Hydrolytic Decomposition of Esters of Nitric Acid. Part V. The Effects of Structural Changes in Aralphyl Nitrates on the S_N and E_{CO} Reactions.*

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Solvolytic and alkaline hydrolytic decomposition of *o*-, *m*-, and *p*-nitrobenzyl, *p*-bromobenzyl, benzyl, *p*-methylbenzyl, *p*-methoxybenzyl, diphenylmethyl, and 1- and 2-phenylethyl nitrates have been studied kinetically in aqueous-ethanolic solvents at several temperatures by methods which make possible the separate evaluation of k_1 (solvolysis), k (S_N2), k ($E_{CO}2$), and, where applicable, k ($E2$). On the basis of these results an analysis has been made of the effects of structural and environmental changes on each separate reaction in terms of the Arrhenius parameters.

In the substitution reaction (by solvent molecules or hydroxide ion) these nitrates closely resemble the corresponding chlorides. In both 90% and 60% aqueous ethanol the first five nitrates follow the S_N2 mechanism, whilst a change to the unimolecular mechanism is observed with *p*-methoxybenzyl, diphenylmethyl, and 1-phenylethyl nitrates. *p*-Methylbenzyl nitrate is a borderline case since it follows the S_N2 mechanism in 90% alcohol but is predominantly S_N1 in the more ionising 60% alcohol.

The specifically bimolecular $E_{CO}2$ reaction is particularly susceptible to structural changes and is favoured (1) by conjugation of the 1-phenyl substituent with the forming carbonyl bond and (2) by strongly electron-attracting substituents in this benzene ring which greatly facilitate the separation of a proton from C_α by increasing the strength of the nitric ester as a pseudo-acid. Introduction of a second α-substituent (alkyl or phenyl), although it may increase the speed of the $E_{CO}2$ reaction, actually greatly reduces its relative proportion because of the concomitant very large increase in the velocity of unimolecular solvolysis, which thus becomes the main reaction.

A sensitive and accurate amperometric titration method for determination of styrene has been applied to the preliminary examination of the olefin-elimination reactions in 1- and 2-phenylethyl nitrates.

Examination of the effect of structural changes in the nitric ester itself on the relative velocities and importance of the nucleophilic substitution (S_N) and carbonyl-elimination (E_{CO}) reactions has so far been restricted to the alkaline hydrolyses of simple alkyl nitrates (Parts I and II, Baker and Easty, *J.*, 1952, 1193, 1208), in which carbonyl elimination never amounted to >10% of the total reaction. It is obviously desirable to examine nitrates in which this reaction path constitutes a larger proportion of the total reaction. In Part IV (*loc. cit.*) it was shown that hydrolytic fission of benzyl nitrate with hydroxide or ethoxide ions gives rise to a high proportion of nitrite and benzaldehyde formation. Nuclear substitution in this ester (in *m*- and *p*-positions) permits a study of the polar effects of such substituents on the relative velocities and importance of the S_N and E_{CO} reactions without complicating steric effects, whilst α-alkyl substitution introduces the third path, olefin elimination, for inclusion in the study. We have prepared a number of nitrates of the general type $X{\cdot}C_6H_4{\cdot}CHR{\cdot}NO_3$ and have determined their rates of solvolysis and of hydrolytic fission with hydroxide or ethoxide ions in various aqueous-ethanolic solvents at different temperatures, by methods which have permitted evaluation of the separate rate coefficients for solvolysis (k_1), for bimolecular substitution [k (S_N2)], and for bimolecular carbonyl elimination [k ($E_{CO}2$)], together with the corresponding values of the Arrhenius equation parameters. We repeatedly confirmed (see p. 629 and Part IV) that, throughout the whole reaction, $[H_3O^+]$ produced or $[OR^-]$ removed is identical with $[NO_3^-]$ produced when substitution is the sole reaction, and with $[NO_3^-] + [NO_2^-]$ when the carbonyl elimination

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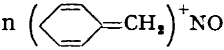
* Part IV, preceding paper.

reaction is also present, and that $[NO_2^-] \equiv [R{\cdot}CHO]$. Subsequently, therefore, reactions were followed by the more rapid acid–alkali titrimetric methods and the rapid and accurate colorimetric determination of nitrite.

The incidence of a fairly rapid solvolysis reaction often made separate evaluation of k (S_N2) and k ($E_{CO}2$) a tedious business: four different methods were used and are described in the experimental section (p. 628). The most accurate values are those (k_1) for solvolysis, for which the probable error is ±2% and about ±300 cal. in the values of the Arrhenius activation energies. The probable errors for k ($E_{CO}2$) are ±3%, but for k (S_N2) they are often quite large (see Table 4). It will be convenient to discuss the effects of structural variation in the nitrate on the solvolysis and the S_N2 and $E_{CO}2$ reactions in turn, on the basis of these separated rate constants. Only a preliminary investigation of olefin elimination ($E2$) in 1- and 2-phenylethyl nitrates is included.

(1) *Solvolysis*

The corrected values of k_1 (sec.$^{-1}$), each of which is obtained from at least ten separate evaluations, for solvolyses in aqueous-ethanolic solutions are given in Table 1.

The results are arranged in order of increasing electron-release by the group R, and comparison of values in either solvent at a specific temperature reveals that this is also the order of increasing velocity of solvolysis. Heterolysis of the $C{-}O{\cdot}NO_2$ bond thus seems to be the more important factor. This is confirmed by the 100-fold increase in velocity caused by the introduction of an α-phenyl substituent into methyl nitrate ($10^5k_1^{60\cdot2}$ in 60% ethanol = 0·0196; Baker and Easty, *loc. cit.*) which permits the facilitating, conjugative polarisation NO_3^-, whereas the introduction of a 2-phenyl substituent into ethyl nitrate ($10^5k_1^{60}$ in 60% ethanol = 0·01; *idem, ibid.*) reduces the velocity, such polarisation not now being structurally possible. In the halide series benzyl is on the borderline of S_N1–S_N2 mechanism, and in our results we find evidence that the aralphyl nitrates traverse the whole range from bimolecular to unimolecular solvolysis.

We consider first the effect of structural changes as the criterion of mechanism. The relative values (CH_2Ph = 1) of k_1 for the solvolysis of RNO_3 at 20°, are given below:

R =	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	p-$C_6H_4Br{\cdot}CH_2$ *	CH_2Ph
90% EtOH	0·089	0·12	0·52	1
60% EtOH	0·036	0·058	0·41	1

R =	p-$C_6H_4Me{\cdot}CH_2$	CHPhMe	p-$MeO{\cdot}C_6H_4{\cdot}CH_2$	$CHPh_2$
90% EtOH	5·91	97·4	12,820	36,950
60% EtOH	13·9	566	—	—

* Estimated from results at 60°.

In 90% aqueous ethanol, from p-nitrobenzyl to p-methylbenzyl nitrate, where decreasing electron-attraction (or increasing release) causes relatively small increases in velocity, the pattern is the familiar one for the S_N2 mechanism. With 1-phenylethyl, p-methoxybenzyl, and diphenylmethyl nitrates the very large velocity increases caused by the further increase in the electron-release of R clearly indicate that the solvolysis of these nitrates is proceeding by the unimolecular mechanism. In the more ionising solvent, 60% ethanol, it is evident that the mechanistic change over has now occurred at the p-methylbenzyl ester, and the differences in behaviour of this compound in 90% and 60% ethanol are quite marked.

These mechanistic conclusions are confirmed by the sensitivity of the solvolysis rates towards added hydroxide ion. The test cannot be applied to the nitrobenzyl nitrates because, in the presence of alkali, carbonyl elimination becomes practically the sole reaction (p. 625), but the specific rates (10^5k_1) for solvolysis alone and for the isolated substitution reaction in the presence of 0·04M-hydroxide ion are given in Table 2.

It is evident that alkali has no significant effect on the rate of hydrolysis of those nitrates for which it was concluded above that the S_N1 mechanism is operative. The different behaviour of the p-methylbenzyl compound in 60% and 90% ethanol is again evident: in the former the reaction is mainly of first order, whilst a second-order reaction is predominant in the less ionising solvent.

