E2$ + $E_{CO}2$) which occurs with the nitrate is considerably less than that of olefin elimination from *iso*propyl bromide under comparable conditions (Hughes, Ingold, and Shapiro, *J.*, 1936, 225); (2) whilst in 90% alcohol the total velocity of alkaline hydrolysis of *iso*propyl nitrate is only about one-seventh of that of ethyl nitrate under the same experimental conditions, in 60% alcohol *iso*propyl nitrate is hydrolysed slightly *faster* than ethyl nitrate, and, moreover, in this solvent elimination reactions are reduced to negligible proportions.

In both solvents there are indications from the limited data available that the rate of neutral solvolysis of the *iso*propyl compound is greater than that of ethyl nitrate, and no appreciable elimination could be detected, substitution accounting for $\nless 99\%$ of the total reaction.

For comparison, the approximate value of the second-order velocity coefficient for the solvolysis of *iso*propyl nitrate (calculated on the basis of solvent concentration) in 60% alcohol at 60° is $\sim 1 \cdot 5 \times 10^{-8}$, *i.e.*, $\sim 10^{-3}$ times that for attack by hydroxyl ion under the same conditions.

More extensive examination of *tert.*-butyl nitrate has been possible because the hydrolytic reactions are sufficiently rapid to be conveniently studied at lower temperatures and in glass vessels. For alkaline hydrolysis the velocity coefficients calculated on the basis of a first-order law are reasonably constant throughout any one experiment, but Expts. Nos. 2 and 3 (Table 6) suggest that change in the initial hydroxyl-ion concentration has a small effect on the velocity. Olefin elimination is also important, both in alkaline hydrolysis and in netural solvolysis, but carbonyl elimination is, of course, structurally impossible. Analysis of the data for both alkaline hydrolysis and neutral solvolysis in 90% alcohol is given in Table 6.

In the presence of 2—4 molecular proportions of alkali the values of both $k_1(S_N1)$ and $k_1(E1)$ are somewhat higher than those for the solvolytic reaction at the same temperature (the disparity being greater in the elimination reaction). When, however, the initial concentration of alkali is only about one-fifth of the initial concentration of *tert.*-butyl nitrate (No. 3), the value of $10^5k_1(S_N1 + E1)$ (4·2) closely approximates to that (3·66) for the solvolytic reaction at the same temperature (No. 6) and, moreover, its value remains essentially constant as the medium changes from alkaline, through neutral, to acid as the reaction proceeds (cf. p. 1207). Addition of tetramethylammomium nitrate caused no detectable alteration in the value of k_1 (cf. No. 7), but this *may* arise from a fortuitous compensation between a velocity-increasing ionic-strength effect and a retarding mass-law effect of the common ion. The question whether the higher velocities in the presence of alkali are due to an ionic-strength effect or to some incursion of a bimolecular mechanism is thus not resolved and further investigations of the effects of added salts are necessary. Lucas and Hammett (*loc. cit.*) only detected acceleration by sodium hydroxide in solvents of high dioxan content. If the presence of excess of alkali gives rise to some bimolecular reaction the values obtained in No. 1 (where the ratio $(KOH]/[Bu^tNO_3] = \sim 4)$ may not be strictly comparable with those of Nos. 2 and 4 (in which the ratio is ~ 2), with consequent repercussions on the derived values of the Arrhenius energies of activation.

TABLE 6. *Alkaline hydrolysis and neutral solvolysis of* tert.*-butyl nitrate in* 90% EtOH.

	Initial concn. (mole l.$^{-1}$)			10^5k_1 (sec.$^{-1}$)			E (kcal./mole)		Reaction proportions, %	
No.	[OH$^-$]	[Bu^{t}NO$_3$]	Temp.	S_N1	$E1$	Total	S_N1	$E1$	S_N1	$E1$
1	0·0877	0·0211	30°	18·5	5·5	24·0	22·3	25·4	77	23
2	0·0876	0·0420	20	$4{\cdot}9_3$	$1{\cdot}5_4$	$6{\cdot}4_7$			76·2	23·8
3	0·0109	0·0486	20	—	—	4·2			—	—
4	0·0883	0·0437	0	0·32	0·06	0·38			84·4	15·6
5	0	0·0298	30	13·9	2·38	16·3	22·6	23·5	85·4	14·6
6	0	0·0245	20	3·10	0·56	3·66			84·8	15·2
7	0	0·0473	0	0·22	$0{\cdot}03_3$	0·25 *			87·2	12·8

* Cf. $10^5k_1 = 0{\cdot}26$ when $0{\cdot}0463\text{M-NMe}_4{}^+\}\text{NO}_3{}^-$ is added.

