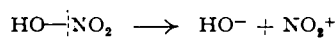


493. Kinetics and Mechanism of Aromatic Nitration. Part II.
Nitration by the Nitronium Ion, NO₂⁺, derived from Nitric Acid.

By E. D. HUGHES, C. K. INGOLD, and R. I. REED.

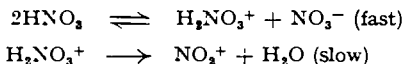
The plan underlying the investigation as developed in this collection of papers, which includes papers of several concurrent series, is explained. The series to which this paper belongs is concerned with the kinetics and products of aromatic nitration. The other series deal with various kinds of physical and synthetical evidence, all bearing directly or indirectly on the subject of nitration. In this paper the kinetics of aromatic nitration by nitric acid are considered. The treatment is divided into Sections, and the following summary of the paper is intended to render any of its Sections intelligible without the necessity of reading the others.

(1) *Kinetic Orders of Aromatic Nitration: The Nitronium Ion* (p. 2402).—Aromatic nitration displays second-order kinetics in sulphuric acid (Martinsen), and first-order kinetics in nitric acid; and in either nitromethane or acetic acid with nitric acid in constant excess, it exhibits zeroth-order kinetics for sufficiently reactive aromatic compounds, and first-order kinetics for sufficiently unreactive compounds. Nothing of special interest concerning mechanism follows from these kinetic results in sulphuric acid, and in nitric acid, though they are consistent with what is deduced; but the zeroth-order kinetics in organic solvents, and its transition to first-order kinetics with diminishing aromatic reactivity, proves without alternative the formation and effectiveness of the nitronium ion, NO₂⁺. The kinetically fundamental process is shown to be localised in nitric acid, to be activated, to be heterolytic, and to produce electron-deficient nitrogen. Therefore it is the bond-fission



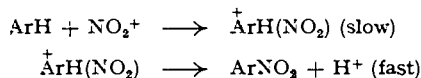
disregarding the associated, instantaneous proton-transfers, which are treated under (2).

(2) *Solute Effects on Nitration Kinetics: Mechanism of Formation of the Nitronium Ion* (p. 2412).—Aromatic nitration in nitric acid, or in nitromethane, or acetic acid, with nitric acid in constant excess, is accelerated by sulphuric acid, and retarded by ionising nitrates, the latter effect being specific, and not a general salt effect. The effect of sulphuric acid on the rate, and that of nitrate ion on the reciprocal of the rate, obey linear limiting laws. The effects occur alike with zeroth- and first-order reactions, always without disturbance to the reaction order. These results show that one proton is employed, and one nitrate ion eliminated, in the conversion of nitric acid into a nitronium ion; and that these changes are reversed. It also follows that they take place in an earlier reaction-step than that which produces nitronium ion, because a zeroth-order nitration only maintains its kinetic order when the latter step is not reversed. Thus the following two-stage mechanism is unequivocally established:

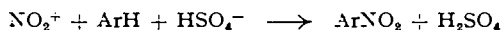


Consistently, the kinetic effect of water in zeroth-order nitration is negligible in comparison with that of nitrate ion. Relatively large amounts of water will retard the nitration by reversing the second of the above reaction-steps; but then the zeroth-order reaction goes over into a first-order reaction. Consistently also, the kinetic effect of water on first-order nitration is comparable to that of nitrate ion. These considerations establish the formation of the nitric acidium ion, H₂NO₃⁺. The function of one of the above-written nitric acid molecules is simply to supply a proton to the other one, which is the actual source of the nitronium ion; and the function of proton-supply will obviously be taken over by a stronger acid than nitric acid, such as sulphuric acid, if such an acid is present.

(3) *Medium Effects on Nitration Kinetics: Mode of Action of the Nitronium Ion* (p. 2423).—Acetic acid, nitromethane, nitric acid, and sulphuric acid, considered as nitration media, form a series in order of increasing polarity. A partial or complete replacement of acetic acid by nitromethane, of either by nitric acid, or of any of these by sulphuric acid, increases nitration rate, independently of reaction order. Such changes to more polar media may also change the order, reducing it from first towards zeroth, as has been illustrated for the replacement of acetic acid by nitromethane, and for its partial replacement by nitric acid. From these results, and the well-established theory of kinetic solvent effects, it follows that, while ionic charges are created in the reactions that produce the nitronium ion, ionic charges are neither formed nor destroyed in the kinetically significant step of the attack by the nitronium ion on the aromatic molecule. The nitrating attack must therefore be a two-stage bimolecular process:

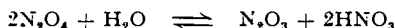


The slowness of the first step is shown by the kinetics, and the relative rapidity of the second is confirmed (Melander) by the absence of a hydrogen-isotope effect on the rate. The recently discussed suggestion that the nitrating attack is a one-stage termolecular process, requiring the collaboration of a base, and especially of an anion, as in the equation



is thus disproved: for this reaction, which destroys charges, should be strongly retarded by polar solvents; and it should show a hydrogen-isotope effect. The very limited kinetic effects which formed the basis of this theory can reasonably be ascribed in part to the secondary influence of charge distribution, and in part to the formation of salt-like complexes by the aromatic compounds under the conditions of the observations (Gillespie, Millen).

(4) *Effects of Nitrous Acid on Nitration Kinetics: Condition of Nitrous Acid in Nitric Acid Solvents* (p. 2430).—The term "nitrous acid" is used to cover all materials in nitric acid which after dilution with water could be together estimated as nitrous acid. Aromatic nitration in nitric acid, or in nitromethane, or acetic acid, with nitric acid in constant excess, is retarded by "nitrous acid," which itself is neither formed nor destroyed, except in some special cases considered elsewhere (Part VI *et seq.*). The effect applies alike to zeroth-order and first-order reactions, and operates always without disturbance to the reaction order. At low nitrous acid concentrations, and in the absence of water, the effect on the reciprocal of the rate is linear with respect to the power one-half of the nitrous acid concentration. At higher nitrous acid concentrations, or in the presence of water, a stronger retarding effect appears. With sufficient nitrous acid and water, the reciprocal of the rate varies with the three-halves power of the nitrous acid concentration. These effects are attributed to the ionisation of oxides of nitrogen by nitric acid. Nitrous acid exists in nitric acid mostly as dinitrogen tetroxide; but an increase of concentration, or the addition of water, increases the small proportion in which it exists as dinitrogen trioxide:



Dinitrogen tetroxide and dinitrogen trioxide are ionised thus:



The nitrate ion deprotonates the nitric acidium ion, as has been described under (2). The nitrite ion acts similarly, but, as the stronger base, its effect is specifically more powerful. Deprotonation by the nitrate ion leads to retardation by the one-half-power law, and deprotonation by the nitrite ion to retardation by the three-halves-power law.

(0) INTRODUCTION TO SOME PAPERS OF SEVERAL CONCURRENT SERIES.

(0.1) *This Paper as a Development of Previous Work on Nitration Kinetics.*—The work now reported is a continuation of the investigation, described in Part I* (Benford and Ingold, *J.*, 1938, 929), into the kinetics of nitration of aromatic compounds by nitric acid in homogeneous solution. We have employed the dilatometric technique used by Benford and Ingold (*loc. cit.*), adding some small refinements which will be mentioned later. As heretofore, the interpretation of the dilatometric results has been controlled by chemical analysis. A short statement of our main results and conclusions has already been published (Hughes, Ingold, and Reed, *Nature*, 1946, 158, 448).

Having established a convenient technique, Benford and Ingold made a general survey of solvents for nitration. These they classified as fast, medium, and slow, according to their effect on nitration rate. Thus sulphuric acid was a fast solvent, nitromethane a medium-rate solvent, and acetic acid was a slow solvent. In consequence of earlier work by Martinsen and others, much was already known about the kinetics of nitration in sulphuric acid; and therefore, Benford and Ingold concentrated upon the medium-rate solvent, nitromethane, leaving for the future the study of slow, and the continued study of fast, solvents.

A further investigation was promised in Part I on the kinetics of nitration in sulphuric acid, and a programme of work on these lines was commenced; but it was abandoned when, later, the information was received that others were engaged in a similar study. However, we continued our investigation of nitration kinetics and mechanism in a large number of other ways, of which the following three are brought together in the present paper.

First, in order to strengthen the evidence concerning fast solvents, we have studied nitration kinetics with nitric acid itself as the solvent: though not so fast as sulphuric acid, nitric acid is certainly to be classed as a fast solvent for nitration.† Secondly, we have extended, and in a sense completed, the kinetic investigation of Benford and Ingold on nitration in the medium-rate solvent, nitromethane. Thirdly, as foreshadowed in Part I, we have carried out a similarly full investigation on the kinetics of nitration in the slow solvent, acetic acid. Judged from the results, the solvents mentioned might fairly be classified into two main groups: sulphuric acid and nitric acid are more or less comparable, and so also are nitromethane and acetic acid, the differences in each case being quantitative rather than qualitative.

* The paper to which we refer as Part I of the present series was published under the specific title "A Dilatometric Investigation of the Kinetics of Aromatic Nitration, especially in Nitromethane Solution."

† Perchloric acid is stated to be a faster solvent for nitration than is sulphuric acid (Robinson, *J.*, 1941, 238), though no detailed report illustrating the comparison is yet available.