There is, of course, no clear-cut division between the two extreme mechanisms (Gleave, Hughes, and Ingold, *J.*, 1936, 236) which are differentiated by different degrees of co-operation of solvent molecules in the rate-determining stage. Both mechanisms involve an increase in charge in the transition state and hence the velocity of both should be increased in the more aqueous solvent. Experience suggests (cf. Baker and Easty, *J.*, 1952, 1211) that such increase is more pronounced for the S_N1 mechanism. Relative velocities in different aqueous ethanolic media are given in Table 3, those in 90% ethanol being taken as standard. Data for methyl nitrate (S_N2) and for *tert.*-butyl and diphenylmethyl chlorides (S_N1) are included as reference standards. Comparisons confirm that, of the nitrates given, only the diphenylmethyl and 1-phenylethyl esters are undergoing solvolysis by the S_N1 mechanism, whilst *p*-methylbenzyl nitrate is on the S_N2–S_N1 borderline.

TABLE 1. *Values of the first-order coefficient* k_1 (*sec.*$^{-1}$) *and Arrhenius parameters for the solvolysis of* RNO_3 *in* x% *aqueous ethanol at various temperatures.*

x	Temp.	10^5k_1	E, kcal./mole	log A
R = Ph·CH$_2$·CH$_2$				
60	75·0°	0·01	—	—
R = p-NO$_2$·C$_6$H$_4$·CH$_2$				
90	96·2	0·853	23·1	8·6
,,	75·0	$0{\cdot}122_5$		
,,	60·2	0·0281		
,,	45·0	$0{\cdot}0052_9$		
60	96·2	2·70	24·1	9·7
,,	75·0	0·361		
,,	60·2	0·0760		
,,	45·0	0·0136		
R = m-NO$_2$·C$_6$H$_4$·CH$_2$				
90	95·0	0·950	22·8	8·5
,,	75·0	0·161		
,,	60·2	0·0366		
60	95·0	3·63	23·7	9·3
,,	75·0	0·577		
,,	60·2	0·1267		
,,	45·0	0·0228		
R = p-BrC$_6$H$_4$·CH$_2$				
90	60·2	0·190	—	—
60	60·2	0·813	—	—
R = Ph·CH$_2$				
90	60·2	0·341	23·4	9·9
,,	45·0	0·0624		
,,	30·0	0·0101		
60	60·2	1·80	23·6	10·8
,,	45·0	0·334		
,,	30·0	0·0527		
R = p-CH$_3$·C$_6$H$_4$·CH$_2$				
90	75·0°	8·71	23·2	10·6
,,	60·2	2·00		
,,	45·0	0·367		
R = p-CH$_3$·C$_6$H$_4$·CH$_2$				
60	60·2	31·6	24·3	12·5
,,	45·0	5·53		
,,	19·85	0·196		
R = Ph·CHMe				
90	60·2	39·6	24·2	12·5
,,	20·0	0·262		
60	20·0	8·32	24·5	14·2
,,	0·0	0·378		
R = p-MeO·C$_6$H$_4$·CH$_2$				
90	20·0	34·5	—	—
R = Ph$_2$CH				
100	30·0	45·0	23·7	13·8
,,	20·0	11·8		
,,	10·0	2·80		
90	20·0	99·4	22·3	13·7
,,	10·0	26·6		
,,	0·0	6·06		

TABLE 2. *Values of specific rates* (10^5k_1 *sec.*$^{-1}$) *for the substitution reaction of* RNO_3 *in* x% *aqueous* EtOH *at* 20° (a) *without alkali and* (b) *with* 0·04M-*alkali.*

R	x = 60		x = 90	
	a	*b*	*a*	*b*
Ph$_2$CH	(11·8	13·2) *	99·4	100
p-MeO·C$_6$H$_4$·CH$_2$	—	—	34·5	34·2
PhCHMe	8·32	8·02	0·262	0·284
C$_6$H$_4$Me·CH$_2$	0·204	0·265	0·0159	0·118
Ph·CH$_2$	0·0147	0·060	0·00269	0·058
p-C$_6$H$_4$Br·CH$_2$	0·0060	0·088	0·0014	0·13

* In 100% EtOH.

In a plot of log k_1 (as ordinates) of substituted benzyl nitrates against Hammett's σ values ("Physical Organic Chemistry," McGraw-Hill, 1940, p. 190) for the nuclear substituents, the values for *m*- and *p*-nitro-, hydrogen, and *p*-bromo- fall on a straight line but *p*-methyl and, especially, *p*-methoxyl introduce a marked upward curvature. Hammett's use of ionisation constants derived from carboxylic acids as a measure of values automatically excludes polarisability effects and it is evident that the facilitating $+E$ effect of *p*-methyl and, particularly that of *p*-methoxyl, will play an important rôle in the solvolysis. Moreover, these effects introduce a change in mechanism which will almost certainly be accompanied by a change in the reaction constant; accordingly, the marked curvature of the Hammett plot confirms conclusions reached on other evidence.

TABLE 3. *Relative velocities of solvolysis of* RNO_3 *at* 20° *in* x% *aqueous* EtOH.

x	R = Ph_2CH	PhCHMe	*p*-$C_6H_4Me{\cdot}CH_2$	$PhCH_2$	*p*-$C_6H_4Br{\cdot}CH_2$
100	0·12	—	—	0·36 *	—
90	1·0	1·0	1·0	1·0	1·0
60	—	32	13	5·5	4·2
45	—	—	—	12·5 *	—

x	*R* = *m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	*p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	CH_3 †	Bu^tCl ‡	Ph_2CHCl ‡
100	—	—	—	0·054	0·11
90	1·0	1·0	1·0	1·0	1·0
60	2·6	2·2	2·7	73·5	—
45	—	—	—	400	—

* Baker and Neale, *loc. cit.* † Baker and Easty, *loc. cit.*

‡ From data collected by Winstein and Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 846; 1951, **73**, 2701.

The intelligible picture presented by the solvolysis rates is in marked contrast to the superficial confusion suggested by the Arrhenius activation energies, for which the continuous transition between two distinct mechanisms is largely responsible. Interpretation of the Arrhenius parameters has been discussed in detail by one of us elsewhere (Heggs, Thesis, University of Leeds, 1954) and only a few salient points can be mentioned here. Differences in the E_A values are small and not very much larger than the estimated experimental accuracy ($\pm0{\cdot}3$ kcal.). In the region of bimolecular solvolysis the polar character of the nuclear substituent will have opposite effects on the ease of breaking of the $C{-}O{\cdot}NO_2$ bond* and the electrostriction of, and bond formation by, the attacking solvent molecule. This dual polar requirement evidently means that such substitution has little overall effect on the value of E_A, the main differences being in the entropy term. The unimolecular solvolysis, however, derives no help from covalent interaction with the solvent molecule and hence if, in a graded series of nitrates with increasing electron-release towards C_α there is, at any point, a rather rapid transition from S_N2 to S_N1, a higher E_A value might well result. In agreement with our earlier deductions, such a definite increase in E_A is observed on passing from *p*-methylbenzyl to 1-phenylethyl nitrate in 90% ethanol and between benzyl and *p*-methylbenzyl nitrates in 60% ethanol. Once in the unimolecular region, further increase in electron supply at the reaction site will decrease the energy required for heterolysis, and the lower E_A values for diphenylmethyl nitrate are understandable. The entropies of activation fit into the same picture. For those nitrates which, as suggested by other evidence, are undergoing essentially a bimolecular solvolysis the values of log A (after allowance for the inclusion of a solvent concentration term) are of the same order of magnitude as those observed in other known bimolecular reactions (*e.g.*, the Menschutkin reaction) of the same charge type. Unimolecular solvolyses frequently have non-exponential terms of the order 10^{13} and it is again significant that such values are observed for those nitrates to which we have assigned the S_N1 mechanism. Benzyl nitrate in 60% and its *p*-methyl derivative in 90% ethanol show distinct transition tendencies. The effect of α-substituents in increasing the entropy of activation in the unimolecular mechanism was ascribed by A. G. Evans and Hamman (*Trans. Faraday Soc.*, 1951, **47**, 25) to a displacement of solvent molecules from the first solvation shell, thereby diminishing

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* *Note added*, 19.1.55—Evidence was given by Baker and Neale (*J.*, 1954, 3225; Part IV, *loc. cit.*) that with benzyl nitrate nucleophilic substitution occurs solely at C_α.

the solvation of the cation. The observed entropy changes (in 80% ethanol) of ~6 e.u. associated with α-methyl substitution (in passing from *p*-methylbenzyl to 1-phenylethyl chloride), and of ~11 e.u. for α-phenyl substitution (in diphenylmethyl chloride), were found to be roughly correlated with the number of water molecules which could be fitted into a volume equal to that of the substituent. For the corresponding nitrates the closely similar figures (in 90% ethanol) of 8 and 13·5 e.u. respectively (calculated from our A values) are found.