Although the trend is somewhat irregular there is a general indication that the proportion of olefin formed increases with rise in reaction temperature, in agreement with the larger energy of activation of the $E1$ compared with that of the S_N1 reaction, and it is clear that the proportion of olefin formed is also greater in alkaline hydrolysis than in neutral solvolysis.

TABLE 7. *Alkaline hydrolysis and neutral solvolysis of* Bu^{t}NO$_3$ *in* 60% EtOH.

Initial concns. (mole l.$^{-1}$)			10^5k_1 (sec.$^{-1}$)			E (kcal./mole)		Reaction proportions, %	
[OH$^-$]	[Bu^{t}NO$_3$]	Temp.	S_N1	$E1$	Total	S_N1	$E1$	S_N1	$E1$
0·106	0·0289	20°	236	29·4	265	25·0	25·6	88·9	11·1
—	—	10	(43·7)	(6·3)	(50) *			(87·4)	(12·6)
0·101	0·0395	$8{\cdot}6_5$	32·6	4·95	37·5			86·8	13·2
0·0866	0·0419	0	10·2	1·1	11·3			90·2	9·8
0	0·0272	30	589	51·9	641	21·2	23·0	91·9	8·1
0	—	20	(170)	(14·6)	(185)			(92·0)	(8·0)
0	0·0330	10	43·2	3·9	47·1			91·7	8·3
0	0·0372	0	12·5	0·80	13·3			94·0	6·0

* The values in parentheses have been calculated from the straight-line plots of $1/T$ against $-\log k$, for comparison with values at corresponding temperatures in the other series.

In the more highly ionising 60% alcohol there is a much closer general parallelism between the results for both alkaline hydrolytic and solvolytic decompositions, indicating that substitution and elimination reactions are proceeding essentially by the same mechanisms in both media. The results are summarised in Table 7.

It will be seen that the proportion of olefin formation in both alkaline and solvolytic reactions is less in 60% than in 90% alcohol (Table 6), but that again it is somewhat higher in the presence of hydroxyl ions.

It should be noted that the velocities of both the alkaline hydrolysis and the solvolysis of *tert.*-butyl nitrate are very much higher in the more highly ionising solvent, 60% alcohol.

EXPERIMENTAL

Solvent.—Absolute ethyl alcohol was dried and purified by refluxing it with sodium and ethyl phthalate (Smith, *J.*, 1927, 1288) and finally distilling it over solid 2 : 4-dinitrophenylhydrazine to remove the last traces of carbonyl derivatives. The resulting alcohol gave no appreciable reaction for aldehyde with Tollens's ammoniacal silver nitrate reagent. The solvent was prepared by mixing x volumes of this dry alcohol with $(100 - x)$ volumes of water to give " x vol.% " alcohol.

Preparation of Organic Nitrates.—Ethyl and *iso*propyl nitrates were prepared by adding ethyl iodide or *iso*propyl bromide, respectively, to dry, finely powdered AnalaR silver nitrate (slightly more than 1 molecular proportion) at 0°. The mixture was gently refluxed, with occasional addition of more powdered silver nitrate, to a total of 2 molecular proportions, until no alkyl halide remained and the liquid ceased to reflux at the b. p. of the alkyl halide. The product was distilled from the reaction mixture at ~50° under reduced pressure, condensed in a well cooled receiver, dried over anhydrous calcium nitrate in the presence of a little powdered calcium carbonate (to ensure freedom from acid), and carefully fractionated over fresh powdered silver nitrate. The main fraction (ethyl nitrate, b. p. 47°/180 mm.; *iso*propyl nitrate, b. p. 47°/105 mm.) was frozen in liquid air, then allowed partly to melt, and the liquid portion was removed by suction through a sintered-glass filter stick. The remaining crystalline material, after melting, was again dried over calcium nitrate and carefully refractionated from a little silver nitrate through a short column. The samples used were: ethyl nitrate, b. p. 49·8—50·0°/180 mm. (Found: C, 26·8; H, 5·9. Calc. for $C_2H_5O_3N$: C, 26·4; H, 5·5%); *iso*propyl nitrate, b. p. 49·5°/100 mm. (Found: C, 34·9; H, 6·8. Calc. for $C_3H_7O_3N$: C, 34·3; H, 6·7%).