(0.2) *Continued Study of Nitration Kinetics in the Accompanying Papers.*—We have extended the kinetic investigation in several further directions. First, the very slow nitration solvent, water, required to be examined, in order to complete the representation of solvent types. The issues here involved are rather distinct, and it thus became convenient to describe this part of the work in a separate paper (Part III). Secondly, all the work so far mentioned is concerned with nitrations effected by the use of nitric acid, either alone or in a solvent; but alkyl and acyl nitrates are also in principle nitrating agents, and thus it seemed desirable to investigate their behaviour. A particularly important special case is that of nitryl nitrate, *i.e.*, dinitrogen pentoxide. Some further papers of the present group deal with this part of the subject (Parts IV and V).

Thirdly, the general kinetic findings, as set out in the present paper, apply without modification to a great variety of aromatic substances; but derivatives of phenol and aniline form a special class, inasmuch as their nitration often involves complications, which affect the kinetics, and sometimes also the products, of nitration. The nature of these disturbances, and their place in the general scheme of aromatic nitration, is examined in other papers of the present collection (Parts VI—VIII). However, our work on the kinetics of nitration of aniline derivatives is still incomplete, and further papers on this section of the subject will be offered later.

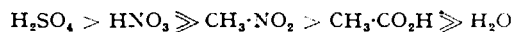
(0.3) *Non-kinetic Study of Nitrating Agents as Reported in Accompanying Papers.*—This explanation of the plan of the present work has referred as yet only to kinetic investigations. In the study of reaction mechanism, it is desirable, where possible, to combine kinetic with non-kinetic evidence; and, accordingly, the papers mentioned above will be found interspersed with a number of others, which largely follow their own general theses, but in doing so contribute evidence of a non-kinetic kind on the mechanism of nitration.

Such evidence has been obtained in several different ways, including the physical examination of nitrating media, the chemical separation of reactive entities contained in such media, and the physical study of the isolated entities. We may refer to accompanying papers, or series of papers, under the serial titles, "Cryoscopic Measurements in Sulphuric Acid," "Cryoscopic Measurements in Nitric Acid," "Chemistry of Nitronium Salts," "Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen," and "Chemistry of Nitroammonium Salts." The physical properties which have been found to be of most service in this problem are freezing-point depressions, Raman spectra, and electrolytic phenomena; and the relevant work by the first two of these methods is being published at this time. Our electrochemical work, however, it still unfinished, as is also some work which employs the method of infra-red absorption spectra. Papers dealing with these divisions of the investigation will be published later. A related crystallographic investigation is proceeding in Professor Cox's laboratory.

(1) KINETIC ORDERS OF AROMATIC NITRATION: THE NITRONIUM ION, NO_2^+ .

(1.0) *Conditions affecting Reaction Order.*—The kinetic results which are the simplest to interpret, and are of the most general significance with respect to the mechanism of nitration, are those which relate to kinetic order, and its variation with the aromatic compound and with the solvent.

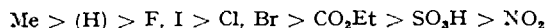
Summarising our previous remarks on the general differences between solvents, we now arrange them, as shown below, in a graded series, according to their effect on reaction rate. The reason for doing this is that the same series forms a useful basis for considering the behaviour of the different solvents in the determination of the kinetic order of nitration, and for discussing the effects of the solvents on reaction mechanism:



For the purpose of discussing the effect of the constitution of the aromatic compound on reaction order and mechanism, it is convenient to grade also aromatic compounds with reference to their influence on nitration rate, *i.e.*, according to the relative rates at which they would be attacked under uniform conditions.

This can be discovered by what we may call the competition method: two aromatic compounds, both in excess, are allowed to compete for a limited amount of a nitrating agent in the same homogeneous solution, and, from the proportions in which they are nitrated, the ratio of the specific rates at which the nitrating entity attacks the competing aromatic molecules is calculated.

Determinations on these lines have been made for benzene and a number of monosubstituted benzenes (Ingold and Shaw, *J.*, 1927, 2918; Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959; Ingold and Smith, *J.*, 1938, 905; Bird and Ingold, *J.*, 1938, 918; Bordwell and Rohde, *J. Amer. Chem. Soc.*, 1948, **70**, 1191; Ingold and Shaw, *J.*, 1949, 575). The numerical results vary with the conditions, but are not very sensitive to them; so that the following statements may be taken as approximately true over a considerable range of temperatures and nitrating media. Toluene is attacked 24 times faster than benzene, fluoro- and iodo-benzene 6 times more slowly than benzene, chloro- and bromo-benzene 30 times more slowly than benzene, and ethyl benzoate 300 times more slowly than benzene. Qualitatively we know that benzenesulphonic acid is attacked still more slowly, and nitrobenzene even more slowly. Thus the relative effects of substituents in activating or deactivating the benzene nucleus towards this type of attack is expressed by the following sequence :



There is reason to believe that, within fairly wide limits, these relationships will hold qualitatively for polysubstituted benzenes; so that, for instance, *p*-xylene is attacked more rapidly than toluene, and *p*-dichlorobenzene more slowly than chlorobenzene. We shall later confirm this expectation by means of rate-constants applying to such examples.

(1.1) Observations on Kinetic Order.

(1.1.1) *Reaction Order in Sulphuric Acid.*—Before the inception of this work, a simple kinetic order for the nitration of aromatic compounds had been established for one solvent only, *viz.*, sulphuric acid. The nitration of benzene itself by nitric acid in sulphuric acid is too rapid for measurement; but in 1904 Martinsen found that the nitration of nitrobenzene in this medium was a straightforward reaction of the second order (*Z. physikal. Chem.*, 1904, **50**, 385); and he later obtained the same result for several other benzene derivatives, such as 2 : 4-dinitrotoluene and the three nitrobenzoic acids (*ibid.*, 1907, **59**, 605). This result has been confirmed by all subsequent investigators. Klemenc and Schöller observed second-order kinetics for the nitration, in sulphuric acid, of several more benzene derivatives, such as 2 : 4-dinitro-*m*-xylene and the chloronitrobenzenes (*Z. anorg. Chem.*, 1924, **141**, 231). Lauer and Oda established corresponding kinetics for the nitration of anthraquinone (*J. pr. Chem.*, 1936, **144**, 176; *Ber.*, 1936, **69**, 1061); as did Oda and Ueda for the nitration of a number of substituted anthraquinones (*Bull. Inst. Phys. Chem. Res., Japan*, 1941, **20**, 335). Westheimer and Kharasch, besides confirming a number of the earlier results, have established second-order kinetics for the nitration in sulphuric acid of some additional nitro-substituted benzenes, and also of some derivatives of benzoic acid and benzenesulphonic acid (*J. Amer. Chem. Soc.*, 1946, **68**, 1871). Bennett, Brand, James, Saunders, and Williams have supplied further confirmation of Martinsen's observation that the nitration of 2 : 4-dinitrotoluene in sulphuric acid is a second-order process (*J.*, 1947, 474).

The general conclusion from all this work may be epitomised thus :

$$\left. \begin{array}{l} \text{Rate in H}_2\text{SO}_4 = k_2[\text{HAr}][\text{HNO}_3] \\ \text{[Shown for nitro-substituted benzenes, for benzoic and benzenesulphonic} \\ \text{acids, and for anthraquinones (lit.)]} \end{array} \right\} \cdot \cdot (1)$$

(1.1.2) *Reaction Order in Nitric Acid.*—With the above conclusion we can associate one, which is derived in the present paper, concerning nitrations in which nitric acid is, not only the nitrating agent, but also the solvent. In these experiments the nitric acid was, of course, in constant concentration. The reactions were found to be of the first order with respect to the aromatic compound, and hence the kinetic equation for nitration in nitric acid is consistent with that given above for nitration by nitric acid in sulphuric acid.

The aromatic compounds studied were nitrobenzene, *p*-chloronitrobenzene, and 1-nitroanthraquinone. The course of a typical run is shown in Fig. 1. From the linear fall with time shown by the logarithm of the concentration of the compound undergoing nitration, it is evident that the first-order rate-law is well obeyed.

Some first-order rate constants for nitration in nitric acid are reported in Table I: other values will be found in Tables VII, XII, XIV, and XXIII, on pp. 2414, 2417, 2418, and 2433 respectively.

TABLE I.

First-order rate constants (k_1 in sec^{-1}) for nitration in nitric acid.

Expt.		$[\text{HNO}_2]$.	Temp.	$[\text{HAr}]_0$.	$10^5 k_1$.
410	Nitrobenzene	0.0015	-13.3°	0.20	547
560	<i>p</i> -Chloronitrobenzene	0.03	+20.0°	0.15	1.37
571	1-Nitroanthraquinone	0.0055	+20.0°	0.24	248

Nitrating solutions nearly always contain what for convenience we call "nitrous acid" and symbolise HNO_2 , that is, lower oxides of nitrogen and all other materials which in the water-diluted solution are collectively estimated as nitrous acid. In most conditions this nitrous acid has a definite (usually a negative) catalytic effect, and therefore it is necessary to include its concentration among the particulars which must be specified when quoting rate constants.

FIG. 1.

Nitration in nitric acid: general kinetic form (illustrated by Expt. 411 on the nitration of nitrobenzene at -13.3°).

