885. *Nitration at Nitrogen and Oxygen Centres. Part II.* Kinetics and Mechanism of the Conversion of Alcohols, Glycols, and Glycerol into their Nitric Esters.*

By EILEEN L. BLACKALL, E. D. HUGHES, SIR CHRISTOPHER INGOLD, and R. B. PEARSON.

The O-nitrations of methyl alcohol, p-nitrobenzyl alcohol, ethylene glycol, trimethylene glycol, and also glycerol with respect to its primary hydroxyl groups, with nitric acid in constant excess in solvent nitromethane of not-too-high water-content, are of zeroth-order and identical in absolute rate with one another and with the N-nitrations of N-methyl-di- or -tri-nitroaniline and with the C-nitrations of benzenoid hydrocarbons under the same conditions. For the nitration of methyl alcohol small concentrations of sulphuric acid increase, of nitrate ions decrease, and of water do not change the zeroth-order rate, whilst larger concentrations of water increase it, and still larger concentrations cause a switch from zeroth- to first-order kinetics with reduction in the absolute rate. In the presence of sufficient water to secure first-order kinetics, the rates of attack of nitronium ion on the unsaturated or unshared electrons of carbon, nitrogen, and oxygen in the substances mentioned were compared.

In conditions similar to those of these zeroth-order nitrations, *neo*pentyl alcohol is nitrated in a kinetic form between zeroth and first order, and at a smaller absolute rate, whilst the secondary hydroxyl group, remaining after the nitration of glycerol has completed its zeroth-order course, is nitrated in first-order form, and at a still smaller rate.

As NOTED in the preceding paper, we expect that, for any one general reaction within the natural family of electrophilic substitutions, for instance, nitration, nitrosation, or chlorination, much the same pattern of available mechanisms will apply to C-, N-, and O-substitutions. In particular, we expect that, since in C-nitration the nitronium-ion mechanism is outstandingly important, this mechanism will probably dominate the picture of N- and O-nitrations.

We are here concerned with O-nitrations, particularly with the conversions of alcohols into alkyl nitrates. Until recently, such esterifications with nitric acid seem not to have been generally regarded, at least not automatically, as nitrations. In 1950 Israelashvili suggested that the conversion of starch into its nitrate might be an O-nitration.[1] In 1951, Klein and Mentser proved, by the use of isotopically labelled oxygen, that the conversion of cellulose into its nitrate was indeed an O-nitration: what was shown was that, for each group C–O–H converted, the replacement was of H by NO_2, with two oxygen atoms from the nitrating medium, not of OH by NO_3, with three oxygen atoms from that source.[2] This work firmly classified the esterifications of alcohols with nitric acid as nitrations, but left untouched the question of nitration mechanism.

The nitronium-ion mechanism of the O-nitration of alcohols was first identified[3] in this research by the kinetic method originally developed (refs. 1 and 2 of preceding paper) for the study of aromatic C-nitration, the principle of which is to show that a conjugate acid of nitric acid is dehydrated to a nitrating entity, which, according to how we adjust the competitive conditions, can either be recaptured by the water or trapped by the substrate, with consequent change in the kinetic order, first or zeroth, with respect to the substrate. Reference was made in the preliminary account[3] to the nitration of methyl alcohol and several other mono- and poly-hydric alcohols, including glycerol. The great

* Part I, preceding paper.

[1] Israelashvili, *Nature*, 1950, **165**, 666.

[2] Klein and Mentser, *J. Amer. Chem. Soc.*, 1951, **71**, 5888.

[3] Blackall and Hughes, *Nature*, 1952, **170**, 972.

technical importance of the nitration of glycerol for more than a century being considered, it seems curious that the kinetics of the reaction should have been established only lately.