For the prepation of *tert.*-butyl nitrate, refluxing must be avoided. *tert.*-Butyl chloride, mixed with an equal volume of pure dry ether, was shaken with an excess of dry powdered silver nitrate in the dark until the liquid was free from chlorine (~3 days). The ethereal solution was filtered from the silver salts, and the ether removed at room temperature under reduced pressure. The residue was distilled from a little powdered silver nitrate and calcium carbonate, the fraction of b. p. 23—25°/10 mm. being collected in a receiver cooled in an alcohol–solid carbon dioxide mixture. Purification was effected by the freezing technique previously described. The sample used had b. p. 21—23°/10 mm., m. p. *ca.* −36°, and gave consistent values ~100% purity by complete hydrolysis. It was stored, frozen solid, in small sealed brown ampoules in solid chest containing carbon dioxide (Lucas and Hammett, *loc. cit.*).

Methyl nitrate was available in accurately standard 0·06M-solutions in the purified 90% and 60% alcohol, which were stored below 0°. Owing to the very slow rate of solvolysis of this nitrate, no significant change occurs in these solutions over long periods at room temperatures. The zero point of each kinetic determination was always determined by actual titration. The infinity values after alkaline hydrolysis corresponded to a purity of ~100%.

Velocity Determinations.—In the case of the slowly reacting methyl, ethyl, and *iso*propyl nitrates, solutions of the nitrate and of potassium hydroxide of appropriate concentrations were mixed at room temperature (~20°) and the required volume of the reaction mixture was measured between calibration marks of a gravity-filled pipette ground into an all-glass apparatus, and suitably connected to a capillary delivery tube, by means of which the reaction vessels were filled. After the vessels had attained temperature equilibrium in the thermostat the concentration was checked by an initial zero reading. At suitable time intervals the vessels were chilled in ice, the lining vessels carefully removed, and the contents washed out with distilled water.

The sample was extracted with neutral ether, to remove unchanged organic nitrate, and the aqueous liquor, together with three aqueous washings of the ethereal extracts, was titrated with standard sulphuric acid (~0·03N) to methyl red, from a calibrated, microburette. The neutralised liquor, after appropriate concentration, was used for the gravimetric determination of nitrate as nitron nitrate. When nitrite was determined, the aqueous extract was made up to a suitable standard volume before titration and an aliquot portion used for the Griess–Ilosvay determination of nitrite, and the remainder was titrated and used for the nitrate determination.

The much greater speed of hydrolysis of *tert.*-butyl nitrate necessitated a different technique. Since the reaction is complete before appreciable alkali attack on glass occurs, the *tert.*-butyl nitrate was weighed directly from a weight-pipette into the appropriate volume of $\sim$0·1N-potassium hydroxide solution in aqueous alcohol in a stoppered glass flask which had previously attained temperature equilibrium in the thermostat. After thorough mixing, a 2-c.c. sample was immediately taken within the first minute, for determination of the initial acidity (always present) of the organic nitrate, and this titre and time were taken as the zero values. In the alkaline hydrolysis in 90% alcohol separation of potassium nitrate occurs as the reaction proceeds and 2-c.c. samples were taken at appropriate time intervals with a pipette to the end of which was attached a sintered-glass filter stick. Time intervals were measured to the nearest second, on a stop-clock. In some alkaline hydrolyses, 0·12% of nitrite was found to be present. According to our suggested mechanisms, the elimination of nitrite (E_{00} reaction) is impossible with this *tert.*-nitrate, and it was found that the amount present did not increase during the reaction and for long periods after its completion. Duplicate experiments in alkali, but on the same sample of *tert.*-butyl nitrate which had previously been allowed to age at room temperature for 2 and 9 days gave, respectively, 0·16 and 4·4% of nitrite, these amounts also remaining unchanged as the hydrolysis went to completion. It is thus evident that the small amount of nitrite formed is not a product of the hydrolytic decomposition but arises from slight decomposition of the initial sample of tertiary nitrate.