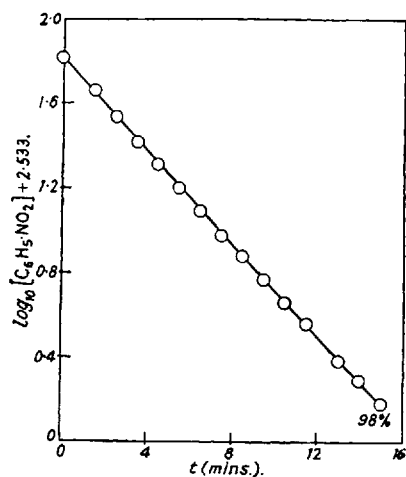
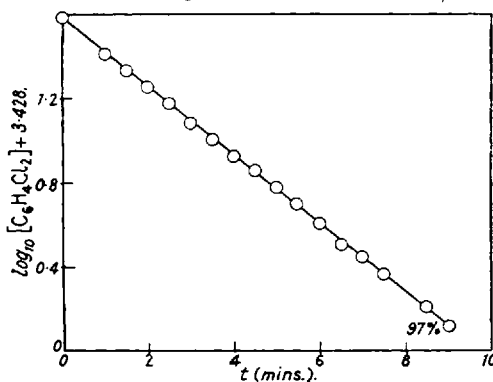


FIG. 2.

Nitration in nitromethane. First-order kinetic form (illustrated by Expt. 301 on the nitration of *p*-dichlorobenzene by 8.5M-nitric acid at 20.0°).



This is done in Table I, and in all the later tables of this paper. But in the experiments of Table I the concentrations of nitrous acid were too small to have significant effects on the rate constants, excepting possibly in the experiment on *p*-chloronitrobenzene.

In the example of 1-nitroanthraquinone we investigated the effect of adding sulphuric acid to the medium, thus tracing part of the transition from a nitric acid to a sulphuric acid solvent. This increased the reaction rate, as we shall note in more detail later; but, the nitric acid being always in constant excess, it made no difference to the reaction order. Moderate additions of water, of certain salts, including nitrates, and of nitrous acid also made no difference to the reaction order.

Thus our general result for nitric acid solvents may be summarised as follows:

$$\left. \begin{array}{l} \text{Rate in } \text{HNO}_3 = k_1[\text{HAr}] \quad ([\text{HNO}_2] = \text{constant}) \\ \text{[Shown for nitrobenzene, } p\text{-chloronitrobenzene and 1-nitroanthraquinone} \\ \text{(this paper).]} \end{array} \right\} \quad \cdot \cdot \quad (2)$$

(1.1.3) *Reaction Orders in Nitromethane.*—The first well-defined kinetic results in any solvent other than sulphuric acid were those reported in Part I (Benford and Ingold, *loc. cit.*). With nitromethane as solvent and nitric acid in constant excess, zeroth-order kinetics were demonstrated for the nitration of benzene and two of its homologues. This means that nitration proceeds at an undiminished rate until the original substance is exhausted, when the reaction has to cease abruptly. Such insensitiveness of the rate to the concentration of the aromatic compound seems to imply an insensitiveness to the nature of the compound, and within limits

this was confirmed: in the same medium and at the same temperature, benzene, toluene, and ethylbenzene were all nitrated at an identical rate:

$$\left. \begin{array}{l} \text{Rate in Me}\cdot\text{NO}_2 = k_0 \quad ([\text{HNO}_3] = \text{constant}) \\ \text{[Shown for benzene, toluene, and ethylbenzene (Part I).]} \end{array} \right\} \dots \dots (3)$$

These relationships appear to be restricted to benzene and those derivatives of benzene, which, if tested by the competition method, would be found to be attacked by nitrating agents more rapidly than benzene. The relationships do not hold for those aromatic compounds which, by the competitive test, would be found to be substantially less reactive than benzene. This was illustrated in Part I with reference to the four halogenobenzenes. These compounds divide themselves into two pairs, just as they do in the rate series based on the competition test. In nitromethane solution with nitric acid in constant excess, fluoro- and iodo-benzene are nitrated at nearly identical rates, which are rather smaller than the common rate applying to benzene, toluene, and ethylbenzene; and the rates for fluoro- and iodo-benzene are not quite constant, but depend slightly on the concentration of the halogeno-compound, the degree of dependence increasing towards the end of reaction. For chloro- and bromo-benzene the rates are again nearly identical, but are notably smaller than for the other two halogeno-compounds; and they now have a greater degree of dependence on the concentration of the halogeno-compound, this dependence increasing nearly to proportionality towards the end of reaction.

Benford and Ingold interpreted these results as indicating kinetics having intermediate character between two simple limiting forms. One limiting form was obviously to be identified with the zeroth-order kinetics which had been established for benzene and two of its homologues. Corresponding to their distribution in the rate series, fluoro- and iodo-benzene took positions fairly close to this limit, while chloro- and bromo-benzene occupied more remote places, nearer the other limit. This second limiting form was hypothetically identified with a first-order type of kinetics, which was assumed to be observable for nitration in nitromethane with still less reactive aromatic compounds, but which Benford and Ingold did not in fact observe directly:

$$\left. \begin{array}{l} \text{Rate in Me}\cdot\text{NO}_2: \text{intermediate between (3) and (5)} \\ \text{[Shown for the four halogenobenzenes (Part I).]} \end{array} \right\} \dots \dots (4)$$

We have confirmed this identification of the second limiting kinetic form by isolating it—how completely can be seen from the example represented in Fig. 2. To achieve this result, all that was necessary was to reduce further the reactivity of the aromatic ring, as it would appear in experiments on competitive nitration, by the introduction of a second halogen atom. The linear time-dependence of the logarithm of the concentration of the substance undergoing nitration shows the reaction to be of the first order.

Some first-order rate constants for *p*-dichlorobenzene and 1:2:4-trichlorobenzene are given in Table II. Other values for the former substance will be found in Tables XI and XXI on pp. 2416 and 2431, respectively. These reactions are sensitive to anti-catalysis by nitrous acid, even at the lowest concentrations here recorded. However, the kinetic order remains unaffected by changes in the concentration of the nitrous acid, or of the nitric acid, within the range of our experiments.

TABLE II.
First-order rate constants (k_1 in sec^{-1}) for nitration in nitromethane.

Expt.	Har.	$[\text{HNO}_3]$.	$[\text{HNO}_2]$.	Temp.	$[\text{Har}]_0$.	$10^5 k_1$.
165	<i>p</i> -Dichlorobenzene	8.5	0.0135	10.0°	0.20	165
166	"	"	"	19.9	"	371
150	"	"	0.0240	20.0	0.10	367
301	"	"	0.0018	"	"	649
300	"	"	"	"	0.17	617
299	1:2:4-Trichlorobenzene	"	"	"	0.10	54.4
156	<i>p</i> -Dichlorobenzene	11.5	0.0269	"	"	2470

The fact that the first-order kinetic form of nitration, which, on deactivating the aromatic ring by successive chlorine substituents, is reached at *p*-dichlorobenzene, is not still transitional, but is a stable limiting kinetic form, is proved by introducing the third chlorine atom of 1:2:4-trichlorobenzene. This makes no difference to the first-order form of the reaction, although, as the rate-constants themselves establish, it does bring about a further reduction in the reactivity of the aromatic ring towards the nitrating agent.

Summarising this series of results in the form already used for other series, we have

$$\left. \begin{array}{l} \text{Rate in Me}\cdot\text{NO}_2 = k_1[\text{HAr}] \quad ([\text{HNO}_3] = \text{constant}) \\ \text{[Shown for } p\text{-di- and 1:2:4-tri-chlorobenzene (this paper).]} \end{array} \right\} \dots \dots (5)$$

(1.1.4) *Reaction Orders in Acetic Acid.*—Benford and Ingold thought that the kinetic forms that they had established for nitration in nitromethane, and, in particular, the zeroth-order kinetics followed by the nitration of benzene and its homologues, were dependent in a special way upon that solvent; but we have now observed all the same kinetic phenomena with acetic acid as the solvent. As compared with nitromethane, the use of acetic acid as solvent produces, not only reduced rates, but also a distinct shift in the distribution of the aromatic compounds among the different reaction orders. Thus, under the conditions we have used, the nitration of benzene itself in acetic acid is not invariably a reaction of zeroth order, as it is in nitromethane. With certain concentrations of nitric acid the reaction is nearly of zeroth order; but at other concentrations the deviations from zeroth-order kinetics are very appreciable; and at yet others they are large. However, the nitration of toluene is definitely of zeroth order over the whole of the investigated range of concentrations, and the same is true for all the higher homologues of benzene that we have examined, *viz.*, ethylbenzene, *p*-xylene, and mesitylene. Fig. 3 illustrates the general form of the kinetic results obtained for the nitration of the alkylated benzenes in acetic acid. The same form of curve is obtained for benzene itself provided that the concentration of nitric acid is above a certain minimum.

Some zeroth-order rate constants applying to nitrations in acetic acid are given in Table III. In Expts. 79 and 80, the concentration of nitric acid was made large in order to secure a zeroth-order reaction for benzene; and then, because of the high resulting rates, the concentration of

TABLE III.