Comparison of available data shows that the bimolecular solvolysis rates of the aralphyl nitrates are of the same order of magnitude as those of the corresponding chlorides. In the S_N1 region, however, the nitrates generally have rather higher velocities than the chlorides, whilst *tert.*-butyl nitrate has an exceptionally high value, closely comparable to that of *tert.*-butyl bromide. Since there is only one configuration of the nitrate group which permits free rotation in *tert.*-butyl nitrate it is possible that some steric acceleration of the unimolecular solvolysis may occur in this case. The values of E_A for the nitrates are ~2—3 kcal./mole higher than for the corresponding chlorides, but the activation entropies of the nitrates are also considerably higher (about 2 in log A). It is probable that the higher heterolytic bond energy of $C-O\cdot NO_2$ compared with C–Cl is an important contributory factor in the higher E_A value, whilst the larger A factor may be correlated with the higher entropy of the nitrate (35·0) in comparison with that of the chloride (13·2 e.u.) ion ("Chemical and Thermodynamic Properties," Circ. 500, Nat. Bur. Stand., 1951, pp. 53, 21). Thus in neutral solvolysis the organic nitrates exhibit no anomalous behaviour.

(2) *Bimolecular substitution*, S_N2

There are several reasons why the separated rate constants for bimolecular substitution by "hydroxide" * ion in aqueous ethanol are the most difficult to determine and are of low accuracy. In alkaline solution either the $E_{CO}2$ reaction may greatly preponderate (*e.g.*, *p*-nitrobenzyl nitrate) or the bimolecular reaction may be accompanied by a dominant first-order solvolysis which necessitates the use of lengthy computational methods which cause all the errors to accumulate in the k (S_N2) value. This applies especially to *p*-methylbenzyl nitrate in 60% ethanol when the main reaction becomes a unimolecular solvolysis. In such cases rather more favourable conditions are obtained by increasing the relative concentration of the alkali used. The true second-order nature of the corrected k (S_N2) constant is illustrated by the following results in 60% ethanol. (All second-order constants in this communication are in mole^{-1} l. sec.$^{-1}$). The last column gives the value of the second-order constant for total substitution at zero time, the deviation from k (S_N2) being entirely accounted for by a variable contribution from accompanying solvolysis. The separate values of k (S_N2), corrected for solvent expansion, for the various nitrates investigated are collected in Table 4.

	$[RNO_3]$	$[OH^-]$	10^5k (S_N2)	10^5k_2 (exp.)
$Ph\cdot CH_2\cdot NO_3$ at 60°	0·035	0·040	75	120
,, ...	0·051	0·106	76	95
p-$C_6H_4Me\cdot CH_2NO_3$ at 45°	0·033	0·044	25·0	150
,, ...	0·054	0·098	24·0	85

The dual polar requirements of a bimolecular nucleophilic substitution of benzyl nitrate have already been noted. Replacement of a neutral solvent molecule by an anion as the nucleophilic reagent should increase the importance of those polar effects which facilitate electrostriction of the attacking reagent, which was of minor significance in neutral solvolysis. It is therefore not surprising to find that, although nuclear substitution in benzyl nitrate causes only small velocity changes, both an electron-releasing methyl group and electron-attracting bromine now increase k (S_N2), which is at a minimum in the unsubstituted parent. Introduction of a 2-phenyl group reduces the velocity of alkaline hydrolysis of ethyl nitrate [10^5k $(S_N2)^{59\cdot 2}$ in 90% EtOH = 4·13; Baker and Easty, *loc. cit.*] about 25-fold, *i.e.*, a much larger effect than in neutral solvolysis.

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* Solutions of sodium hydroxide in aqueous ethanol: the equilibrium $HO^- + EtOH \rightleftharpoons H_2O + OEt^-$ (Baker and Neale, *J.*, 1954, 3225) means that the actual nucleophilic reagent is indeterminate.

TABLE 4. *Values of k* (S_N2) *for the reactions of* OH^- *with* RNO_3 *in* x% *aqueous* EtOH *at various temperatures.*

Temp.	x	10^5k (S_N2)	Estimated error	Temp.	x	10^5k (S_N2)	Estimated error
		R = Ph·CH$_2$				R = p-C$_6$H$_4$Me·CH$_2$	
60·2°	90	97	± 10%	60·2°	90	194	± 8% E_A = 20·1 kcal./mole
45·0	,,	27·5		45·0	,,	38·3	
30·0	,,	4·6		30·0	,,	8·1	
20·0	,,	1·38		20·0	,,	2·52	
60·2	60	76	± 8% E_A = 19·6 kcal./mole	60·2	60	116	± 25%
45·0	,,	15·8		45·0	,,	25	
30·0	,,	3·7		30·0	,,	5·4	
20·0	,,	1·20		20·0	,,	1·7	
		R = p-C$_6$H$_4$Br·CH$_2$				R = Ph·CH$_2$·CH$_2$	
20·0	90	3·3	± 20%	60·2	90	0·16	(Preliminary figure)
20·0	60	2·2	± 5%				

Consistently with the requirements of a bimolecular reaction between a negative ion and a neutral molecule in which the charge becomes dispersed in the transition state, increase in the water content of the solvent now causes a small decrease in velocity. This is clearly established by the data in Table 4 and by the more complete range (uncorrected for solvent expansion) for benzyl nitrate given below :

Solvent, x% EtOH	x = 100	90	60	45
10^5k $(S_N2)^{60\cdot2}$	100 *	93	74	50 *

* Part IV, *loc. cit.*

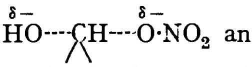
For those nitrates where neither unimolecular solvolysis nor bimolecular carbonyl elimination largely monopolises the reaction course, the relative importance of the bimolecular substitution and carbonyl elimination reactions is shown in Table 5. Electron-repelling substituents increase, and electron-attracting ones decrease, the proportion of the S_N2 reaction, but it will be seen (Section 3) that the ratio is essentially governed by the much greater sensitivity of the $E_{CO}2$ reaction to structural changes. The dispersal of the negative charge will be greater in the transition state of the $E_{CO}2$ reaction, $\overset{\delta-}{HO}\cdots H\cdots C\overset{\cdots}{=}O\cdots \overset{\delta-}{NO_2}$, than in that of the S_N2 reaction,  $\overset{\delta-}{HO}\cdots CH\cdots\overset{\delta-}{O}\cdot NO_2$ and, in harmony with this, it will be noticed that the proportion of substitution increases in the more aqueous solvent, in the same manner as that in which the ratio $E_2/(E_2 + S_N2)$ for olefin elimination in the action of hydroxide ion on, say, *iso*propyl bromide decreases as the water content of the alcohol solvent is increased (Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, pp. 457, 459).

TABLE 5. *Ratio* 100k (S_N2)/[k (S_N2) + k ($E_{CO}2$)] *for* RNO_3 *in* x% *aqueous* EtOH *at* 20°.

x	R = CH$_2$Ph	p-C$_6$H$_4$Me·CH$_2$	p-C$_6$H$_4$Br·CH$_2$	x	R = CH$_2$Ph	p-C$_6$H$_4$Me·CH$_2$	p-C$_6$H$_4$Br·CH$_2$
60	34	66	9·7	90	13	46	3·7

As indicated in Table 2, addition of sodium hydroxide causes no superimposition of any significant second-order reaction to the first-order solvolysis of the other nitrates studied, but certain complexities noticed in the case of diphenylmethyl nitrate are noteworthy, although we can offer no completely satisfactory explanation. Although the presence of 0·04N-sodium hydroxide in 90% aqueous ethanol caused no increase in the solvolytic constant k_1 of this nitrate, a similar concentration of potassium hydroxide produced quite a marked acceleration; the following values exclude any $E_{CO}2$ reaction :

	10^5k_1 (sec.$^{-1}$)			10^5k_1 (sec.$^{-1}$)	
Reagent	0°	10°	Reagent	0°	10°
90% EtOH	6·06	26·6	90% EtOH + 0·04N-KOH	6·75	28·4
90% EtOH + 0·04N-NaOH ...	5·93	26·5			

Diphenylmethyl chloride is solvolysed in 100% ethanol at a rate which is independent of alkali concentration (Ward, *J.*, 1927, 2294) but we found that 0·04N-sodium ethoxide increased the rate of solvolysis of the corresponding nitrate in the same solvent:

	10^5k_1 (sec.$^{-1}$)				10^5k_1 (sec.$^{-1}$)		
Reagent	10°	20°	30°	Reagent	10°	20°	30°
100% EtOH	2·80	11·8	45·0	100% EtOH + 0·04N-NaOEt	3·30	13·2	51·0

It was proved by a blank experiment ($10^5k_1^{20} = 11{\cdot}9$) that the higher figures in the presence of alkali are not due to adventitious absorption of water by the hygroscopic solvent during the necessary additional operations involved in the use of alkali. It is perhaps significant that in the cases where higher velocities were observed in the presence of alkali, and only in these, separation of the alkali-metal nitrate occurred during the reaction. The resultant reduction in the [NO_3^-] might decrease the speed of recombination of R^+ and NO_3^- ions, thus increasing the observed velocity of the rate-determining ionisation $RNO_3 \longrightarrow R^+ + NO_3^-$, but no discontinuity was detected in the reaction rate such as would be expected if this were the correct explanation.