In the rapid neutral solvolysis, addition of calcium carbonate was considered unnecessary and the reaction was followed by acid–alkali titration, with only an occasional check by gravimetric determination of nitrate ion formed in experiments in 60% aqueous alcohol where the whole of the potassium nitrate formed remained in solution.

(1) *Nitrite.* The standard procedure was to treat 20 c.c. of the nitrite solution ($\sim$0·4—4·0 $\times$ 10^{-5}M) with 1 c.c. of each of the Griess–Ilosvay reagent solutions, warm the whole for 1·5 minutes at 70°, cool it to room temperature, allow it to stand for 2 minutes, and then determine the percentage transmission in a 1-cm. cell, using a OB1 blue light filter in a Hilger absorptiometer. The nitrite concentration was determined from a calibration curve based on the following data, obtained under identical experimental conditions, from standard solutions of AnalaR potassium nitrite.

$10^5[NO_2^-]$ (mole l.$^{-1}$)	7·55	3·77	2·83	1·89	0·94$_4$	0·37$_7$
Transmission, %	39·2	59·4	66·2	76·6	87·4	94·2

(2) *Nitrate.* A solution, $\sim$0·025M in NO_3^-, was concentrated on a steam bath to 4·0 c.c. (after filtration, where necessary, to remove traces of precipitated indicator). To the hot solution 3 drops of glacial acetic acid were added, followed by 25 drops of a standard solution containing 10 g. of nitron in 100 c.c. of 5% acetic acid, stored in the dark. The tube was stoppered and the mixture allowed to cool in the dark for 20 minutes and then kept at 0° for 30 minutes. For concentrations $<$0·025M, the volume of solution and the quantity of reagent were decreased proportionately and a longer period was allowed for crystallisation of the nitron nitrate. The precipitated nitron nitrate was collected in a weighed, sintered-glass microcrucible, washed several times with small volumes of a saturated aqueous solution of nitron nitrate, dried at 112° for 30 minutes and weighed on a semi-micro-balance. With the factor NO_3^-/nitron nitrate = 0·1654, this technique gave the values NO_3^- = 61·2, 61·6, 60·6 (mean = 61·1) for AnalaR potassium nitrate (Calc. : NO_3^-, 61·4%), and was shown to be reliable when a 0·04995M-KNO_3 solution in 60% alcohol containing 0·03028M-ethyl nitrate was put through the usual ether-extraction technique (Found : NO_3^-, 0·04989M). A second sample containing 0·00509M-NO_3^- gave an equally satisfactory result (Found : NO_3^-, 0·00508M). Nitrite, when also present, was first destroyed with hydrazine sulphate or sulphamic acid. By this method a solution originally 0·0301M in potassium nitrate and 0·0189M in potassium nitrite gave NO_3^- = 0·0309M.

(3) *Olefin determination.* Three techniques were employed.

(i) Using sealed glass bulbs for the reaction. This was an earlier technique employed before the method (iii) (below) was developed, or in cases where alkali attack on glass was slight as in rapid reactions or neutral solvolysis. Sample bulbs (*B*) of the reaction mixture were removed from the thermostat after various times, then chilled, a small glass collar (*C*) was slipped over the neck of the bulb, and the whole dropped carefully into the lower section of the stoutly constructed glass apparatus shown in Fig. 2, which contained sufficient 2N-sulphuric acid to neutralise the alkali present in the reaction mixture, and 5 c.c. of carbon tetrachloride. After the whole had been cooled in ice the point of the stout glass plunger *P* was inserted between the collar and the neck of the bulb and a sharp blow on the top of the plunger then *simultaneously* broke the bulb and closed the gas-tight glass stoppered joint *S* securely into its seat, thus completely sealing the lower portion of the vessel and preventing any possible escape of volatile olefin. The top portion was immediately sealed by means of the tightly fitting rubber stopper *A*.† The lower section was then well cooled in ice and a known (excess) volume of a 0·05N-solution of bromine in carbon tetrachloride saturated with hydrogen bromide was introduced through *T* into the top section. By slightly raising the stopper *S* this solution was sucked into the lower half, *S* being closed whilst a small volume of the solution still remained in the top half. A solution of potassium iodide was then introduced through *T* to ensure that no bromine escaped from this excess bromine solution. The olefin solution was allowed to react with the added bromine for 30 minutes, and, by using the same technique, the potassium iodide solution was then sucked in. The vessel was then opened, the whole contents were washed out, and the liberated iodine was titrated with 0·05N-sodium thiosulphate. The method was tested with weighed amounts of trimethylethylene (sealed in glass bulbs). Determinations gave 95, 93, 94, 96, 104% of olefin.