Zeroth-order rate constants (k_0 in $\text{sec.}^{-1} \text{ g. mol.}^{-1}$) for nitration in 99.8% acetic acid.

Expt.	HAr.	[HNO ₃].	[HNO ₂].	Temp.	[HAr] ₀ .	10 ⁴ k ₀ .
79	Benzene	12.4	0.497	10.7°	0.35	97
80	Toluene				0.33	103
54	“	7.0	0.0024	20.0	0.20	6.28
55	“	“	0.0044	“	0.10	6.43
60	“	“	0.0050	“	0.10	5.90
53	“	“	0.0060	“	0.05	6.50
56	Ethylbenzene	“	0.0027	“	0.04	6.00
61	“	“	0.0046	“	0.10	6.20
57	“	“	0.0143	“	0.10	5.65
62	<i>p</i> -Xylene	“	0.0046	“	0.10	6.17
51	“	“	0.0192	“	0.07	5.70
50	Mesitylene	“	0.0037	“	0.05	5.63
63	“	“	0.0046	“	0.10	5.62
52	“	“	0.0073	“	0.09	5.48
48	<i>p</i> -Xylene	5.0	0.0096	“	0.06	0.433
49	Mesitylene	“	0.0137	“	0.07	0.417

nitrous acid was also made unusually large in order to bring the rates down to values which could be measured conveniently. In all the other experiments of Table III the kinetic effect of nitrous acid is small if not negligible.

The most severe test for a zeroth-order reaction is that the rate shall be independent, not only of the concentration of the substance nitrated, but also of the nature of that substance, provided that the nitration medium and temperature remain the same. Table III shows that this criterion is satisfied within the range of our experiments.

We may summarise these findings in the following statement:

$$\left. \begin{array}{l} \text{Rate in HOAc} = k_0 \quad ([\text{HNO}_3] = \text{constant}) \\ \text{[Shown conditionally for benzene, and generally for toluene, ethylbenzene,} \\ \quad p\text{-xylene, and mesitylene (this paper).]} \end{array} \right\} \dots \dots (6)$$

When the kinetics of the nitration of benzene in acetic acid containing nitric acid in constant excess differ appreciably from those of a zeroth-order reaction, the deviation is always in the direction of one which would be caused by an admixed first-order reaction; and the first-order character becomes more marked towards the end of reaction. Fig. 4 illustrates the course of a nitration of benzene in acetic acid with such a concentration of nitric acid that the deviation

from zeroth-order kinetics is large. In order to show the character of the deviation, both the concentration of the benzene and the logarithm of its concentration have been plotted against time. Though the reaction has no definite kinetic order, a resemblance to first-order kinetics can be recognised: a quoted first-order rate constant, based on the latter part of the reaction, would have some rough significance.

FIG. 3.

Nitration in acetic acid. Zeroth-order kinetic form (illustrated by Expt. 57 on the nitration of ethylbenzene by 7M-nitric acid at 20.0°).

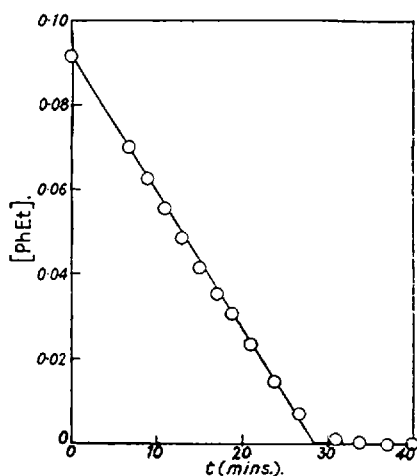


FIG. 5.

Nitration in acetic acid. Nearly complete transition to first-order kinetics (illustrated by Expt. 176 on the nitration of chlorobenzene by 10.0M-nitric acid at 20.0°).

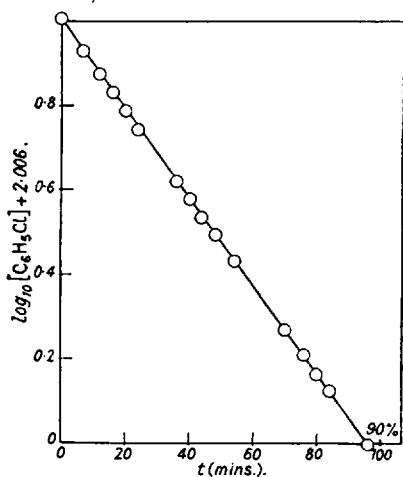


FIG. 4.

Nitration in acetic acid. Mixed-order kinetics (illustrated by Expt. 110 on the nitration of benzene by 9.7M-nitric acid at 20.0°).

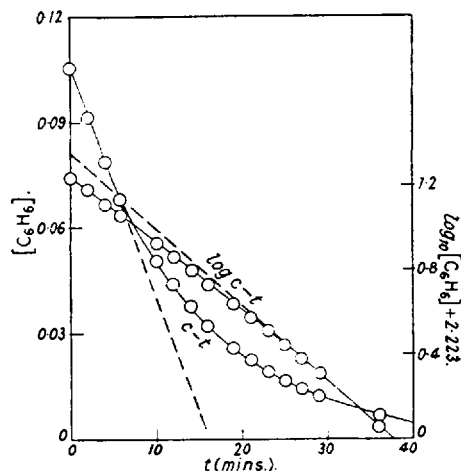
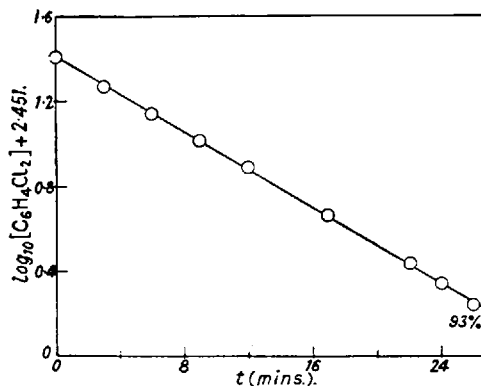


FIG. 6.

Nitration in acetic acid. First-order kinetic form (illustrated by Expt. 164 on the nitration of p-dichlorobenzene with 12M-nitric acid at 19.9°).



Kinetically, the nitration of benzene in acetic acid is somewhat similar to that of fluoro- or of iodo-benzene in nitromethane. The nitration of these two halogenobenzenes in acetic acid, containing a constant excess of nitric acid, follows a kinetic form which is intermediate between zeroth and first order, but under most conditions, and especially towards the end of reaction, is close enough to the latter to give approximate significance to a quoted first-order

rate constant. Thus the nitrations of fluoro- and iodo-benzene in acetic acid are kinetically rather similar to the nitrations of chloro- and bromo-benzene in nitromethane. The nitrations of the last two halogenobenzenes in acetic acid, containing a constant excess of nitric acid, follow first-order kinetic forms in fairly close approximation, as is illustrated for chlorobenzene by the linearity of the logarithmic plot in Fig. 5. The fact that the reaction order is still not quite integral can, however, be shown by comparisons among first-order rate constants derived from experiments, similar to that illustrated, but with different initial concentrations of the halogenobenzene.

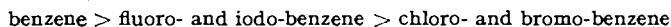
Table IV contains a number of approximate first-order rate constants computed for such mixed-order nitrations of benzene and the halogenobenzenes in acetic acid as have kinetic forms sufficiently close to that of a first-order reaction to allow such a representation. Other similar values for chlorobenzene will be found in Table XXII on p. 2432.

TABLE IV.

Approximate first-order rate-constants (k_1 in sec.^{-1}) for mixed-order nitrations in 99.8% acetic acid.

Expt.	HAr.	[HNO ₃] ₀	[HNO ₂] ₀	Temp.	[HAr] ₀	10 ⁴ k ₁
Series A :						
120	Benzene	8.0	0.0015	20.0°	0.10	118
257	"	"	0.0035	"	0.10	126
124	"	"	0.0042	"	0.10	113
262	Fluorobenzene	"	small	"	0.10	30
264	"	"	small	"	0.10	30
259	"	"	0.0041	"	0.10	26
252	"	"	0.0043	"	0.16	25
267	Iodobenzene	"	0.0039	"	0.10	30
266	"	"	0.0043	"	0.10	27
258	"	"	0.0057	"	0.16	27
256	"	"	0.0072	"	0.10	29
Series B :						
277	Fluorobenzene	9.0	0.0043	20.0	0.10	114
278	"	"	"	"	0.20	100
275	Iodobenzene	"	"	"	0.10	137
274	Chlorobenzene	"	"	"	0.10	52
271	Bromobenzene	"	"	"	0.10	45
279	"	"	"	"	0.20	39
Series C :						
293	Chlorobenzene	10.0	0.0022	20.0	0.05	365
291	"	"	"	"	0.10	325
292	"	"	"	"	0.23	294
294	"	"	"	"	0.30	281
Series D :						
108	Benzene	9.7	0.457	20.0	0.10	167
107	"	"	"	"	0.17	137
105	"	"	"	"	0.17	133
110	"	"	"	"	0.21	124
109	"	"	"	"	0.30	85
113	"	"	"	"	0.34	75

The experiments of Series A and B in Table IV show that benzene and the halogenobenzenes arrange themselves with reference to nitration rate into three groups, as follows:



The grouping is the same as in Benford and Ingold's kinetic experiments in nitromethane, and the same as in Bird and Ingold's comparisons by the competition method (*loc. cit.*).