In such work it is usual, for greater convenience in arranging the necessary competitive balance, to work in a medium based on a polar but non-aqueous solvent with a somewhat low content of adventitious or added water, usually not above 1M. However, in 1952, Bunton and Halevi extended the kinetic method of diagnosing mechanism in aromatic nitration to nitrations in aqueous nitric acid, although, of course, in these conditions the standard of competition for nitronium ion set by the water is very much more severe; they were able to show that the nitronium-ion mechanism is still responsible for C-nitration, even in these highly aqueous conditions.[4] Concurrently, with Llewellyn, and by the use of isotopically labelled water, they attacked the problem of the mechanism of oxygen exchange between nitric acid and water, that is, of the O-nitration of water, in the same aqueous nitric acid media. And from the identity of the absolute rate of exchange in such a medium with the absolute rate in the same medium of an aromatic nitration, so organised that the organic substrate captures almost all the nitronium ion, the kinetic order in substrate becoming zero, they were able to prove that, in aqueous nitric acid containing, say, 60 moles % of water, the nitronium-ion mechanism is responsible for the O-nitration of water.[4,5]

Bonner and Frizel recently furnished evidence for the nitronium-ion mechanism in the O-nitration of alcohols by nitric acid in an aqueous solution of a very strong acid. They showed that the rate of O-nitration of *iso*pentyl alcohol by nitric acid in about 50—60% aqueous perchloric acid varies with acidity according to a form of *J* function.[6] Such evidence is generally accepted as indicating that a protonated species is being dehydrated in the rate-controlling portion of the mechanism. Strong indirect evidence in favour of Bonner and Frizel's thesis is afforded by the work summarised in the preceding paragraph, since it is inconceivable that the nitronium-ion mechanism could be responsible for both C- and O-nitration in aqueous nitric acid, with no added strong acid, and yet fail to take charge of O-nitration in the presence of a considerable concentration of perchloric acid.

In the experiments now described, various mono- and poly-hydric alcohols were nitrated with a constant excess of nitric acid in nitromethane, without or with initial additions of water or other solutes. As is usual in this laboratory, the kinetics were followed dilatometrically. We had become so accustomed to associating nitration with large contraction that the smallness of the volume changes accompanying O-nitration of alcohols was a surprise, though it should not have been since a nitro-group is only transferred from one oxygen atom to another and in the O-nitration of water there could be no volume change. In the O-nitration of methyl alcohol there is a contraction of only about 1/40 of that accompanying the C-nitration of toluene, and about 1/10 of that accompanying the N-nitration of N-methyl-2 : 4 : 6-trinitroaniline. Naturally, this involved our making dilatometers more sensitive by at least an order of magnitude than those used previously, and also a thermostat of similarly greater precision. Furthermore, a better method of setting up runs had to be adopted, and the previously inappreciable disturbances due to reaction heat, which now appeared prominently, had to be avoided. However, due care having been taken, the dilatometry of the small volume changes proved about as easy and accurate as that of the relatively large ones hitherto followed.

(A) *Conversion of Methyl Alcohol into Methyl Nitrate.*—(1) *Kinetic form: Effect of substrate concentration.* In initially dry nitromethane, with methyl alcohol concentrations not above 0·05M and nitric acid concentrations much larger but not above 2·5M, one obtains the typical volume–time curve of a zeroth-order nitration. After some initial irregularity while a steady temperature is being attained, a straight line of negative slope is traced,

[4] Bunton and Halevi, *J.*, 1952, 4917.
[5] Bunton, Halevi, and Llewellyn, *J.*, 1952, 4913.
[6] Bonner and Frizel, *Nature*, 1957, **179**, 1022.

which at a certain point turns sharply to one of zero slope. At this point the chemical reaction is over. The negative slope gives its zeroth-order rate-constant.

In other conditions, disturbances can be noticed. With substantially higher initial concentrations of methyl alcohol, *e.g.*, 0·1M or more, the downward-sloping part of the volume–time curve is not absolutely straight, its initial gradient being appreciably greater, *e.g.*, 10%, than its gradient over the latter part. The cause of this is not established, but it may be due to some kinetic solvent effect of the methyl alcohol (cf. sub-section *A*4, where it is shown that added water accelerates zeroth-order nitration).