(ii) This technique was used for rapid hydrolytic reactions, such as those of *tert.*-butyl nitrate, in which the reaction is complete before any appreciable alkali attack on the glass vessel occurs. The actual reaction was carried out (to completion) in the lower section of an apparatus very similar to that depicted in Fig. 2, but without the plunger *P*. The olefin formed was then determined in the whole reaction mixture by a similar technique. The presence of acetone in concentrations far in excess of any likely to be produced by any $E_{CO}2$ reaction, was shown not to introduce an error greater than that of the accuracy of the method. This technique was also tested with a standard alcoholic solution of *iso*butene, which was determined (*a*) by direct titration and (*b*) after submission to the reaction conditions in the thermostat for 70 hours. The following results show the amount of olefin in a 2-c.c. sample in terms of c.c. of ~0·01N-thiosulphate :

Method (*a*)	19·84	19·94	19·94	19·94
Method (*b*)	22·35	22·25 *	21·96	21·64 *
Found, %	113	112	110	109

Results marked * were obtained with olefin solution which had been mixed with an equal volume of 0·03M-nitric acid in alcohol whilst in the thermostat. The agreement with the other values shows that no appreciable loss of olefin by hydration occurs under the acid conditions produced in the solvolysis experiments.

(iii) An aspiration method was developed using a " Polythene " " test-tube ", constructed from " Polythene " rod of 1" diameter, and sealed with a two-holed rubber stopper through which passed a " Polythene " delivery tube, reaching to the bottom, and a glass exit tube (Fig. 3). A glass tube extension to the " Polythene " tube was secured by means of rubber. The reaction mixture was placed in the " Polythene " test-tube, the rubber stopper was sealed with wax, and the two glass tubes were drawn out and sealed at *A* and *B*. The vessel was immersed in the thermostat for the necessary period. To determine the olefin formed, *A* was connected to a supply of pure nitrogen and *B* was attached through an efficient trap, cooled to −12°, to a bubbler train containing a known volume of a standard solution of bromine in carbon tetrachloride and a guard-tube bubbler containing potassium iodide solution. The sealed glass tips *A* and *B* were then broken inside the connecting rubber tubing and a slow stream of nitrogen was passed through for 1 hour. The excess of bromine was determined with potassium iodide and standard thiosulphate solution in the usual manner. A " blank " correction for any alcohol vapour carried over into the bromine solution was carried out, with only solvent alcohol in the reaction vessel and the same rate of passage of nitrogen. The method was tested with a standard solution of pure propylene in alcohol against the olefin concentration determined by direct titration. In two experiments, the olefin in a 2-c.c. sample required the following volumes (c.c.) of 0·01N-bromine : Direct method, 8·53, 8·83. Aspiration method (iii), 9·38 (110%), 9·94 (113%).

Kinetic Results.—Details of typical kinetic experiments are recorded as illustrative of the general results. The data so given have not been corrected for solvent expansion.

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† Initially a second glass-stoppered joint was employed here, but the resultant rigidity of the apparatus resulted in frequent fracture during breaking of the bulb and simultaneous closing of both glass-stoppered joints.

Methyl nitrate.

(*a*) *Alkaline hydrolysis in* 60% EtOH *at* 60·2° *in* " *Polythene* " *vessels.*

Initial [$MeNO_3$] = 0·0301; [KOH] = 0·0854M. Reaction followed by titration with 0·0378N-H_2SO_4 and by gravimetric determination of NO_3^- as nitron nitrate.