The data of Series C in Table IV show that the nitration of chlorobenzene in 10M-nitric acid is not accurately a reaction of the first order. No doubt it would be very nearly of first order in sufficiently dilute solution; but as the initial, and therefore the average, concentration of the aromatic compound is increased in successive experiments, the average reaction-order falls, and therefore the computed average first-order rate constant falls. This is consistent with the observation that, in any one experiment, the instantaneous reaction-order rises as the

concentration of the chlorobenzene falls towards the end of the experiment. The figures of Series D show the same thing for the nitration of benzene in 9.7M-nitric acid. As Fig. 4 illustrates, this reaction is certainly not accurately obeying a first-rate law.

We may express these findings in a summarising statement, as follows :

$$\left. \begin{array}{l} \text{Rate in HOAc : Intermediate between (6) and (8)} \\ \text{[Shown for benzene and the four halogenobenzenes (this paper).]} \end{array} \right\} \dots (7)$$

As was explained above, one of the two limits which bound this range of intermediate kinetic forms, *viz.*, the zeroth-order form, has been established as a stable limit for nitration in acetic acid by the study of benzene homologues containing from one to three activating alkyl groups. The other limit, *viz.*, the first-order form of reaction, has been similarly established as a stable limit by the study of benzene derivatives containing from one to three deactivating chlorine substituents. The same first-order form is preserved in the presence of the more strongly deactivating carbethoxyl substituent. In acetic acid, with nitric acid in constant excess, the nitrations of *o*-, *m*-, and *p*-dichlorobenzene, of 1 : 2 : 4-trichlorobenzene, and of ethyl benzoate, all display first-order kinetics. The course of a typical run is shown as the usual logarithmic plot in Fig. 6.

A number of first-order rate constants for nitration in acetic acid are assembled in Table V. The rates show that the three chlorine atoms successively introduced in the chlorinated benzenes studied exert deactivating effects, which, although not equal to one another, are of the same order of magnitude. They show also that the deactivating effect of a carbethoxyl group is of the order of that of two chlorine atoms.

TABLE V.

First-order rate constants (k_1 in sec.^{-1}) for nitrations in 99.8% acetic acid.

Expt.	Har.	[HNO ₃]	[HNO ₂]	Temp.	[Har] ₀	10 ⁵ k ₁
282	<i>o</i> -Dichlorobenzene	10.5	0.0029	20.0°	0.10	25.7
283	<i>m</i> -Dichlorobenzene	"	"	"	"	49.8
281	<i>p</i> -Dichlorobenzene	"	"	"	"	20.0
280	Ethyl benzoate	"	"	"	"	15.5
161	<i>p</i> -Dichlorobenzene	12.0	0.0030	10.0	0.10	67.6
164	"	"	"	19.9	"	165
310	"	12.2	0.0034	20.0	0.10	223
311	1 : 2 : 4-Trichlorobenzene	"	"	"	"	18.0

The differences between the rates for the isomeric dichlorobenzenes, in particular the greater rate of nitration of *m*-dichlorobenzene than of its isomers, may possibly be correlated with the circumstance that both the chlorine atoms of *m*-dichlorobenzene are, like the single chlorine atom of chlorobenzene, in *ortho*- or *para*-positions with respect to the principal positions into which the nitro-group enters; whereas only one of the two chlorine atoms in *o*- or in *p*-dichlorobenzene, and only two of the three in 1 : 2 : 4-trichlorobenzene are in *ortho*- or *para*-positions with respect to the main positions in which nitration occurs in these substances. One chlorine atom in each of these three compounds necessarily occupies a *meta*-position with respect to the principal positions of nitration. From the orientational effects of halogens, one must expect deactivation by chlorine to be stronger in the *meta*-position than in other positions. On the other hand, the figures themselves show that the deactivating actions of the different chlorine atoms in the polysubstituted compounds are by no means independent of one another.

We summarise this group of the results in the following statement :

$$\left. \begin{array}{l} \text{Rate in HOAc} = k_1[\text{Har}] \quad ([\text{HNO}_3] = \text{constant}) \\ \text{[Shown for } o\text{-, } m\text{- and } p\text{-dichlorobenzene, 1 : 2 : 4-trichlorobenzene,} \\ \text{and ethyl benzoate (this paper).]} \end{array} \right\} \dots (8)$$

(1.2) Discussion (Part 1). The Kinetic Orders : Formation and Effectiveness of the Nitronium Ion.

(1.2.1) Significance of the Changes of Kinetic Order : The Nitronium Ion.—The following facts requires explanation. Nitration is rapid, and exhibits second-order kinetics in sulphuric acid (equation 1) : it is rather rapid, and exhibits first-order kinetics in nitric acid (equation 2). In the organic solvents, nitromethane and acetic acid, with nitric acid in constant excess, nitration is relatively slow; and it exhibits zeroth-order kinetics if the aromatic compound is

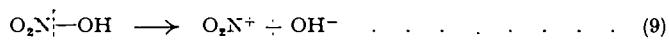
sufficiently reactive in electrophilic substitutions (equations 3 and 6), first-order kinetics if the aromatic compound is sufficiently unreactive in such substitutions (equations 5 and 8), and mixed zeroth-to-first-order kinetics for aromatic compounds having intermediate reactivity (equations 4 and 7).

The second-order nitration in sulphuric acid and the first-order nitration in nitric acid could be held to be consistent with many theories of mechanism. These kinetics indicate nitration either by the nitric acid molecule itself, or by any reactive entity whose concentration throughout nitration bears a constant ratio to the stoichiometric concentration of nitric acid. In the latter alternative, the nitrating entity might be formed nearly completely, partially, or in minute proportion; but it must be formed rapidly in comparison with the rate of its involvement in nitration. That is all that can be said on the basis of these particular kinetic results: they are of too normal a type to give any specific indication of mechanism.

On the other hand, the observation of zeroth-order kinetics for nitration in nitromethane and in acetic acid is highly significant. It has for nitration the same kind of importance as Lapworth's discovery of the first-order bromination of acetone had for prototropy, a general reaction which we now know to be rate-controlled by a protolysis. Again, the observation that, for nitration in these solvents, the kinetic order changes during a graded series of constitutional changes related to the reactivity of the aromatic molecule for electrophilic substitution, has the same significance for nitration as the discovery of a similar change of kinetic order, during a progressive change of alkyl structure in nucleophilic aliphatic substitution, had for the mechanism of that general reaction. In the latter case, the accepted interpretation is that the alkyl derivative undergoes a heterolysis which, if sufficiently facilitated by internal polar effects, becomes rate-determining for the substitution, independently of co-operation by the second reactant.

Apart from the lead given by these known analogies, the conclusion indicated by the changes of kinetic order is clear. Nitration depends on some preliminary process which does not involve the aromatic compound, and which, by the use of solvents such as nitromethane and acetic acid, can be made slow enough to be rate-determining, provided that a sufficiently reactive aromatic compound is employed. The preliminary change cannot be in the solvent, because solvents which have little in common with respect to their general chemistry behave similarly. Hence it must be in the nitric acid itself. Benford and Ingold's original assumption that, for nitration in nitromethane, the preliminary change consisted in the prototropic isomerisation of the solvent is easily shown to be incorrect. For if it were true, the rate of a zeroth-order nitration in nitromethane should be equal to the rate at which nitromethane would be brominated in identical conditions, apart from the replacement of the aromatic compound by bromine. Actually the former reaction is enormously faster than the latter. Further, the rates of the two processes are changed in opposite ways by changes in the concentration of nitric acid.

A measurably slow change in nitric acid cannot depend only on proton transfers, which are instantaneous in oxy-acids. Moreover, a slow, and therefore activated, process must involve the breaking of a bond. The orientation laws for nitration, and the effects of substitution on aromatic reactivity in competitive nitration, clearly establish that nitration is an electrophilic substitution. Hence the bond fission must be heterolytic, not homolytic; and hence, also, it must take such a direction as will yield an electrophilic nitrating agent—an entity having the appropriate atomic grouping with an electron-deficient nitrogen atom. Disregarding for the moment, as an easily adjustable detail, the distribution of instantaneously transferable protons, the fundamental heterolysis, the kinetic effect of which stands isolated in zeroth-order nitration, can only be the following:



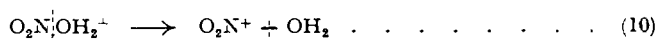
The active product for nitration is the *nitronium ion*, NO_2^+ , and the heterolysis which yields it is clearly analogous to the heterolysis which, in the chemistry of alkyl compounds, gives the alkyl cation, and stands kinetically isolated in unimolecular nucleophilic substitution and elimination. Our kinetic result is a demonstration, jointly, of the *formation and effectiveness of the nitronium ion*. Further demonstrations of its formation will be given in other papers of this group.