In their examination of alkyl nitrates, Baker and Easty (*loc. cit.*) commented on the very slow rates of hydrolysis by the bimolecular mechanism, by comparison with the corresponding bromides. The more extended series of nitrates now studied makes possible comparison with various other esters of the same aralphyl groups, and it is evident that for both solvolysis and alkaline hydrolysis the rates of the nitrates closely resemble those of the corresponding chlorides. It was tentatively suggested that a possible reason for the slow rate in the case of the nitrates might be a repulsion of the nucleophilic reagent by the negative charge on the oxygen atoms of the nitric ester. The wider comparison now available makes this view untenable since, in all cases, the ratio k_2 (RNO_3)/k_2 (RCl) undergoes little change when the reagent is changed from a neutral alcohol molecule to a negatively charged bromide (Baker and Nathan, *J.*, 1936, 236) or hydroxide ion with which, if they were important, such repulsive forces should be very much greater. There is thus nothing abnormal about the slow rates of alkaline hydrolysis observed with some nitric esters.

(3) *The carbonyl-elimination reaction*, $E_{CO}2$.

Reasons were given in Part III (Baker and Neale, *J.*, 1954, 3225) for the belief that the E_{CO} reaction can occur only by a bimolecular mechanism $\overset{\curvearrowright}{\bar{X}}\ H\!-\!\overset{\curvearrowright}{CHR}\!-\!O\!-\!\overset{\curvearrowright}{N}O_2 \longrightarrow HX + R{\cdot}CH{:}O + NO_2^-$, and we always find that this reaction is of true second order. This is illustrated by the representative results in Table 6. Except for small variations, partly accounted for by salt effects, the second-order velocity coefficient is evidently independent of concentration. Unlike those of k (S_N2), the values of k ($E_{CO}2$) can be determined with considerable accuracy whatever rate law governs the total reaction. This is because of the extreme sensitivity of the colorimetric NO_2^- determinations, a concentration of 3×10^{-5}M being readily determined to an accuracy of ±2%.

TABLE 6. *Initial values of* 10^5k ($E_{CO}2$) (*mole*$^{-1}$ *l. sec.*$^{-1}$) *for the alkaline hydrolysis of* RNO_3 *in* x% *aqueous* EtOH.

	R = m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$; $x = 90$; $T = 0°$.				R = CH_2Ph $x = 60$; $T = 60°$.		R = p-$C_6H_4Me{\cdot}CH_2$; $x = 60$; $T = 45°$	
$10^4[RNO_3]$ ...	616	282	387	4·57	344·7	515	335	545
$10^4[NaOH]$ ...	358	361	886	1130	403	1060	440	979
10^5k ($E_{CO}2$) ...	370	361	352	330	189	177	14·7	14·6

The separated values of k ($E_{CO}2$) obtained for the various nitrates studied are given in Table 7. The much greater sensitivity of the $E_{CO}2$ reaction to structural changes is immediately apparent.

Baker and Easty (*loc. cit.*) gave theoretical reasons why electromeric effects might predominantly control bimolecular carbonyl elimination from organic nitrates. The limited information then available for alkyl substitution was in harmony with this view, although disturbances due to inductive effects were also evident. The wider range of results now available makes a re-assessment of the position possible. Values of k ($E_{\text{CO}}2$) (mole^{-1} l. sec.$^{-1}$) under comparable conditions of solvent and temperature are given in Table 8. Consideration of the transition stage $\overset{\delta-}{\mathrm{HO}}\text{---}\mathrm{H}\text{---}\mathrm{CR}\overset{\cdots}{=}\mathrm{O}\text{---}\overset{\delta-}{\mathrm{NO_2}}$ suggests two features which should be primarily concerned with the ease of the carbonyl elimination reaction. They are (1) the positive character of the eliminated hydrogen, *i.e.*, the strength of the nitric ester as a pseudo-acid, and (2) conjugation (or hyperconjugation) of the α-substituent group R with the forming carbonyl double bond.

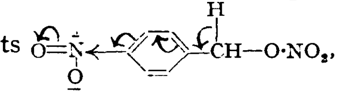
TABLE 7. *Values of k* ($E_{\text{CO}}2$) (*corr.*) *in the alkaline hydrolysis of nitric esters* $R{\cdot}NO_3$.

R	Temp.	Solvent	10^5k ($E_{\text{CO}}2$)
CH_2Ph	60·2°	90% EtOH	847
,,	45·0	,,	175
,,	30·0	,,	31·6
,,	20·0	,,	9·24
,,	60·2	60% EtOH	183
,,	45·0	,,	41·0
,,	30·0	,,	7·90
,,	20·0	,,	2·45
p-$C_6H_4Me{\cdot}CH_2$	60·2	90% EtOH	306
,,	45·0	,,	61·5
,,	30·0	,,	9·85
,,	20·0	,,	2·90
,,	60·2	60% EtOH	74·2
,,	45·0	,,	15·0
,,	30·0	,,	2·99
,,	20·0	,,	0·866
m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	20·0	90% EtOH	4,560
,,	10·0	,,	1,310
,,	0·0	,,	365
,,	−10·0	,,	87·4
,,	0·0	60% EtOH	91·9
p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	10·0°	90% EtOH	106,000
,,	0·0	,,	34,800
,,	−10·0	,,	10,100
,,	0·0	60% EtOH	7,400
o-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	0·0	90% EtOH	24,400
,,	0·0	60% EtOH	5,180
p-$C_6H_4Br{\cdot}CH_2$	20·0	90% EtOH	85·2
,,	,,	60% EtOH	20·4
p-$MeO{\cdot}C_6H_4{\cdot}CH_2$	20·0	90% EtOH	1·91
$CHPh_2$	30·0	100% EtOH	159
,,	20·0	,,	52·5
,,	10·0	,,	16·1
,,	20·0	90% EtOH	31·7
,,	10·0	,,	10·7
,,	0·0	,,	2·98
CHPhMe	20·0	90% EtOH	0·127
$Ph{\cdot}CH_2{\cdot}CH_2$	60·2	90% EtOH	0·33

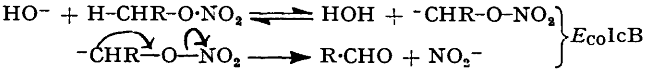
TABLE 8. *Values of* 10^5k ($E_{\text{CO}}2$) *for alkaline hydrolysis of* RNO_3 *in* 90% *aqueous* EtOH.

R =	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	o-$NO_2{\cdot}C_6H_4{\cdot}CH_2$ *	m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	p-$C_6H_4Br{\cdot}CH_2$	
10^5k ($E_{\text{CO}}2$)^{20}	340,000	240,000	4560	85·2	
10^5k ($E_{\text{CO}}2$)^{60}	—	—	—	—	
R =	$CHPh_2$	CH_2Ph	p-$C_6H_4Me{\cdot}CH_2$	p-$MeO{\cdot}C_6H_4{\cdot}CH_2$	
10^5k ($E_{\text{CO}}2$)^{20}	31·7	9·24	2·90	1·91	
10^5k ($E_{\text{CO}}2$)^{60}	—	847	306	—	
R =	CHPhMe	$Ph{\cdot}CH_2{\cdot}CH_2$	Et †	Pr^i †	CH_3 †
10^5k ($E_{\text{CO}}2$)^{20}	0·127	—	—	—	—
10^5k ($E_{\text{CO}}2$)^{60}	—	0·33	0·2	0·1	negligible

* Estimated from experiments at 0°. † Baker and Easty (*loc. cit.*).