As with all zeroth-order nitrations, the rate rises, as a steep function of the nitric acid concentration. A new disturbance arises if this concentration is increased above 3M to produce somewhat fast runs: a special kind of discontinuity then appears at the end of the downward-sloping branch of the volume–time curve. Instead of turning abruptly
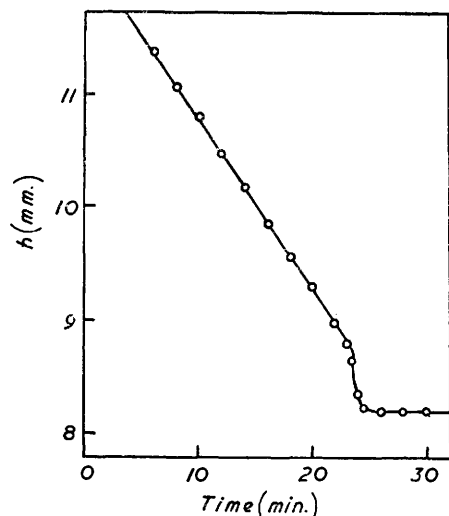

FIG. 1. *Volume–time curve in a nitration of methyl alcohol* (0·2M) *by nitric acid* (4M) *in nitromethane at* 25°. *The reaction is of zeroth order, and the short exponential segment of curve, here interposed between the usual two linear branches of the volume–time curve of such a reaction, is a cooling curve.*

horizontal, it turns, just as abruptly, to a much more steeply downward-sloping direction, and then, after a short exponential course, becomes horizontal (Fig. 1). This is regarded as a thermal effect, arising from dissipation of the heat of reaction. It is not seen in the less sensitive types of dilatometer, nor in the sensitive dilatometers unless the runs are fast. While nitration proceeds, heat is generated at a constant rate. During the first few minutes of a run, the dilatometer contents will attain a steady temperature such that the generated heat is lost to the thermostat at the same constant rate. When nitration abruptly stops, because no more methyl alcohol is left, the temperature of the dilatometer contents must fall to that of the thermostat. The resultant cooling-curve appears as the exponential contraction.

Apart from the disturbances mentioned, all runs on the nitration of methyl alcohol with a constant excess of nitric acid in initially dry nitromethane followed the zeroth-order

TABLE 1.—*Zeroth-order rate-constants* (k_0 *in moles* $l.^{-1}$ $sec.^{-1}$) *for the nitration of methyl alcohol by* 1·5M-*nitric acid in nitromethane at* 25°.

$[MeOH]_0$	0·0233	0·0236	0·0244	0·0356	0·0400	0·0524	0·0580	0·0653	0·0830
$10^5 k_0$	1·65	1·61	1·69	1·74	1·69	1·62	1·72	1·66	1·74

kinetic form with satisfactory precision. It is consistent that, within the same limitations, the zeroth-order rate-constants derived from different runs started with different concentrations of methyl alcohol, other conditions being the same, were identical (Table 1), the mean value of k_0 being 1·68 × 10⁻⁵ moles l.⁻¹ sec.⁻¹

As the contents of a dilatometer did not provide enough material for satisfactory isolation of the nitration product, a larger-scale "dummy" kinetic run was conducted in a flask. Methyl nitrate was isolated from this and identified.

(2) *Rate comparison with aromatic nitration.* Since the mechanism of aromatic nitration is known, a comparison of the absolute rate of the zeroth-order nitration of methyl alcohol with the rate under the same conditions of the nitration of such aromatic compounds as follow the zeroth-order law provides important evidence concerning the mechanism of the O-nitration. That the zeroth-order rates are the same in the same conditions for the nitration of methyl alcohol, benzene, toluene, and ethylbenzene is shown in Table 2. These experiments on the hydrocarbons were carried out at the same time and with the same materials as those on methyl alcohol, in order to make the whole series comparable.