The idea that, in certain conditions of nitration, the actual nitrating agent might be the nitronium ion was advanced as early as 1903 by Euler (*Annalen*, 1903, **330**, 280). It has since been supported by Euler himself (*Z. angew. Chem.*, 1922, **35**, 580), by Walden (*ibid.*, 1924, **37**, 390), by Ri and Eyring (*J. Chem. Physics*, 1940, **8**, 433), by Price (*Chem. Rev.*, 1941, **29**, 51), by Kharasch and Westheimer (*J. Amer. Chem. Soc.*, 1946, **68**, 1871), by Bennett, Brand, and

Williams (*J.*, 1946, 869), by Norman Jones, Thorn, Lyne, and Taylor (*Nature*, 1947, **159**, 163), and by Norman Jones and Thorn (*Canadian J. Res.*, 1949, *B*, **27**, 580), but for the most part on evidence less direct than that offered in the present group of papers (and, of course, in our earlier summarising publications, *viz.*, *Nature*, 1946, **158**, 448, 480, 514). A fuller account of the history will be found in a recent article by Gillespie and Millen (*Quart. Reviews*, 1948, **2**, 277).

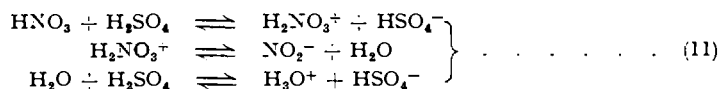
(1.2.2) *Preliminary Consideration of the Initial Proton Transfer.*—We shall allow our discussion of the proton transfers, which require to be associated with the above fundamental heterolytic process for the purpose of completing a representation of the reactions involved in the formation of the nitronium ion, to rest temporarily on general chemical arguments, reserving a more specific demonstration on the matter for treatment in Section (2.4.1) of this paper.

Consider the following analogy. In the formation of an alkyl cation from an alcohol in strongly acid conditions, a proton uptake certainly precedes heterolysis. This is shown by the acid catalysis of those substitutions, olefin eliminations, and Wagner rearrangements of which the starting substances are alcohols. The heterolysis leading to R^+ thus takes place, not in ROH itself, but in the alkyloxonium ion $R-OH_2^+$, doubtless because the group $-OH_2^+$ attracts electrons much more strongly than the group $-OH$. We shall almost certainly be correct if we assume that, analogously, a proton uptake precedes the formation of the nitronium ion, the actual heterolysis taking place, not in the nitric acid molecule itself, but in the derived oxonium cation. The heterolysis of system (10) must be much more facile than that of system (9), and thus it is highly plausible that equation (10) should represent the actual route by which the nitronium ion is produced :

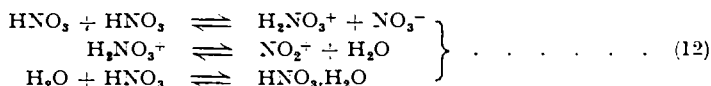


The reactive entity on the left of this equation is a form of the nitric acidium ion, $H_2NO_3^+$. It may not be the most prevalent form, which possibly has a more evenly distributed arrangement of the protons; but all the prototropic forms will be in mobile equilibrium, owing to the rapidity of proton migrations in oxy-acids; and the form represented above will certainly be that most prone to the particular heterolysis which yields the nitronium ion.

The proton which adds itself to a nitric acid molecule must be expected to come chiefly from the strongest acid present in sufficient quantity in the system. Hence the nature of the main process of proton transfer will be different according as there is, or is not, in the solution an acid which is stronger than nitric acid itself. Perchloric acid, sulphuric acid, and selenic acid are all stronger acids than nitric acid; and in the presence of a very strong acid, such as any of these, we may expect equilibria of the kind illustrated in equations (11) in the example of sulphuric acid:



On the other hand, in the absence of any acid stronger than nitric acid, the latter will itself take on the role of proton donor; and the resulting equilibria will be as follows :



Equations (12) take into account the known fact that no transfer of protons occurs on any considerable scale from nitric acid to small concentrations of water, and that, with nitric acid in large excess, the water forms a hydrogen-bond complex of considerable stability (Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722; cf. Gillespie and Millen, *loc. cit.*, p. 277).

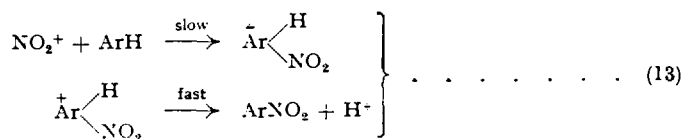
It has been shown that, in sulphuric acid, nitration is of the second order, that in nitric acid it is of the first order, and that in organic solvents it is still of the first order if the aromatic compound is sufficiently unreactive, but of zeroth order if the aromatic compound is sufficiently reactive. It has been made clear that the first three of these results could be accommodated to many theories of nitration, but that the fourth is sharply diagnostic of a preliminary heterolysis to the nitronium ion. However, the first three results are consistent with the same theory provided that due account is taken of the relative rates of formation and destruction of the nitronium ion in the different conditions.

In sulphuric acid, the nitronium ion is formed quickly and completely. Physical evidence concerning this is presented in accompanying papers (*J.*, 1950, papers nos. 499 and 500). The second-order kinetics of nitration in sulphuric acid are a necessary consequence of this situation.

In nitric acid, the nitronium ion is still formed rapidly, but now only in small equilibrium concentration. This can be estimated in various ways to be of the order of 1%, as is shown in Section (2.4.2) of this paper, and in accompanying papers (*J.*, 1950, papers nos. 504 and 510). It follows that the concentration of nitronium ion will remain constant during nitration in nitric acid, and that the reaction will thus exhibit first-order kinetics. In organic solvents, with nitric acid in constant excess, the situation is essentially the same so far as concerns the nitration of sufficiently unreactive aromatic compounds; for even though the small equilibrium concentration of nitronium ion may now be established much more slowly than before, the rate of its establishment is still, by the use of a sufficiently unreactive aromatic compound, rendered much larger than the rate at which the formed nitronium ion is consumed by the aromatic compound. Once again, the nitronium ion will be present in a stationary concentration, closely approximating to its equilibrium concentration, and first-order kinetics will result. But if, in those organic solvents in which the nitronium ion is only slowly formed, we nitrate a sufficiently reactive aromatic compound, this will immediately combine with the nitronium ion as the latter is produced. It follows that the rate of nitration will be equal to the rate of production of the nitronium ion, and this will be constant, if the nitric acid is in constant excess: thus the nitration will be of zeroth order.

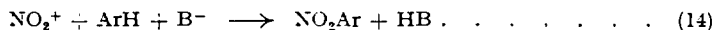
(1.2.3) *Preliminary Consideration of the Nitration by the Nitronium Ion.*—The consideration of this process involves another problem concerning proton movements, which we shall here discuss in an introductory manner in preparation for the more careful treatment to be given in Section (3.2). Two main types of mechanism are conceivable, which are as follows.

The first possibility is that, very quickly after the uptake of the nitronium ion, the aromatic proton is ejected into the solvent, there to be passed from molecule to molecule until it, or some proton displaced by it, eventually reaches its most stable situation in combination with the strongest available base. This is a two-stage process, of which the first stage is rate-determining. We may represent it by means of equation (13), calling it "bimolecular" since two original molecules are undergoing covalency change in the transition state of reaction:



In this mechanism the proton-loss has no kinetic significance: and there is no acceleration of the reaction by solute bases.

The second possibility may be developed from the same formulæ by regarding the first reaction as rapid and rapidly reversible, and by assuming that the resulting pre-equilibrium is followed by a slow, and therefore rate-determining, extraction of the aromatic proton by some sufficiently powerful base. Such a reaction may be called "termolecular": whether the transition state is built up by successive bimolecular encounters, or by a single termolecular encounter, it will contain three original species all undergoing covalency change, *viz.*, the nitronium ion, the aromatic molecule, and the necessary base (which might, *e.g.*, be a hydrogen sulphate, or a nitrate ion). Writing B⁻ for the base, this mechanism may, for all kinetic purposes, be expressed by the single equation (14):



This process is evidently base-accelerated; and the proton-loss has in this case definite kinetic importance.

We shall later develop the thesis that for nitration by nitric acid in sulphuric acid, nitric acid, nitromethane, and acetic acid solvents, the "bimolecular" mechanism (13) prevails (cf. Section 3).

(Discussion continued on p. 2419.)

(2) SOLUTE EFFECTS ON NITRATION KINETICS: MECHANISM OF FORMATION OF THE NITRONIUM ION.

(2.0) *Significance of the Kinetic Effects of Solutes.*—This Section brings together our work on the kinetic effects produced by three added substances in particular, *viz.*, sulphuric acid, potassium nitrate, and water. The reason for collectively treating the kinetic effects of these three solutes is that it is through their study that we have sought for evidence concerning the

nature of the reactions by which the nitronium ion is formed, on which nitration has been shown to depend. We may expect in this way to discover at what stage proton transfers enter into the process, at what stage nitrate ion appears in the sequence of changes, and at what stage water is produced, or, alternatively, such products as water would give by interaction with the medium; and from this information we may expect to be able to reconstruct the sequence of reactions. Following the presentation of our results on the solute effects mentioned, a discussion will be given along these lines.

There is a fourth solute the kinetic effects of which have been studied in some detail, *viz.*, nitrous acid. Because this work tends in a different direction, it is described and discussed in a later Section. The principal unknown here was the constitution of the nitrous acid, and it is mainly on this problem that the kinetic evidence bears.