Electron attraction by the group R by a $-I$, and especially by a $-T$, effect should greatly increase the acid strength of the nitric ester. α-Phenyl groups should thus facilitate the reaction on both counts, whereas alkyl groups, although weakly hyperconjugating with the forming double bond will, by their inductive effects, reduce the positive character of the α-hydrogen by direct action on the C_α to which it is attached. Comparison of benzyl with ethyl nitrate at once reveals that phenyl is approximately 4×10^3 times as efficient as methyl in promoting carbonyl elimination, whilst the very small effect of a β-phenyl substituent (in 2-phenylethyl nitrate) is clear evidence that it is the conjugative effect of phenyl which is important. Introduction of a second α-substituent brings in a statistical factor since there is now only one α-hydrogen for attack by the nucleophilic reagent but, allowing for this, a second α-phenyl (to give diphenylmethyl nitrate) further increases the velocity by only seven-fold, whilst an α-methyl group (to give 1-phenylethyl nitrate) actually reduces the velocity to about 1/40 of the value for benzyl nitrate. Once the essential " phenyl-forming double bond " conjugation is present it would seem that further polar substituents in the ring function mainly by virtue of their effect on the acid strength of the nitrate. Electron-attracting groups (Br, NO_2) greatly increase and electron-releasing groups (Me, MeO) decrease the rate of the $E_{CO}2$ reaction by altering the electron-density at C_α and hence the ease of fission of the C_α–H bond. The results obtained with such nuclear substitution provide a striking illustration of the importance of polarisability phenomena. *p*-Methoxybenzyl nitrate is simultaneously decomposed by two different reactions with different polar requirements. The strongly electron-demanding substitution reaction (S_N1) utilises the powerful $+E$ effect of the methoxyl group , causing a large increase in velocity, whereas the concomitant $E_{CO}2$ reaction makes no such demand and it is only slightly impeded by the relatively small mesomeric electron-release of this group. A similar argument is valid for the weaker hyperconjugative effect of a *p*-methyl substituent. The strong acceleration of the $E_{CO}2$ reaction by a *m*-nitro-group shows the importance of the inductive effect in increasing the acid strength of the nitrate, but the real counterpart in carbonyl elimination, of the *p*-methoxy-group in the substitution reaction, is the *p*-nitro-group which, by full operation of both its inductive ($-I$) and electromeric ($-E$) effects , increases the velocity of the $E_{CO}2$ reaction by a factor of 4×10^4 so that it now becomes the sole reaction. The importance of the electromeric effect of the *p*-nitro-group and, incidentally, the uniformity of the mechanism of the E_{CO} reaction throughout the whole range of nitrates $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO_3$ examined, is confirmed by the good straight-line Hammett plot of $\log k/k_0 = 3{\cdot}40\sigma$ which is obtained providing Hammett's higher value 1·27 (which takes into account its tautomeric effect) is used for the *p*-nitro-group.

The evident importance of the acidity of the nitric ester raises the question of the alternative mechanism



$$\left.\begin{array}{l} HO^- + H{-}CHR{-}O{\cdot}NO_2 \rightleftharpoons HOH + {}^-CHR{-}O{-}NO_2 \\ {}^-CHR{-}O{-}NO_2 \longrightarrow R{\cdot}CHO + NO_2^- \end{array}\right\} E_{CO}1cB$$

in which reaction occurs through the conjugate base. At the moment we have no definite evidence to exclude this possibility, but the isotopic test (Skell and Hauser, *J. Amer. Chem. Soc.*, 1945, **67**, 1661) excluded it in the corresponding olefin-elimination reaction. Our system is, however, one in which such an alternative mechanism is inherently probable (Ingold, *op. cit.*, p. 423, foonote).

A more detailed picture of the effects of substitution on the $E_{CO}2$ reaction results from examination of the Arrhenius parameters. Those available are given in Table 9.

TABLE 9. *Arrhenius parameters for the* $E_{CO}2$ *reaction of* RNO_3 *in* x% *aqueous* EtOH.

R	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	CH_2Ph		p-$C_3H_4Me{\cdot}CH_2$		$CHPh_2$	
x	90	90	90	60	90	60	100	90
E, kcal./mole ...	17·92	20·65	21·80	20·90	22·6	21·16	19·52	18·98
log *A*	13·9	14·1	12·28	10·99	12·28	10·74	11·31	10·7

With nuclear-substituted benzyl nitrates the velocity sequence from the rate constants is confirmed by the Arrhenius E_A values p-NO_2 < m-NO_2 < H < p-CH_3, but the introduction of the polar nitro-group both lowers E_A and increases the entropy term. Introduction of a second α-phenyl group to give diphenylmethyl nitrate does considerably lower the activation energy, and the relatively small increase in the velocity of the $E_{CO}2$ reaction is determined by the simultaneous decrease in log A. This may be due to the considerable rigidity likely in the transition state for the formation of benzophenone with both phenyl groups tending to conjugate with the forming double bond. The activation energy is lower in the more aqueous solvent, and the observed *decrease* in velocity is due to the decrease in the entropy term. The most important feature in this reaction is the destruction of charge, and consequent change in solvation, of the attacking hydroxide ion in the transition state, and the direction and magnitude of both energy and entropy changes are in harmony with the values obtained by Latimer and Slanksky (*J. Amer. Chem. Soc.*, 1940, **62**, 2019) for the heats and entropies of solution of potassium bromide and chloride in aqueous methanol mixtures. As already indicated (p. 621) the greater charge distribution which occurs in the transition state for the $E_{CO}2$ reaction compared with that in the S_N2 reaction causes a greater relative decrease in velocity with increase in the ionising power of the solvent. This is directly confirmed by the following ratios of the velocities of the two reactions for various nitrates, $X{\cdot}C_6H_4{\cdot}CH_2NO_3$, in 90% and 60% ethanol at 20° :

X =	*p*-CH_3	H	*p*-Br	*m*-NO_2 *	*o*-NO_2 *	*p*-NO_2 *
k ($E_{CO}2$), 90%/*k* ($E_{CO}2$), 60%	3·4	3·8	4·2	4·5	5·2	5·3
k (S_N2), 90%/*k* (S_N2), 60%	1·5	1·1	1·5	—	—	—

* Estimated from results at 0°.

Increasing electron-attraction in the ring causes higher positive polarity of the α-hydrogen atoms, which will result in greater destruction of charge on the attacking hydroxide ion in the transition state, and this trend is reflected in the more pronounced alteration in rate on passing from 60% to 90% ethanol noted for the nitrates to the right of the above table.

The presence of contemporaneous reactions of different kinetic order means that the percentage of $E_{CO}2$ reaction varies with the concentration of added base and with the solvent and hence bears no *simple* relation to structure. In a medium of low ionising power, such as 90% ethanol, not favourable to solvolytic reaction, the overall picture is given in Table 10. Thus a necessary (but not sufficient) condition for the $E_{CC}2$ reaction to constitute a large proportion of the total reaction is that the nitrate should be prone to reaction by the bimolecular mechanism. With nitrates which undergo solvolysis by the unimolecular mechanism the speed of this reaction is such that the $E_{CO}2$ reaction only constitutes a few per cent. of the total reaction. The value of *k* ($E_{CO}2$) for diphenylmethyl nitrate is actually 3—4 times that for benzyl nitrate, but against this the value of k_1 for the solvolysis (substitution) reaction is 4×10^4 times as great, thus causing a reduction in the proportion of carbonyl elimination from 87% to 1%.

TABLE 10. *Percentage of* $E_{CO}2$ *reaction in the weakly alkaline hydrolysis of* RNO_3 *in* 90% *aqueous* EtOH *at* 20°.

R	$E_{CO}2$ (%)	Remarks
p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	>96	From $[\overline{\mathrm{NO}}_2]$ at infinity : is probably the sole reaction
m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	>96	
o-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	100	
p-$C_6H_4Br{\cdot}CH_2$	96	100*k* ($E_{CO}2$)/[*k* (S_N2) + *k* ($E_{CO}2$)]
CH_2Ph	87	
p-$CH_3{\cdot}C_6H_4{\cdot}CH_2$	54	
p-$MeO{\cdot}C_6H_4{\cdot}CH_2$	0·2	Predominant solvolysis : 100*k* ($E_{CO}2$)/total reaction
CHPhMe	3·0	
$CHPh_2$	1·0	
$Ph{\cdot}CH_2{\cdot}CH_2$	~5	At 60°
Et	2·0	At 30° (Baker and Easty, *loc. cit.*)

Baker and Neale (Part III, *loc. cit.*) showed that the $E_{CO}2$ reaction with different basic reagents follows the Brönsted law, and hence replacement of an attacking hydroxide ion by the very much weaker base, a water or alcohol molecule, will result in an enormous fall in the reacton rate. Only with a highly reactive compound like *p*-nitrobenzyl nitrate might such solvolytic E_{CO} reaction possibly be detected. The nitrate is so susceptible to attack by alkali, even from glass, that the test had to be conducted in Fluon vessels (Part I). In the solvolysis of a 0·033M-solution in 90% ethanol at 75° only very small amounts of nitrite were detected, but their irregularity suggested no relation to time of reaction, and they most probably arose from slight reduction, by the alcoholic solvent, of the liberated nitric acid. After 36% reaction (96 hr.) the final NO_2^- was only 34×10^{-6}M, which, if significant, would correspond to only 0·3% elimination and *k* ($E_{CO}2$) =

3×10^{-9} mole^{-1} l. sec.$^{-1}$. An order-of-magnitude calculation based on the relative values of the catalytic coefficients $k_{OH}/k_{H_2O} = 5 \times 10^{10}$ (Bell, "Acid-Base Catalysis," Oxford Univ. Press, 1941, p. 92) suggests that the pseudo-first-order coefficient for carbonyl elimination by water molecules in 90% ethanol at 75° is $\sim 10^{-13}$ sec.$^{-1}$, a rate much too small to detect.