TABLE 2. *Zeroth-order rate-constants (k_0 in moles l.$^{-1}$ sec.$^{-1}$) for the nitration of methyl alcohol and of benzenoid hydrocarbons by 2·5M-nitric acid in nitromethane at 25°.*

	[MeOH]$_0$, As Table 1	[C$_6$H$_6$]$_0$, 0·110	[Ph·Me]$_0$, 0·0748	[Ph·Et]$_0$, 0·0675
$10^5 k_0$	1·68 (mean)	1·72	1·70	1·66

(3) *Kinetic effects of acid, base, and salts.* The object of these experiments was to confirm the nitronium-ion mechanism with respect to step (1) of the mechanism, as expressed in scheme (I) of the preceding paper (p. 4358). It is expected that acids will accelerate reaction strongly, and neutral salts will do so mildly, but that bases will retard

FIG. 2. *Effect of added sulphuric acid on the zeroth-order rate of nitration of methyl alcohol (0·025M) by nitric acid (1·5M) in nitromethane at 25°.*
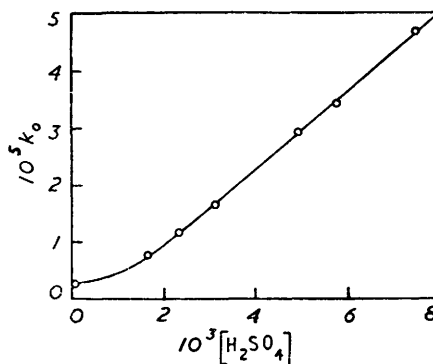
reaction. The solvent throughout this group of experiments was initially dry nitromethane, and the nitration was in consequence of zeroth-order form, step (2) of scheme (I) being rate controlling. This kinetic form was preserved throughout these particular experiments, even under the retarding addition of a base.

The added acid was sulphuric acid, which is so much stronger than nitric acid that, even in somewhat low concentration, it wholly takes the place of that one of the two nitric acid molecules, written as the factors of step (1) in scheme I, which acts as proton-donor to the other. The observed zeroth-order rates are in Table 3. On the progressive addition of sulphuric acid, the accelerating effect is at first small but soon grows to its maximum. This can be understood because although the sulphuric acid protonates the nitric acid, this in turn will cause formed nitric acidium ion so to combine with original autoprotolytic nitrate ion that the ionic product of the nitric acid remains constant. Only when most of the pre-existing nitrate ion has been thus destroyed will the further addition of sulphuric acid produce its equivalent in an increased concentration of nitric acidium ion, and so will produce the linear increase, shown in Fig. 2, in the rate of formation of nitronium ion, and hence in rate of zeroth-order nitration.

As Table 3 shows, the addition of sodium perchlorate accelerates nitration. This is expected as a normal salt effect; for, according to the nitronium-ion mechanism, ions are being produced from neutral species in the kinetically significant part of the mechanism,

i.e., up to and including the rate-controlling step. Other salts are expected to act similarly, unless they exert superposed specific effects. Added potassium nitrate certainly does this, because it markedly retards nitration, as is also shown in Table 3. Although our figures are not extensive enough to permit a quantitative analysis of the superposed effects, the qualitative conclusion seems assured that the observed retarding effect is the net result of a normal-salt acceleration and a stronger specific retardation arising from the basic nature of the nitrate ion, which, as the lyate ion of the system, is the strongest base that can be introduced in quantity. According to the nitronium-ion mechanism, the nitrate ion must deprotonate such nitric acidium ion as is autoprotolytically formed in pre-equilibrium, and must thereby reduce the stationary concentration to which the rate of formation of nitronium ion, measured as zeroth-order nitration rate, is proportional.

TABLE 3. *Effects of added sulphuric acid, sodium perchlorate, and potassium nitrate on the zeroth-order rate-constants (k_0 in moles l.$^{-1}$ sec.$^{-1}$) of nitration of methyl alcohol (initially 0·025 M) by nitric acid in nitromethane at 25°.*

$[HNO_3]$ $\{$ $[H_2SO_4]$	0	0·00161	0·00231	0·00308	0·00492	0·00576	0·00744
= 1·5M $\{$ $10^5 k_0$	0·276	0·767	1·17	1·63	2·91	3·40	4·71
$[HNO_3]$ $\{$ $[NaClO_4]$	0	0·00231	0·00287	0·00409	0·00676		
= 2·5M $\{$ $10^5 k_0$	1·65	1·71	1·74	1·91	2·08		
$[HNO_3]$ $\{$ $[KNO_3]$	0	0·00131	0·00194	0·00297	0·00467	0·00538	0·00661
= 2·5M $\{$ $10^5 k_0$	1·65	1·30	1·19	1·05	0·99	0·98	0·88