(2.1) *Observations on the Kinetic Effects of Sulphuric Acid.*

(2.1.1) *Effect of Added Sulphuric Acid on Zeroth-order Rates of Nitration.*—Except for nitration in very strongly acidic solvents, such as sulphuric acid, and nitration in basic solvents such as water, the rule is general that small concentrations of added very strong acids, such as perchloric acid, sulphuric acid, or selenic acid, greatly increase rates of nitration. We have investigated this phenomenon quantitatively in the example of added sulphuric acid, treating both zeroth-order and first-order reactions.

Small concentrations of added sulphuric acid strongly accelerate zeroth-order nitrations, without detectably disturbing their zeroth-order form, within the range of our observations. This has been established for the nitrations of benzene and toluene in nitromethane as solvent, with several concentrations of nitric acid, and in the presence of various amounts of nitrous acid. The observed forms of acceleration are somewhat dependent on the proportion of nitrous acid present. Such forms are illustrated by reference to two series of experiments in Table VI. The rate constants of the first series are plotted as a function of the concentration of the added sulphuric acid in Fig. 7.

TABLE VI.

Effects of added sulphuric acid on zeroth-order rate constants (k_0 in $\text{sec.}^{-1} \text{g.-mol.l.}^{-1}$) for nitrations by nitric acid in nitromethane.

[HNO ₃] = 3.0M. Temp. = -10.0°.											
Expt.	H.Ar.	[HAr] ₀	[HNO ₂]	[H ₂ SO ₄]	10 ⁵ k ₀	Expt.	H.Ar.	[HAr] ₀	[HNO ₂]	[H ₂ SO ₄]	10 ⁵ k ₀
Series A :											
230	PhH	0.115	0.0034	none	0.103	236	PhH	0.115	0.0034	0.0329	4.71
235	"	"	"	"	0.104	233	"	"	"	0.0424	6.38
231	"	"	"	0.0053	1.05	232	"	"	"	0.0452	6.33
234	"	"	"	0.0206	3.10						
Series B :											
242	PhMe	0.150	0.0793	none	0.053	245	PhMe	0.150	0.0793	0.0631	1.41
244	"	"	"	0.0144	0.128	246	"	"	"	0.0842	1.86
243	"	"	"	0.0418	0.712						

When the nitrous acid is present in quantities greater than, or about equal to, the quantity of added sulphuric acid, it notably reduces the accelerative effect of the latter. This can be seen by comparing the rate constants of Series B in Table VI with those of Series A. It would appear that nitrous acid, if not too dilute, is able largely to destroy the catalytic effect of an amount of sulphuric acid comparable to its own amount. However, nitrous acid, when present in quite dilute solution, and in quantities considerably smaller than the quantities of added sulphuric acid, has no significant influence on the kinetic effect of the latter; and it is in these conditions that the linear relation appears, which is illustrated in Fig. 7. Although the quantity of nitrous acid, in the experiments here represented, is too small seriously to influence the rates obtained in the presence of sulphuric acid, it is sufficient to reduce the rates in the comparison experiments without added sulphuric acid by about one-third. However these rates are so small in comparison with the catalysed rates that the effect mentioned does not upset the general linearity shown.

A similar plot of the results of Series B would furnish a curve, which, as compared with the curve of Fig. 7, is much more nearly horizontal, and is distinctly concave to the rate axis. This illustrates the effect of increasing the concentration of nitrous acid. It can be understood on the basis that nitrous acid inactivates a certain amount of sulphuric acid by reacting with it, nearly completely when the acid is in deficit, but only partly when the acid is in excess.

Therefore we take the most significant result of these experiments to be the linear catalysis illustrated by Series A. Two factors probably contribute to the simplicity of the result: one is that the concentration of added sulphuric acid is small; and the other is that the total catalytic effect is large, *i.e.*, that the catalysed rates are many times larger than the uncatalysed.

The sensitivity of the reaction to catalysis by sulphuric acid may be specified by stating that a 0.001M-concentration of the acid doubles the rate. This figure assumes the absence of disturbances by nitrous acid, a correction having been applied for the effect of nitrous acid on the rate of the uncatalysed reaction in the experiments of Series A.

(2.1.2) *Effect of Added Sulphuric Acid on First-order Rates of Nitration.*—Like zeroth-order nitrations in nitromethane, first-order nitrations are accelerated notably by small concentrations of added sulphuric acid, without detectable disturbance to the kinetic form of the reaction. It has been found that in all qualitative respects the effect of sulphuric acid on first-order reactions is closely parallel to its effect on zeroth-order reactions under similar conditions.

Considerable quantitative differences appear in the effect as it applies to first-order nitrations with nitric acid as both solvent and reagent. In these conditions there are no known zeroth-

FIG. 7.

Effect of sulphuric acid on zeroth-order nitration rates: nitration of benzene by 3M-nitric acid in nitromethane at -10.0° .

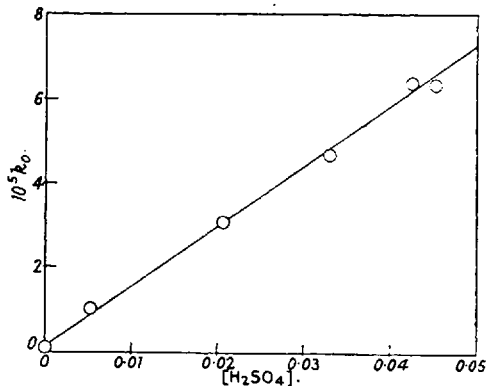
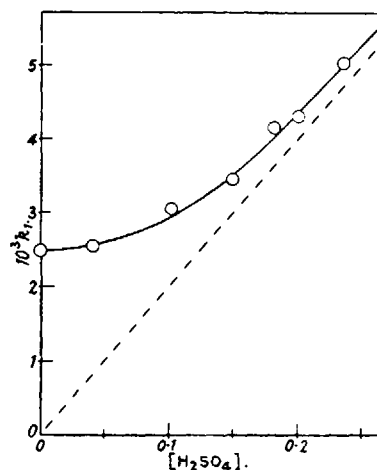


FIG. 8.

Effect of sulphuric acid on first-order nitration rates: nitration of 1-nitroanthraquinone in nitric acid at 20.0° .



order reactions for comparison. In illustration of the effect, we give in Table VII a series of first-order rate constants for the nitration of 1-nitroanthraquinone in nitric acid, with and without added sulphuric acid.

TABLE VII.

Effect of added sulphuric acid on first-order rate constants (k_1 in sec^{-1}) for the nitration of 1-nitroanthraquinone in nitric acid at 20.0° .

Expt.	[C ₁₄ H ₇ O ₄ N] ₀	[HNO ₂]	[H ₂ SO ₄]	10 ⁵ k ₁	Expt.	[C ₁₄ H ₇ O ₄ N] ₀	[HNO ₂]	[H ₂ SO ₄]	10 ⁵ k ₁
571	0.0241	0.0055	none	248	575	0.0238	0.0065	0.176	419
572	0.0263	0.0085	0.044	253	576	0.0255	0.0150	0.201	431
573	0.0252	0.0090	0.101	309	577	0.0260	0.0070	0.234	503
574	0.0252	0.0097	0.147	343					

In these experiments the influence of nitrous acid is small enough to be neglected. A plot of the rate constants against the concentration of sulphuric acid is shown in Fig. 8. Evidently, added sulphuric acid accelerates the reaction. But in proportion to the uncatalysed rate, the observed accelerations are much smaller than those found for nitrations in nitromethane, when in this solvent effects of nitrous acid may be neglected. In particular, the concentration of sulphuric acid which is required in order to double the rate in nitric acid is 0.23M, *i.e.*, it is about 200 times greater than in the experiments in nitromethane already quoted.

As Fig. 8 shows, the accelerations observed in solvent nitric acid are far from linear. The sensitivity of the reaction to the catalysis is small at low catalyst concentrations, but it rises as the concentration of sulphuric acid increases. In the upper part of the investigated range of

concentrations, we find some approach to linear acceleration, and this leads us to think that the form of the catalysis in nitric acid is not different in principle from the form observed in nitromethane. We assume that, if the curve of Fig. 8 could be continued, without losing simplifying effects due to the dilution of the sulphuric acid, until the catalysed reaction were many times faster than the uncatalysed, then the total curve would be linear over nearly all its length, like the curve in Fig. 7; and that, if the magnified lower extremity of the curve of Fig. 7 could be investigated sufficiently minutely, it would be found to turn before meeting the rate axis, like the curve of Fig. 8. We shall discuss these assumed relationships later [Section (2.4.2)].

(2.2) *Observations on the Kinetic Effects of Nitrates.*

(2.2.1) *The General Salt Effect and the Specific Nitrate Ion Effect.*—Exploratory experiments have shown that an appreciable general salt effect influences both zeroth- and first-order nitration in nitromethane. The effect is exerted typically by the alkali-metal salts of very strong acids—salts such as potassium perchlorate and potassium hydrogen sulphate. The effect is accelerative, as we should expect if it be a primary salt effect, bearing in mind the general parallelism between primary salt effects and solvent effects, and the known direction of the solvent influence on nitration rate. However, this salt effect is small; in particular, it is small enough to be neglected in comparison with the specific salt effect next to be mentioned.