In the alkaline hydrolysis of *m*- and *p*-nitrobenzyl nitrates a marked downward drift was observed in the value of the second-order rate constant as the reaction proceeded. This drift was the more pronounced the lower the initial concentration of alkali. Examination, using the *meta*-isomer, showed that (1) in the presence of a large initial concentration of *m*-nitrobenzaldehyde the velocity coefficient was much smaller but remained constant throughout the run, and (2) that with a large excess (200-fold) of alkali (0·1M) a strictly first-order rate law was observed, showing that retardation by the aldehyde formed was negligible under these conditions. All three nitrobenzaldehydes are soluble in alkali with slow decomposition but are reprecipitated by immediate acidification of the solution, and it is evident that the decreasing second-order coefficient arises simply from the reduction in the concentration of the attacking alkali by the aldehyde produced acting as a neutralising acid. Extrapolation of the velocity coefficient to zero time was therefore necessary.

(4) *Olefin elimination* (E)

Only a few preliminary results have been obtained for the olefin-elimination reaction with 1- and 2-phenylethyl nitrate. The use of an extremely sensitive amperometric method for the determination of styrene (see p. 627) has permitted a reliable estimate of the very small amounts of this olefin formed in the solvolysis of these nitrates. For unimolecular elimination in the solvolysis of 1-phenylethyl nitrate in *x*% ethanol the percentages of styrene formed are

x =	90	60	*x* =	90	60
At 60°	1·19	—	At 20°	0·59	0·2

Hughes *et al.* (*J.*, 1940, 908) found ~0·5% of styrene produced in the solvolysis of the corresponding bromide in 100% ethanol at 55°. The closely similar proportion of olefin in both esters is expected, since it is determined in the subsequent fast reaction of the same carbonium ion in both cases. The effects of temperature and solvent composition are closely similar to those observed with the halides and are doubtless similarly accounted for (Ingold, *op. cit.*, pp. 459, 463).

The limited results obtained for bimolecular olefin elimination with both 1- and 2-phenylethyl nitrates are given, together with those for corresponding bromides for comparison, in Table 11. The facilitating effect of phenyl substitution, especially in the β-position, is evident. With 1-phenylethyl nitrate in 90% ethanol at 20° there is approximately 4% of carbonyl and 1% of olefin formation, but in the alkaline hydrolysis of 2-phenylethyl nitrate in the same solvent, at 60°, approximately 94% of the total reaction is olefin elimination, 4% carbonyl elimination, and only 2% substitution, the corrected values of the rate coefficients being 10^5k $(E_2) = 8{\cdot}1$, 10^5k $(E_{CO}2) = 0{\cdot}345$, and 10^5k $(S_N2) = 0{\cdot}17$; all in mole^{-1} l. sec.$^{-1}$.

TABLE 11. *Values of* 10^5k (E_2) *per branch for* RX.

X =	NO_3 [a]	Br	X =	NO_3 [a]	Br
CHPhMe at 20°	0·016	0·79 [c]	Et at 60°	0·08 [b]	1·6 [d]
$Ph{\cdot}CH_2{\cdot}CH_2$ at 60°	8·1	561 [d]	Pr^i at 60°	0·05 [b]	7·6 [d]

[a] In 90% EtOH. [b] Baker and Easty, *loc. cit.* [c] In 100% EtOH at 25°. [d] In 100% EtOH at 55°.

EXPERIMENTAL

Preparation of Materials.—We were unaware of the homogeneous method for the preparation of nitrates from the halides and silver nitrate (Ferris *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 4078) until quite late in this investigation and hence most of our nitrates were prepared by the heterogeneous reaction in ether. Benzyl nitrate, b. p. 78°/3 mm., n_{D}^{20} 1·5204, was prepared as described in Part III (*loc. cit.*) (Found: C, 54·8; H, 4·4. Calc. for $C_7H_7O_3N$: C, 54·9; H, 4·6%). Hydrolysis showed 100% purity by both acid and nitrate-ion determinations.

p-*Methylbenzyl nitrate.* The bromide, m. p. 35·8°, in ether was treated at 0° with powdered silver nitrate, then kept at room temperature for 12 hr., and finally refluxed at 70° for 6 hr. Purification by fractionation and partial freezing gave a sample, b. p. 78°/0·6 mm., n_{D}^{20} 1·5178 (Found: C, 57·0, 57·4, 58·2; H, 4·75, 4·9, 5·3; N, 8·05, 7·9. Calc. for $C_8H_9O_3N$: C, 57·5; H, 5·4; N, 8·4%). The mean of six complete solvolyses under different reaction conditions showed 99·31% purity, and whenever infinity values were not available this factor was used to correct the initial weight of ester used. The trace of impurity was shown to be without effect on the kinetics.

Diphenylmethyl nitrate. An ethereal solution of the chloride, b. p. 115—116°/0·4—0·5 mm., was shaken in the dark at room temperature with finely powdered silver nitrate and a little calcium carbonate, until freedom from unreacted chloride was established. The pale yellow liquid obtained by evaporation of the filtered ethereal solution, solidified at −70°. The *nitrate* crystallised from ligroin (b. p. 40—60°) in colourless needles, m. p. 36·7—37·2° (Found: C, 68·2; H, 4·7; N, 5·9. $C_{13}H_{11}O_3N$ requires C, 68·15; H, 4·8; N, 6·1%). Complete solvolysis showed 100% purity (cf. Baker and Heggs, *Chem. and Ind.*, **1954**, **464**).

p-*Methoxybenzyl nitrate.* Similarly obtained from the chloride (prepared from the alcohol by Swain and Langsdorf's method, *J. Amer. Chem. Soc.*, **1951**, **73**, 2813) was an orange oil which decomposed when molecular distillation was attempted but was obtained reasonably pure by crystallisation from ether at −70°. It was used immediately for kinetic experiments, the concentration being determined from infinity values.

o-*Nitrobenzyl nitrate*, by refluxing the chloride with finely powdered silver nitrate in ether for 7 days, was obtained as a red oil. Extraction of the oil with ligroin gave a solution which deposited white needles after being kept at −70°. Two further crystallisations from the same solvent gave a 10% yield of the nitrate, m. p. 28° (Found: C, 42·6; H, 3·3; N, 14·1. $C_7H_6O_5N_2$ requires C, 42·4; H, 3·0; N, 14·1%).

m-*Nitrobenzyl nitrate*, pale yellow crystals, m. p. 42·5—43·0° (Found: C, 42·6; H, 3·3; N, 13·9%), and p-*nitrobenzyl nitrate*, m. p. 68·2° (Found: C, 42·5; H, 2·9; N, 13·9%), were readily prepared in good yields by a similar method. p-*Bromobenzyl nitrate* was similarly obtained from the bromide as a colourless oil, the ligroin (b. p. 40—60°) solution of which deposited crystals at −70°. Recrystallisation under the same conditions gave the pure nitrate, m. p. 17°, to a colourless oil, n_{D}^{20} 1·5639 (Found: C, 36·45; H, 2·6; N, 5·95; Br, 34·7. $C_7H_6O_3NBr$ requires C, 36·2; H, 2·6; N, 6·0; Br, 34·45%).