(4) *Kinetic effect of water: change from zeroth to first order.* The object of these experiments was so to promote reversal of dehydration of the nitric acidium ion, that the formation of nitronium ion in step (2) of scheme (I) becomes included in the pre-equilibrium part of the mechanism, with the result that the nitronium ion is held in stationary concentration, and the rate at which it is removed by methyl alcohol becomes the nitration rate: our former zeroth-order will then give place to first-order kinetics. Once the change in kinetic order is fully accomplished the water, apart from any general medium effect which it may have as a polar co-solvent, should exert a specific retarding effect on the nitration, since it has now become one of the products of the extended pre-equilibrium [cf. scheme (I)].

The observations (Table 4) are as follows. Small or moderate initial additions of water have no detectable effect on the rate of zeroth-order nitrations started in otherwise dry nitromethane. By moderate, we mean amounts comparable with the amount of water produced in the nitration, and hence already much larger than the amounts of the acid, base, and salts which, in the preceding sub-sections, were shown to produce large kinetic effects. However, when water is added in quantities such as 0·1M which are substantially larger than those in which it is produced in the nitrations (0·025M) but still smaller than would make total water sufficiently competitive with the methyl alcohol to effect any large degree of re-hydration of formed nitronium ion, then, although the pre-equilibrium remains restricted to step (1) of scheme (I), and the zeroth-order form of nitration is accordingly preserved, the nitration is actually accelerated by the added water. Though this is contrary to one's preconceptions, *e.g.*, those based on descriptions in text-books of nitration, as to how water usually affects their rate, it can be understood as a general medium effect of water as a polar co-solvent; for in zeroth-order nitration, according to the nitronium-ion mechanism, ions, namely, nitronium and nitrate, are being produced from the neutral species, nitric acid molecules, in the kinetically significant part of the mechanism, namely steps (1) and (2) of scheme (I). Therefore, added water should accelerate zeroth-order nitration by its medium effect. However, when the water content is raised to 0·2M and above the rate begins to fall, and the reaction order in substrate simultaneously begins to rise from zero towards one, at first in the later part of the course of the reaction, but eventually throughout. At 0·8M-water the rate is still falling, but the reaction is practically completely converted into first-order form. Thereafter, if the concentration of water is

further increased, the first order rate-constant becomes steadily reduced; but now the kinetic form remains the same. We understand this as meaning that the co-solvent effect of water is less important than the specific retarding effect which water now acquires from having become included in the pre-equilibrium products of the combined stages (1) and (2), as rate-control is shifted from step (2) to step (3) of scheme (I), as happens when the kinetic order changes from zero to unity.

(5) *Mechanism of* O-*nitration.* Assuming that proton-loss from the conjugate acid of

TABLE 4. *Zeroth- and first-order rate-constants (k_0 in moles l.$^{-1}$ sec.$^{-1}$ and k_1 in sec.$^{-1}$) of nitration of methyl alcohol (0·025M) by nitric acid (2·5M) in nitromethane containing initially added water.*

[H_2O] *	$10^5 k_0$	Order	[H_2O] *	$10^5 k_0$	Order	[H_2O] *	$10^4 k_0$	Order
—	1·65	0	0·249	~1·9	~0	0·779	~11·9	~1
0·068	1·88	0	0·392	~1·7	impure	0·882	8·53	1
0·122	2·25	0	0·511	~1·6	impure	1·00	4·22	1
0·188	2·07	0				1·13	1·92	1

* *Added* water.

methyl nitrate would be rapid, in agreement with step (4) of scheme (I) (X = OMe), the preceding evidence satisfies all the critical kinetic requirements of that scheme. Thus the O-nitration of alcohols certainly proceeds by attack of pre-formed nitronium ion on non-bonding oxygen electrons of the alcohol.