Time (mins.)	Vol. (c.c.) of H_2SO_4 for 4-c.c. sample	10^2x (mole l.$^{-1}$)		10^4k_2 (mole^{-1} l. sec.$^{-1}$)	
		OH^-	NO_3^-	OH^-	NO_3^-
0	9·047	—	—	—	—
36	8·953	0·089	0·125	(1·66)	2·41
101	8·722	0·307	0·332	2·14	2·29
150	8·592	0·430	0·467	2·06	2·28
305	8·167	0·831	0·821	2·18	2·15
497	7·766	1·209	1·16	2·19	2·07
1320	6·848	2·076	1·96	2·04	1·81
∞ (11 days)		3·07 (102%)		(Mean) 2·14	2·17

Nitrite was only just detectable, ~0·1% of total reaction.

(*b*) *Solvolysis in* 90% EtOH *at* 96·2° (*mean temp. of boiling-water bath in* " *Monax* " *glass bulbs*).

Initial [$MeNO_3$] = 0·0300M.

Time (hours)	10^2x (mole l.$^{-1}$)		10^6k_1 (sec.$^{-1}$)	
	H_3O^+	NO_3^-	H_3O^+	NO_3^-
13·18	0·338	0·367	2·53	2·77
21·25	—	0·562	—	2·70
27·00	0·695	0·710	2·73	2·78
42·67	0·921	0·940	2·38	2·45
50·50	1·15	1·04	2·66	2·34
			Mean 2·58	2·61

The weighed amount of pure AnalaR calcium carbonate was different in each bulb, being graded to the amount of acid liberated at the time the sample was to be removed from the thermostat. Illustrative data for the sample taken at 13·18 hours in the above experiment are as follows:

(1) For determination of [H_3O^+] produced. Wt. of $CaCO_3$ = 0·00083 g. ≡ 1·66 c.c. of 0·010N-HCl. 2-C.c. reaction sample required 0·984 c.c. Therefore, acid produced on hydrolysis ≡ 0·676 c.c. of 0·01N-HCl, whence x = 0·676 × 0·01 × 500/1000 = 0·00338 mole/l.

(2) For determination of [NO_3^-] formed. Wt. of $CaCO_3$ = 0·00079 g. Acidified with acetic acid. Wt. of nitron nitrate from 2-c.c. sample = 0·00275 g., whence [NO_3^-] = 0·00275 × 0·1654 × 500/62 = 0·00367 mole/l.

Ethyl nitrate.

(*a*) *Alkaline hydrolysis in* 60% EtOH *at* 60·2° *in* " *Fluon* " *vessels.*

Initial [$EtNO_3$] = 0·0306; [KOH] = 0·0904M. Reaction followed by titration with 0·0287N-H_2SO_4 and by gravimetric determination of NO_3^- as nitron nitrate.

Time (hours)	Vol. (c.c.) of H_2SO_4 for 4-c.c. sample	10^2x (mole l.$^{-1}$)		10^5k_2 (mole^{-1} l. sec.$^{-1}$)	
		OH^-	NO_3^-	OH^-	NO_3^-
0	12·589	—	—	—	—
8·13	12·313	0·198	0·197	2·58	2·58
17·00	12·114	0·341	0·374	2·17	2·37
32·00	11·740	0·609	0·640	2·21	2·34
49·50	11·321	0·910	0·935	2·32	2·42
70·00	11·006	1·14	1·20	2·20	2·36
93·50	10·680	1·37	1·38 (NO_2^- = 0·013)	2·13	2·16
118·2	10·339	1·61	1·65	2·16	2·25
				Mean 2·25	2·35

(*b*) *Solvolysis in* 90% EtOH *at* 59·3° *in* " *Monax* " *glass bulbs.*

Initial [$EtNO_3$] = 0·0323M.