1-*Phenylethyl nitrate.* The (±)-bromide, b. p. 38°/0·2 mm., n_{D}^{20} 1·5622 (20 g.), dissolved in dry, redistilled acetonitrile (50 c.c.), was added slowly to a solution of silver nitrate (30 g.) in acetonitrile (50 c.c.) at 0°, and the mixture kept at room temperature for 12 hr., the solvent was then removed *in vacuo* from the filtered solution. The residue separated into two layers and the upper layer was fractionated to constant refractive index to yield the *nitrate*, b. p. 49°/0·2 mm., n_{D}^{20} 1·5092 (Found: C, 57·6; H, 5·4; N, 8·4. $C_8H_9O_3N$ requires C, 57·5; H, 5·4; N, 8·4%). By a similar method the isomeric bromide, b. p. 38°/0·2 mm., n_{D}^{20} 1·5580, was converted into 2-*phenylethyl* (*phenethyl*) *nitrate*, b. p. 65°/0·5 mm., n_{D}^{20} 1·5162 (Found: C, 57·9; H, 5·3; N, 8·4%). Neither of these nitrates could be induced to crystallise at temperatures down to −70°.

Aqueous-alcoholic solvents were prepared from 100% ethanol, dried as described in Part III (*loc. cit.*); " x vol. % ethanol " has the same meaning as in previous parts of this series.

Kinetic Techniques and Analytical Processes.—Kinetic techniques and analytical processes were essentially those described in Part III. In gravimetric determinations of benzaldehyde as its 2 : 4-dinitrophenylhydrazone, nitrous acid interferes. Nitrogen evolved when removal with sulphamic acid prior to precipitation is used causes difficulties by adhering tenaciously to the precipitate, and the best method was found to be the use of a very large excess (200 ml. per mmole of aldehyde) of the reagent (0·125 g. of 2 : 4-dinitrophenylhydrazine in 2·5 ml. of concentrated sulphuric acid diluted to 50 ml. with water). By this technique 99·5% recovery of benzaldehyde was effected even in presence of large amounts of nitrite.

Determination of Styrene.—The production of alkyl aryl ketones in our reactions means that determination of olefin by addition of excess of bromine and back titration is likely to be inaccurate because of side reactions. We have therefore used a direct bromine-titration method, using an electrometric method to find the equivalence point (Kolthoff and Bovey, *Ind. Eng. Chem. Anal.*, **1947**, **19**, 498). We found Kolthoff's original procedure quite satisfactory and, in fact, addition of mercuric chloride actually decreased the rate of attainment of equilibrium in the cell after each addition of the bromate–bromide solution.

Methanol for the titrating medium was treated with bromine for 12 hr., excess of bromine was destroyed by zinc dust, and the decanted solution was distilled through a Dufton column, the last 15% being rejected. The olefin-containing sample (2 ml.) was added to 30 ml. of the titrating medium (methyl alcohol, 750 ml.; water, 250 ml.; conc. HCl, 100 ml.; "AnalaR" potassium bromide, 10 g.), and the mixture kept at 0° during titration. The cathode consisted of a 3-cm. piece of 0·5-mm. diameter platinum wire bent into a circle and rotating at 1000 rev./min. The anode was a square piece of platinum with surface area of ~0·5 cm.². A polarising voltage of 0·1 v was applied to these by means of a U2 dry cell in series with a high resistance and connected to a radio-potentiometer. The current between the electrodes was measured with a micro-ammeter fitted with suitable shunts, maximum sensitivity being 100 divisions per micro-amp. The solution was titrated with either 0·00017 or 0·0017M-potassium bromate which was 0·1M with respect to potassium bromide. As the end-point was approached 30 sec. were allowed for the attainment of equilibrium after each small addition of the bromate–bromide solution. Blanks were always carried out on the titrating medium before the addition of the sample. The possible disturbing effects of various materials which might be present were tested, and the reliability of the method was established by the following results.

Amperometric determination of styrene.

Added material	Styrene, mg.: taken	Styrene, mg.: found	Error, %	Added material	Styrene, mg.: taken	Styrene, mg.: found	Error, %
Nil	0·196	0·199	+1·4	2 Ml. 0·03M-KNO_3	0·4950	0·4941	−0·2
,, ...	0·196	0·203	+3·8	5 Mg. Ph·COMe	,,	0·4967	+0·3
,, ...	0·4950	0·4957	+0·1	16 Mg. Ph·CHMe·NO_3 * +2 ml. 0·025M-KNO_2...	,,	0·5052	+2·0
,, ...	0·4950	0·4957	+0·1				
2 Ml. 0·025M-KNO_2 ...	,,	0·4963	+0·3	5 Mg. Ph·COMe .... +2 ml. 0·030M-KNO_3...	,,	0·4977	+0·5
1 Ml. 0·025M-KNO_2 ...	,,	0·4989	+0·8				

* Ph·CHMe·NO_3 was slightly impure and may have contained a trace of unsaturated material.

Calculation of Rate Constants.—Solvolysis constants k_1 were calculated by the usual first-order rate equation, the initial concentration being determined either by direct weighing or from the infinity values, and were checked periodically by Guggenheim's method (*Phil. Mag.* 1926, 2, 538). The two procedures gave values agreeing within the experimental error. To illustrate the accuracy and the agreement between $[H_3O^+]$ and $[NO_3^-]$ produced, alternate determinations up to 95% reaction in the solvolysis of 0·02872M-benzyl nitrate in 60% EtOH at 45° are recorded below. In alkaline hydrolyses four methods were used to extract the separate values of k (S_N2) and k ($E_{CO}2$) from the total reaction, followed by determination of loss of alkalinity or production of nitrate, and nitrite.

Time (hr.)	14·25	21·5	38·1	51·5	69·25	93·5	185·5	194·1	213·6	254·5
$10^2[H_3O^+]$	4·51	6·52	10·42	13·04	16·14	19·32	25·56	25·81	26·43	27·24
$10^2[NO_3^-]$	4·81	6·61	10·55	13·21	16·42	19·70	25·86	26·55	26·80	27·41
10^6k_1, sec.$^{-1}$	3·32	3·32	3·28	3·26	3·31	3·31	3·30	3·27	3·29	3·23

Mean (of 20 determinations) $10^6k_1 = 3{\cdot}31$ sec.$^{-1}$; by Guggenheim's method 3·34 sec.$^{-1}$.

(1) Hughes, Ingold, and Shapiro's method (*J.*, 1936, 51) was used when the reaction was predominantly of second order. The total second-order rate constant k_2 was determined from $k_2 = {}^ik_2 - k_1/(b - x) + t \, . \, \mathrm{d}\,{}^ik_2/\mathrm{d}t$, where ${}^ik_2$ is the experimental integrated second-order rate constant and b is the initial concentration of base. The last term was usually evaluated graphically. The proportion of the reaction x_1 proceeding by the first-order path was then determined from the relationship

$$x_1 = (k_1/k_2)\ \ln\{(k_1/k_2) + b\ [(k_1/k_2) + b - x]\}$$

and hence the total amount of bimolecular reaction was found by difference. The value of the constant for total bimolecular reaction was then split into k (S_N2) and k ($E_{CO}2$) according to the proportion of nitrite produced.

(2) A much more rapid and simplified treatment was to obtain k ($E_{CO}2$) by direct multiplication of ${}^ik_2$ by the carbonyl elimination fraction of the *total* reaction, *i.e.*, $k\ (E_{CO}2) = {}^ik_2[NO_2^-]/x$. The value ${}^ik_2 - k\ (E_{CO}2) = k_2'$ then gives the total second-order constant for substitution

(including solvolysis), whence k (S_N2) = $k_2' - (k_1/\text{mean}[OH^-])$. It can be shown that this simplified method is valid when $(b - x)$ changes only slightly, and hence more accurate values values result when rather higher initial concentrations of alkali are used. When solvolysis is important the values of k ($E_{CO}2$) tended to drift downward slightly towards the end of the run and were always extrapolated to zero time. In practice, it was repeatedly found that this method gave the same values for k ($E_{CO}2$) and k (S_N2) as those obtained by the more rigorous but much more laborious method (1) and hence the simplified method was generally employed.

The following typical results for the hydrolysis of 0·05148M-benzyl nitrate with 0·1056M-potassium hydroxide in 60% EtOH at 60·2° show the equivalence of $[H_3O^+]$ and $[NO_3^-] + [NO_2^-]$ and the values of k (S_N2) and k ($E_{CO}2$) obtained by methods (1) and (2).