(6) *Comparison of substrate reactivities in* C-, N-, *and* O-*nitration.* The rates of attack of nitronium ion on methyl alcohol and on toluene were compared by measuring first-order rate-constants for the nitration of methyl alcohol and of toluene in identical conditions in which both reactions follow first-order kinetics. At 25° in nitromethane containing 1·09M-water, the first-order constant for the nitration with 2·5M-nitric acid of methyl alcohol was $2·5 \times 10^{-4}$ sec.$^{-1}$, and of toluene was $2·0 \times 10^{-4}$ sec.$^{-1}$. If we take figures from the preceding paper (Section *A*6), in order to bring the N-nitration of N-methyl-2 : 4 : 6-trinitroaniline into comparison with the O-nitration of methyl alcohol and the C-nitration of simple aromatic hydrocarbons, we can set up the following scale of kinetic reactivities for nitronium ion of the unsaturated or unshared electrons of carbon, nitrogen, and oxygen in these substrates: Benzene, 1; N-methyl-2 : 4 : 6-trinitroaniline, 1·4; toluene, 24; methyl alcohol, 30. The corresponding figure for water probably lies between one and two orders of magnitude below that for benzene, and therefore about three orders below that for methyl alcohol.

(B) O-*Nitration of Other Mono- and Poly-hydric Alcohols.*—(1) p-*Nitrobenzyl alcohol.* The nitro-substituent in this compound serves the two purposes of preventing nitration in the aromatic ring, and reducing the tendency to oxidation in the side-chain. It is expected also, by its inductive effect, to reduce the reactivity of the unshared oxygen electrons towards nitronium ion.

However, the alcohol is readily nitrated by nitric acid in constant excess in initially dry nitromethane. The accompanying contraction is about the same as that applying in the nitration of methyl alcohol, a fact which itself is evidence that an O-nitration is under observation, as was confirmed by the isolation of *p*-nitrobenzyl nitrate.

The reaction is substantially of zeroth-order, although the volume–time graph remains strictly linear for only the first 90% of the total reaction and then undergoes some rounding as it runs into the horizontal branch representing completed reaction. This probably means that the intrinsic reactivity of the alcohol towards nitronium ion is only just high enough to permit the observation of zeroth-order kinetics. One observes the same thing in the nitration of benzene, though not in that of toluene or more reactive derivatives. It can be understood that, when the specific rate of reaction of the substrate with nitronium ion is, say, more than ten but less than a hundred times larger than the specific rate of the corresponding reaction of water, then, towards the end of reaction, when there is present

more than ten times as much water as there is of substrate, the water will have some success in its competition with the substrate for nitronium ion, which will no longer be captured wholly by the substrate; thus we find in this part of the reaction a departure from zeroth-order kinetics.

As shown in Table 5, the absolute rate of the zeroth-order nitration of *p*-nitrobenzyl alcohol is nearly the same as of methyl alcohol. The slightly smaller figure obtained for the nitro-alcohol may be simply a sign that, with this substance, we are near the lower limit of reactivity at which zeroth-order nitration can be observed.

TABLE 5. *Zeroth-order rate-constants* (k_0 *in moles* $l.^{-1}$ *sec.*$^{-1}$) *for the nitration of methyl and* p-*nitrobenzyl alcohols by nitric acid* (2·25M) *in nitromethane at* 25°.

Methyl alcohol .... $[ROH]_0 = 0.231$, $10^5 k_0 = 1.08$
p-Nitrobenzyl alcohol .... $[ROH]_0 = 0.400$, $10^5 k_0 = 1.00$

(2) neo*Pentyl alcohol.* In *O*-nitration, this alcohol is considerably less reactive than the other alcohols so far mentioned. In initially dry nitromethane, the nitration of *neo*-pentyl alcohol by nitric acid in constant excess shows a strong departure from zeroth-order form, and an absolute rate much below that of the zeroth-order nitrations. The kinetic order is not first, but between zeroth and first, approximating more closely to first on the whole, and especially in the later part of reaction.