Time (hours)	10^2x (mole l.$^{-1}$)		10^8k_1 (sec.$^{-1}$)	
	H_3O^+	NO_3^-	H_3O^+	NO_3^-
278·9	0·0947	—	2·98	—
998·5	0·277	0·353	2·50	3·22
1861	0·536	0·620	2·71	3·18
3087	1·16	1·02	(4·01)	3·41
			Mean 2·73	3·27

Olefin determination [method (iii) (p. 1204)]. Alkaline hydrolysis of ethyl nitrate in 90% EtOH at 59·3°. Initial $[EtNO_3]$ = 0·0343; [KOH] = 0·0975M. 10 C.c. of reaction mixture in thermostat at 59·3° for 71·58 hours: 15 c.c. of standard bromine solution in carbon tetrachloride required (1) initially 17·40, (2) after aspiration of ethylene 16·68, and (3) blank (solvent only) 17·52 c.c., whence ethylene formed ≡ 0·72 c.c. of 0·0090N-sodium thiosulphate. Analysis of the reaction mixture for nitrate and nitrite gave $[NO_3^-]$ = 0·0165, $[NO_2^-]$ = 0·0009, $[C_2H_4]$ = 0·00033 mole/l., whence NO_2^- = 5, C_2H_4 = 2% of total reaction.

iso*Propyl nitrate.*

(*a*) *Alkaline hydrolysis in* 90% *alcohol at* 60° *in " Polythene " vessels.*

Initial $[Pr^iNO_3]$ = 0·0343; [KOH] = 0·0983M. Titration with 0·0247N-H_2SO_4.

Time (hours)	Vol. (c.c.) of H_2SO_4 for 2-c.c. sample	10^2x (mole l.$^{-1}$) OH^-	NO_3^-	NO_2^-	NO_3^- $+NO_2^-$	10^6k_2 (mole^{-1} l. sec.$^{-1}$) Total OH^-	Total NO_3^- $+NO_2^-$	$E_{CO}2$ NO_2^-	S_N2 $+E2$
0	19·873	—	—	—	—	—	—	—	—
65	18·528	0·666	0·360	(0·056)	0·416	(9·72)	6·27	0·84	5·43
137	18·023	0·915	0·662	(0·102)	0·764	6·73	5·93	0·89	5·14
209·5	17·418	1·22	0·983	(0·152)	1·135	6·32	6·38	0·86	5·52
306·5	16·279	1·78	1·26	(0·194)	1·450	7·52	6·16	0·82	5·34
83 days	13·59	3·11	2·48	(0·387) *	2·732	—	—	—	—
∞	12·77	3·52	2·75	0·425	3·172	—	—	—	—
					Mean	(6·84)	6·18	0·85	5·36
							±0·14	±0·02	±0·12

* The values of $10^2[NO_2^-]$ in parentheses have been calculated from the experimental values of $10^2[NO_3^-]$ by using the ratio NO_2^-/NO_3^- determined at infinity, which is regarded as the most reliable. Actual determination of the value at 83 days gave $10^2[NO_2^-]$ = 0·350.

Olefin determinations for above reaction. The aspiration method (iii) was used.

(1) Initial $[Pr^iNO_3]$ = 0·0433; [KOH] = 0·0983M. After 72·97 hours at 60°, 10 c.c. of reaction mixture absorbed bromine ≡ 2·55 c.c. of 0·00903N-$Na_2S_2O_3$; blank (solvent only) required 0·76 c.c.; whence olefin ≡ 1·79 c.c. ≡ 0·81 × 10^{-3} mole/l.

(2) Initial $[Pr^iNO_3]$ = 0·0422; [KOH] = 0·102M. After 71·42 hours at 60°, 10 c.c. of reaction mixture absorbed bromine ≡ 2·37 c.c. of 0·000903N-$Na_2S_2O_3$; blank (solvent only) required 0·48 c.c.; whence olefin ≡ 1·89 c.c. ≡ 0·85 × 10^{-3} (mole/l.). Analysis of the same reaction samples for NO_3^- thus gave

Time (hours)	10^2x (mole/l.) NO_3^-	C_3H_6	100 $E2/(S_N2 + E2)$
(1) 72·97	0·495	0·081	16·3 Mean = 16·8%
(2) 71·42	0·490	0·085	17·4

which, combined with above values for $10^6k(E_{CO}2)$ and $10^6k(S_N2) + E2$ gives

$10^6k(E2)$ = 0·90 = 14·5% of total reaction
$10^6k(S_N2)$ = 4·46 = 71·8% ,, ,,
$10^6k(E_{CO}2)$ = 0·85 = 13·7% ,, ,,

(*b*) *Alkaline hydrolysis in* 60% *aqueous alcohol at* 60·2° *in " Fluon " vessels.*

Initial $[Pr^iNO_3]$ = 0·0347; [KOH] = 0·0916M.