Time (min.)	13	21	34	38	42	46	50
$10^3[NO_3^-]$	2·75	5·61	7·94	8·14	8·78	9·49	9·90
$10^3[NO_2^-]$	7·28	10·45	14·37	15·30	16·35	17·16	17·81
$10^3([NO_3^-] + [NO_2^-])$	10·03	16·06	22·31	23·44	25·13	26·65	27·71
$10^3[H_3O^+]$	10·88	15·40	21·80	23·10	24·62	26·69	27·36
10^3k ($E_{CO}2$) (1)	1·75	1·78	1·77	1·76	1·77	1·77	1·73
10^3k ($E_{CO}2$) (2)	1·75	1·78	1·79	1·77	1·78	1·78	1·75
10^3k (S_N2) (1)	0·79	0·72	0·78	0·74	0·74	0·78	0·78
10^3k (S_N2) (2)	0·79	0·72	0·76	0·73	0·73	0·77	0·76

Time (min.)	55	60	66	73	90	113	∞
$10^3[NO_3^-]$	—	10·85	11·18	11·82	13·12	14·57	19·08
$10^3[NO_2^-]$	18·89	19·90	20·80	22·00	23·66	26·00	32·70
$10^3([NO_3^-] + [NO_2^-])$	—	30·75	31·98	33·82	36·78	40·57	51·78
$10^3[H_3O^+]$	28·74	30·28	31·84	33·40	36·40	39·83	51·79
10^3k ($E_{CO}2$) (1)	1·74	1·76	1·75	1·76	1·70	1·73	—
10^3k ($E_{CO}2$) (2)	1·76	1·78	1·78	1·79	1·73	1·76	—
10^3k (S_N2) (1)	0·75	0·76	0·77	0·75	0·75	0·73	—
10^3k (S_N2) (2)	0·73	0·74	0·74	0·72	0·72	0·74	—

Whence the mean values, after correction for solvent expansion, are 10^3k ($E_{CO}2$) = 1·83; 10^3k (S_N2) = 0·76 l. mole⁻¹ sec.⁻¹.

(3) When the only assumption made is that the carbonyl elimination reaction is always bimolecular, we have $d[NO_2^-]/dt = k\ (E_{CO}2)(a - x)(b - x)$, whence $k\ (E_{CO}2) = [NO_2^-]_0^t / \int_0^t (a - x)(b - x)\ .\ dt$. The numerator was obtained directly from nitrite determinations and the denominator was evaluated graphically. Again a tedious method, it was used only to check the validity of values obtained by other methods.

(4) When the reaction was mainly of first order a method similar to (2) was employed; although strictly valid only when there is $\ngtr$1% bimolecular reaction, it was found to give identical values with those obtained by rigorous methods even when there was 10% of carbonyl elimination. If ${}^ik_1$ is the experimental, integrated, first-order constant, then the value of k ($E_{CO}2$) was obtained by multiplying it by the carbonyl-elimination fraction of the total reaction and dividing by the mean $[OH^-]$. Again, the value was extrapolated to zero time.

Time (min.)	0	35·9	79·3	125·5	192·7	243·8
$[OEt^-]$	6·638	6·200	5·664	5·182	4·542	4·180
10^5k_1	—	(3·70)	3·92	3·90	3·95	3·84
NO_2^-, %	—	16·8	15·78	15·85	14·53	14·34
10^4k ($E_{CO}2$) (3)	—	1·54	1·59	1·66	1·63	1·63
10^4k ($E_{CO}2$) (4)	—	1·54	1·59	1·66	1·63	1·61

Time (min.)	303·5	363·5	423·0	487·5	580·7	1458
$[OEt^-]$	3·780	3·384	3·082	2·800	2·440	1·125
10^5k_1	3·80	3·85	3·82	3·80	3·80	3·77
NO_2^-, %	14·18	13·30	12·75	12·68	12·03	10·09
10^4k ($E_{CO}2$) (3)	1·66	1·63	1·58	1·61	1·59	—
10^4k ($E_{CO}2$) (4)	1·64	1·62	1·59	1·62	1·60	1·55

Whence 10^5k ($E_{CO}2$) = 16·1 mole⁻¹ l. sec.⁻¹.

The following results for the hydrolysis of 0·0380M-diphenylmethyl nitrate with 0·04372M-sodium ethoxide in 100% EtOH at 10° illustrate the application of methods (3) and (4) when the main substitution reaction is of first order. The $[OEt^-]$ is expressed in ml. of 0·01009N-sulphuric acid per 1·597-ml. sample.

Treatment of a more difficult case, when solvolysis accounts for only about 60% of the total reaction, is illustrated by the following results for the alkaline hydrolysis of 0·0540M-*p*-methylbenzyl nitrate with 0·09793M-potassium hydroxide in 60% aqueous EtOH at 45°.

Time (min.)	$10^3[H_3O^+]$, mole l.$^{-1}$	$10^5 . {}^ik_1$, sec.$^{-1}$	$10^4 . {}^ik_2$, mole^{-1} l. sec.$^{-1}$	NO_2^-, %	10^4k ($E_{CO}2$) (4)	(2)	(3)	10^5k_1, sec.$^{-1}$	10^4k (S_N2)	10^4k (S_N2)
30	8·04	9·27	10·10	14·51	1·45	1·47	1·45	9·20	2·72	2·60
55	13·11	8·75	9·82	14·78	1·44	1·45	1·46	8·62	2·29	2·13
80	18·02	8·82	10·20	14·16	1·43	1·44	1·43	8·64	2·60	2·57
105	22·01	8·67	10·36	13·85	1·41	1·43	1·42	8·43	2·49	2·27
140	26·70	8·52	10·58	13·68	1·40	1·45	1·42	8·20	2·45	2·20
170	30·29	8·51	10·89	13·58	1·42	1·48	1·44	8·12	2·51	2·24
200	33·46	8·52	11·21	13·03	1·39	1·46	1·41	8·07	2·65	2·35
240	36·55	8·52	11·42	12·88	1·37	1·47	1·40	7·95	2·68	2·46
280	39·33	8·33	11·78	12·41	1·35	1·46	1·40	7·70	2·45	2·30
320	41·49	8·24	12·08	12·48	1·36	1·51	1·39	7·51	2·24	2·23
400	44·71	8·18	12·40	11·98	1·31	1·47	1·36	7·19	(1·93)	2·14
440	46·75	8·18	13·65	11·79	1·33	(1·61)	1·37	7·7	(1·97)	2·30

The expected drifts in ${}^ik_1$ and ${}^ik_2$ due to the superimposition of first- and second-order reactions are obvious. The values of k ($E_{CO}2$) in the three columns have been calculated by the methods shown at the head. Substitution constants in the last column have been calculated by multiplying ${}^ik_1$ by the fraction of substitution reaction and subtraction of the solvolysis constant to give a value accounted for by second-order substitution, and division of this by the mean $[OH^-]$ to give k (S_N2). The values of k (S_N2) in col. 10 were evaluated from the equation $k_1 = {}^ik_1 + t \,.\, d{}^ik_1/dt - [k\ (S_N2) + k\ (E_{CO}2)]\ [OH^-]$, where k_1 is the instantaneous first-order rate constant, the values of which are listed in col. 9. The final corrected values are 10^5k ($E_{CO}2$) = 14·9 and 10^5k (S_N2) = 24 mole^{-1} l. sec.$^{-1}$.

The hydrolysis of 0·043M-1-phenylethyl nitrate with 0·093M-sodium hydroxide in 90% aqueous EtOH at 20° illustrates a run in which both carbonyl and olefin elimination occur. The $[OH^-]$ is expressed in ml. of 0·01009N-sulphuric acid per 1·007-ml. sample :

Time (hr.)	21·25	33·06	45·5	56·83	72·00	99·5	127·5	
$[HO_2^+]$	0·88	1·30	1·68	2·00	2·39	2·95	3·29	4·31
NO_2^- (%)	3·89	3·71	3·53	3·48	3·31	3·08	3·12	—
$Ph{\cdot}CH{:}CH_2$ (%)	—	1·02	1·04	—	1·07	0·99	—	—
$10^6\,{}^ik_1$ (sec.$^{-1}$)	3·01	3·02	3·02	3·05	3·12	3·22	3·14	—
10^6k ($E_{CO}2$)	1·30	1·27	1·24	1·27	1·29	1·25	1·26	—
10^7k ($E2$)	—	1·5	1·6	—	1·8	1·6	—	—

Whence 10^5k ($E_{CO}2$) = 0·127 and 10^7k ($E2$) = 1·6 mole^{-1} l. sec.$^{-1}$.

${}^ik_1$ is calculated with the usual integrated first-order equation with use of the experimental infinity value as initial concentration : k ($E_{CO}2$) is computed by method (4). The value of k ($E2$) is estimated by use of the expression $k\ (E2) = {}^ik_1\{\%\ \text{styrene} - 0{\cdot}59\}/100\ \text{mean}[OH^-]$ (since 0·59% of styrene is produced in solvolysis) and is, of course, subject to a moderately large error (~30%).

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