The position of *neo*pentyl alcohol among the alcohols in *O*-nitration is comparable to that of chlorobenzene among benzene derivatives with respect to *C*-nitration. The nitration of chlorobenzene in nitromethane has the kinetic characteristics described in the preceding paragraph for the nitration of *neo*pentyl alcohol. We have made a rough comparison of the relative specific rates of reaction of *neo*pentyl alcohol and of chlorobenzene with nitronium ion, by comparing the first-order rate-constants that can be obtained for the nitration of either substrate with a constant excess of nitric acid in nitromethane containing small amounts of water. It appears that *neo*pentyl alcohol has a kinetic reactivity for nitronium ion about $\frac{3}{4}$ of that of chlorobenzene. It has been estimated, from experiments on competitive aromatic nitration, that the specific rate of reaction of chlorobenzene with nitronium ion is about 1/30 of that of the reaction of benzene. We might therefore extend the scale of reactivities for nitronium ion given at the end of the preceding section by assigning to *neo*pentyl alcohol a value about 1/40 of that of benzene, or 1/1200 of that of methyl alcohol.

(3) *Ethylene glycol.* The *O*-nitration with nitric acid in constant excess in initially dry nitromethane, follows a zeroth-order kinetic law, holding smoothly to the complete formation of the final product, ethylene dinitrate. The zeroth-order rate constant for overall conversion of the glycol is one-half of the constant applying to the nitration of methyl alcohol in identical conditions (Table 6).

This relation between the rate constants is natural, for it is implied in the kinetic form that the mononitration of the glycol and of its mononitrate occur at the same zeroth-order rate, *i.e.*, that the first and second hydroxyl groups in a glycol molecule take up nitronium ion independently of each other and just as fast, in each case, as nitronium ion becomes available. Therefore, in order to secure the complete conversion of a glycol molecule, we must wait for the formation of two nitronium ions, twice as long as we have to wait for such conversion of a methyl alcohol molecule; thus the rate is reduced to one-half.

(4) *Trimethylene glycol.* The same description applies. Zeroth-order rate-constants for the nitration of both glycols, and for glycerol, are included in Table 6.

TABLE 6. *Zeroth-order rate-constants* (k_0 *in moles* $l.^{-1}$ *sec.*$^{-1}$) *for the nitration of mono- and poly-hydric alcohols by* 2·5M-*nitric acid in nitromethane at* 25°.

	$[MeOH]_0$, 0·0244	$[C_2H_4(OH)_2]_0$, 0·0274	$[C_3H_6(OH)_2]_0$, 0·0169	$[C_3H_5(OH)_3]_0$, 0·0151
$10^5 k_0$	1·69	0·83	0·84	0·88

(5) *Glycerol.* The *O*-nitration with nitric acid in constant excess in nitromethane passes through two kinetically well-separated phases, a zeroth-order succeeded by a first-order course. More particularly, the reaction proceeds to about two-thirds of its total extent at a constant rate almost equal to the rate of nitration of the glycols (cf. Table 6), after which the reaction is completed at a much reduced and exponentially diminishing rate.

Our interpretation is that two nitronium ions are trapped by the glycerol molecule as fast as they become available. Presumably they are taken up at the primary-alcoholic centres to form propan-2-ol 1 : 3-dinitrate. In this compound, the secondary alcoholic centre is relatively unreactive, and becomes the less successful competitor with water for formed nitronium ion, which it draws off only slowly from a stationary concentration, so accomplishing, with first-order kinetics, the last stage of esterification in the formation of glycerol trinitrate. First-order rate-constants for this last stage are given in Table 7. Although we have not directly compared rates, propan-2-ol 1 : 3-dinitrate appears to be considerably less reactive in first-order nitration than is *neo*pentyl alcohol.

TABLE 7. *First-order rate-constants* (k_1 *in sec.*$^{-1}$) *for the third step in the trinitration of glycerol by nitric acid in nitromethane at 25°.*

[HNO$_3$]$_0$ = 4·0   [Glycerol]$_0$ = 0·168 10^4k_1 = 1·36   [HNO$_3$]$_0$ = 5·0   [Glycerol]$_0$ = 0·062 10^4k_1 = 4·50

EXPERIMENTAL

Apparatus.—Owing to the smallness of the volume changes in *O*-nitration a particularly good thermostat as well as sensitive dilatometers were required.