[This experiment clearly illustrates the greatly improved agreement between determinations of OH^- and NO_3^- in " Fluon " vessels. Nitrite formation ($E_{CO}2$) is only ~1% and no olefin formation could be detected after 92 hours (~50% reaction).]

Time (hours)	10^2x (mole l.$^{-1}$) OH^-	NO_3^-	NO_2^-	10^5k_2 (mole^{-1} l. sec.$^{-1}$) OH^-	NO_3^-	10^6k_1 (sec.$^{-1}$) NO_3^-
40·7	1·05	1·07	—	2·86	2·93	2·46
50·2	1·22	1·26	—	2·82	2·95	2·40
65·0	1·46	1·50	—	2·80	2·91	2·33
88·7	1·82	1·87	0·018	2·87	3·00	2·33
117·3	2·18	2·19	—	2·99	3·01	2·34

tert.-*Butyl nitrate.*

(*a*) *Alkaline hydrolysis in* 60% EtOH *at* 0°.

Initial [Bu^tNO_3] = 0·0419; [KOH] = 0·0866M.

	10^2x (mole l.$^{-1}$)			
Time (mins.)	OH^- (found)	OH^- (corr.) *	NO_3^-	10^4k_1 (sec.$^{-1}$)
0	1·16	0	—	—
8·75	1·36	0·20	—	1·26
18·62	1·53	0·37	—	1·15
25·97	1·59	0·43	—	0·96
34·27	1·78	0·62	—	1·10
58·17	2·18	1·02	—	1·17
∞ (20 hrs.)	4·56	—	4·36	—
				Mean 1·13

(*b*) *Solvolysis in* 60% EtOH *at* 10°.

Initial [Bu^tNO_3] = 0·0330M.

	10^2x (mole l.$^{-1}$)			
Time (mins.)	H_3O^+ (found)	H_3O^+ (corr.)*	NO_3^-	10^4k_1 (sec.$^{-1}$)
0	1·041	0	1·01	—
4·0	1·22	0·179	—	(3·45)
9·63	1·58	0·539	—	4·71
15·01	1·80	0·759	—	4·55
19·98	2·02	0·979	—	4·73
24·57	2·28	1·14	—	4·78
29·51	2·33	1·29	2·23	4·80
				Mean 4·71

* 10^2x (corr.) ≡ true amount of reaction subsequent to zero reading.

(*c*) *Hydrolysis in* 90% EtOH *at* 20° *in solution initially alkaline and becoming acid.*

Initial [Bu^tNO_3] = 0·0486; [KOH] = 0·0109M.

	10^2x (mole l.$^{-1}$)			
Time (mins.)	H_3O^+ (found)	H_3O^+ (corr.)	NO_3^-	10^5k_1 (sec.$^{-1}$)
0	0·707	0	—	—
11·85	0·885	0·178	—	(6·15)
35·75	1·060	0·353	—	4·13
56·75	1·23	0·527	—	3·98
93·53	1·61	0·904	—	4·38
119·5	1·77	1·07	—	4·15
246·9	2·68	1·96	—	4·31
∞ (43 hrs.)	5·08	—	4·85	—
				Mean 4·19

Olefin determinations in above reactions. Owing to the higher b. p. of *iso*butene the aspiration method could not be used. Method (ii) (p. 1204) was used and it was found essential to cool the bottom half of the vessel to *ca.* −15° and then to admit sufficient acid to neutralise the alkali present immediately before admission of the bromine solution. Since all the samples of *tert.*-butyl nitrate used showed considerable acidity, and rapid hydrolysis occurs immediately the nitrate is added to the alkali solution, the percentage of olefin formed was calculated on the unchanged *tert.*-butyl nitrate present at zero time as determined by the initial acidity correction. In view of such necessary corrections the olefin values for this nitrate are rather less certain, but the general orders of magnitude are considered to be essentially correct.

THE UNIVERSITY LEEDS.

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