The thermostat regulator contained, in two connected flat spirals of 1 cm. tubing, toluene sufficient to give a movement of mercury in the capillary of 1 metre per degree. The usual hot-wire switch having been found subject to a possible time-lag of several seconds, an electronic relay was constructed which worked very quickly, though it required frequent maintenance. The 25 w regulator-controlled heater supplemented a permanent heater so adjusted that it was just insufficient to maintain the temperature of 25°. Careful attention was paid to stirring and to thermal insulation of the 100-l. bath, particularly to insulation over the lid. In practice the temperature variation was about 0·0005°.

For aromatic nitrations, the ordinary tapless dilatometers of Benford and Ingold's type C [7] were used. For *O*-nitration, some tapless dilatometers were developed which had the required sensitivity, but also the disadvantage that they took about 15 min. to fill by suction through the fine capillary tube. Therefore we re-introduced taps (2 mm. vacuum) into our dilatometers of the types called " D " and " E ". Above a tap was a length of ordinary 2 mm. capillary tube attachable through a ball-and-socket joint to a capillary tube of similar diameter and an inverted U form, through which filling was accomplished. Below the tap, the dilatometer D contained a simple U of thin-walled quill tubing, 5 ml. in total capacity; and above the other limb of this U was a vertical length of 0·5 mm. precision-bore capillary tubing for the volume readings. The dilatometer E was identical with D except that the simple U of quill tubing was replaced by a helix of 20 ml. total capacity. Ordinary L grease was used for the taps, the attack on it by nitric acid being minimised by care in restricting it to the ground surface. Dilatometers were cleaned, and the grease was removed, after every run. The scale readings were made with a cathetometer, ±0·01 mm. The constants of the dilatometers, *i.e.*, the fractional volume changes per unit scale length were as follows: C = 0·00195, D = 0·000190, E = 0·0000564 cm.$^{-1}$.

Procedure.—The empty dilatometer was placed in the thermostat. The nitric acid, just above its m. p., was weighed from a vacuum-jacketed pipette into nitromethane, just above its m. p., contained in a standard flask. This was placed in the thermostat and, after sufficient time for adjustment of the temperature, was made up to the mark with nitromethane. Meanwhile the organic substrate was weighed into 2 ml. of nitromethane in another weighed standard flask, thereby avoiding unaccounted loss by volatilisation when the substrate was methyl alcohol. This flask was now placed in the thermostat and allowed to attain its temperature. The nitric acid solution was now transferred to a small separating funnel above the other flask,

[7] Benford and Ingold, *J.*, 1938, 929.

and at once run into the latter, up to its mark, while the stop-watch was started. Then the reaction solution, well mixed, was sucked into the dilatometer, and the cathetometer readings were started.

Materials.—Methyl alcohol was purified by a standard method.[8] *p*-Nitrobenzyl alcohol, crystallised from water, had m. p. 92—93°. Ethane-1 : 2-diol, fractionated under low pressure, had n_D^{25} 1·4300. Similarly distilled propane-1 : 3-diol had n_D^{25} 1·4384, and glycerol n_D^{25} 1·4725. Purification of nitric acid and of nitromethane is described in the preceding paper.

Products.—Methyl nitrate was isolated as follows. The nitromethane solution in which methyl alcohol had been nitrated was washed with small volumes of ice-cold water and ice-cold saturated aqueous sodium chloride, and was then neutralised with sodium hydrogen carbonate, filtered, and dried (MgSO$_4$). The filtered solution was fractionated at 12 mm. pressure through a 30 cm. packed column, and the methyl nitrate was trapped at $-80°$ and redistilled at a similar pressure. It gave a strong positive test for nitrate and a negative one for nitrite (n_D^{25} 1·3720; Found: C, 15·8; H, 4·2. Calc. for CH$_3$O$_3$N: C, 15·6; H, 3·9%). *p*-Nitrobenzyl nitrate, recovered by crystallisation after a nitration, had m. p. 67—68° (Found: C, 42·6; H, 3·4. Calc. for C$_6$H$_4$O$_5$N$_2$: C, 42·4; H, 3·0%).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
    UNIVERSITY COLLEGE, LONDON, W.C.1.   [*Received, July 25th*, 1958.]

[8] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 169.