The specific effect has been established for a number of alkali-metal and ammonium nitrates. It consists in a strong negative catalysis. It has been observed to influence both zeroth-order and first-order nitrations, without detectably disturbing the kinetic form of either. This anticatalytic behaviour seems to be specific to nitrates; and the cation of the salt appears to have very little concern with the effect, which we presume to originate in the nitrate ion itself.

Data for some of the exploratory runs are given in Table VIII: they refer to the zeroth-order nitration of toluene in nitromethane. Though the disturbances caused by the nitrous acid are not inappreciable, the figures given suffice to show the direction and relative magnitude of the two salt effects. They show, for instance, that whilst the increase of rate produced by 0.01M-potassium perchlorate is only just detectable, a similar concentration of lithium or potassium nitrate will reduce nitration rate by factors of the order of one-half.

TABLE VIII.

Effects of certain salts on the zeroth-order rate constants (k_0 in $\text{sec.}^{-1} \text{g.} \cdot \text{mol.}^{-1}$) of nitration of toluene in nitromethane.

[HNO ₂] = 7.0M. Temp. = -10.0°.											
Expt.	[HNO ₂]	[C ₇ H ₈] ₀	Salt.	[Salt]	10% <i>k</i> ₀	Expt.	[HNO ₂]	[C ₇ H ₈] ₀	Salt.	[Salt]	10% <i>k</i> ₀
202	0.0046	0.100	none	—	9.78	206	0.0043	0.093	LiNO ₃	0.0084	6.02
204	"	"	KClO ₄	0.0107	10.30	212	0.0070	"	KNO ₃	0.0123	4.30
207	"	"	KNO ₃	0.0065	6.58						

In the course of our work on the kinetics of nitration in acetic acid, we made an attempt to eliminate the disturbing effect of nitrous acid by the addition of urea. Since nitrous acid depresses nitration rates, the expectation was that the addition of urea would lead to a larger rate. Actually it led to a smaller rate, as is shown in Table IX. We concluded that urea nitrate was producing an anticatalytic effect stronger than that of the original nitrous acid. It was clear that the effect must be powerful, because urea nitrate is only slightly soluble in acetic acid. We assume the effect to be due to the nitrate ion.

TABLE IX.

Effect of urea nitrate on first-order rate constants (k_1 in sec.^{-1}) for the nitration of benzene in acetic acid.

Expt.	[HNO ₂]	[HNO ₂]	[C ₆ H ₆] ₀	Temp.	CH ₃ O ₄ N ₂	10% <i>k</i> ₁
401	7.8	0.0013	0.10	0.0°	none	37.9
400	"	none	"	"	saturated	18.1

Acetic acid is a poor solvent for alkali-metal nitrates. In the more detailed study of the nitrate-ion effect now to be described, we therefore investigated nitration in nitromethane, or in nitric acid itself, finding them more convenient than acetic acid as solvents for the salts employed.

(2.2.2) *Effect of Added Potassium Nitrate on Zeroth-order Rates of Nitration.*—The form of the effect of added potassium nitrate on the rate of a zeroth-order nitration may be illustrated by the block of experiments recorded in Table X, which relates to the nitration of toluene by

7M-nitric acid in nitromethane. The disturbances caused by the small amounts of nitrous acid, which were present in the solutions, are negligible in relation to the effect under observation. The anticatalytic effect of the potassium nitrate is evidently powerful, a 0.004M-concentration being sufficient to halve the reaction rate.

TABLE X.

Effect of added potassium nitrate on the zeroth-order rate constants (k_0 in $\text{sec.}^{-1}\text{g.}\cdot\text{mol.l.}^{-1}$) for the nitration of toluene in nitromethane.

$[\text{HNO}_3] = 7.0\text{M}$. $[\text{HNO}_2] = 0.0013\text{--}0.0024\text{M}$. (extreme values).

$[\text{C}_6\text{H}_5]_0 = 0.09\text{M}$. Temp. = -10.0° .

Expt.	$[\text{KNO}_3]$.	10^3k_0 .	Expt.	$[\text{KNO}_3]$.	10^3k_0 .	Expt.	$[\text{KNO}_3]$.	10^3k_0 .
581	none	8.93	584	0.02312	2.18	587	0.1124	1.57
591	"	8.85	585	0.02702	2.23	588	0.2799	1.30
582	0.00346	4.78	586	0.04306	1.87	589	0.6302	0.94
583	0.00587	3.89						

A plot of the reciprocal of the rate against the concentration of the added salt is shown in Fig. 9. The reason for choosing this particular form of graphical representation will be

FIG. 9.

Effect of potassium nitrate on zeroth-order rates of nitration of toluene by 7M-nitric acid in nitromethane at -10.0° .

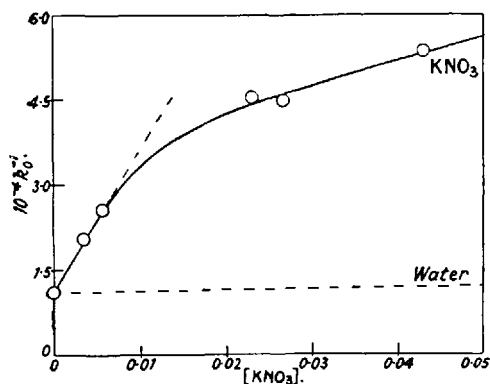
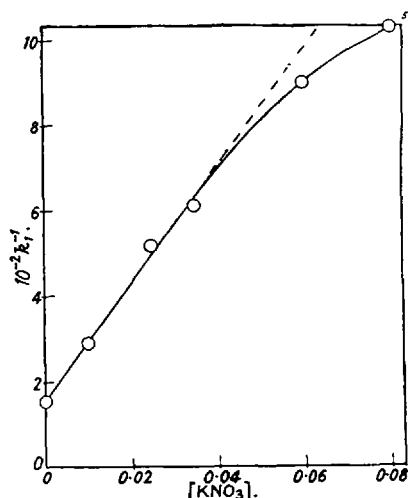


FIG. 10.

Effect of potassium nitrate on first-order rates of nitration of *p*-dichlorobenzene by 8.5M-nitric acid in nitromethane at 20.0° .



explained later. The results are consistent with the idea, to which other groups of experiments point more definitely, that in the low concentration range the effect of the added salt on the reciprocal of the rate is asymptotically linear.

Added water is well known to reduce nitration rates. The broken line near the bottom of the diagram represents the effect of replacing the added potassium nitrate by its molecular equivalent of added water. It will be seen how much more sensitive the rate is to potassium nitrate than it is to water. We shall return to this point later [Section (2.4.1)].

(2.2.3) *Effect of Added Potassium Nitrate on First-order Rates of Nitration.*—The form of the effect of added potassium nitrate on the rate of a first-order nitration is illustrated by the block of experiments recorded in Table XI. They relate to the nitration of *p*-dichlorobenzene by

TABLE XI.

Effect of added potassium nitrate on the first-order rate constants (k_1 in sec.^{-1}) for the nitration of *p*-dichlorobenzene in nitromethane.

$[\text{HNO}_3] = 8.5\text{M}$. $[\text{H}_2\text{O}]_0 = 0.3\text{M}$. $[\text{C}_6\text{H}_4\text{Cl}_2]_0 = 0.10\text{M}$. $[\text{HNO}_2] = 0.008\text{M}$. Temp. = 20.0° .

Expt.	$[\text{KNO}_3]$.	10^3k_1 .	Expt.	$[\text{KNO}_3]$.	10^3k_1 .	Expt.	$[\text{KNO}_3]$.	10^3k_1 .
301	none	649	303	0.0250	193	306	0.0606	111
307	0.0100	348	302	0.0349	164	305	0.0809	97

means of 8.5M-nitric acid in nitromethane. The disturbance caused by the nitrous acid present in these experiments is negligible in relation to the effect under observation.

The relation between the reciprocal of the first-order rate constant and the concentration of the salt is shown graphically in Fig. 10. The result is somewhat similar to that obtained in the corresponding representation of zeroth-order rates shown in Fig. 9; but there are two differences. For the first-order reactions, the linear relation between the reciprocal of the rate-constant and the concentration of the salt holds up to a larger salt concentration, *viz.*, 0.05M. Also the sensitivity of the first-order reactions to the effect of nitrates is smaller, a salt concentration of 0.01M. being needed to halve the rate constant.

When the concentration of the nitric acid is increased until the acid is essentially the solvent as well as the nitrating agent, the nitration rates are still reduced by added potassium nitrate,

FIG. 11.

Effect of potassium nitrate in first-order rates of nitration of nitrobenzene in nitric acid at 0.0°.

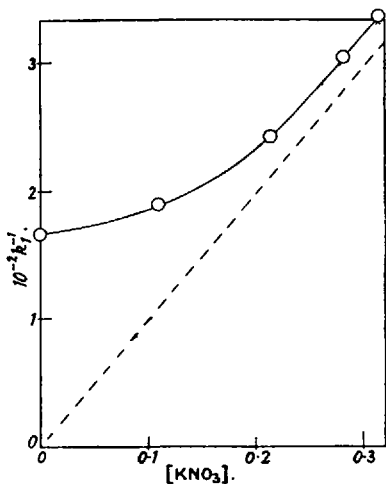
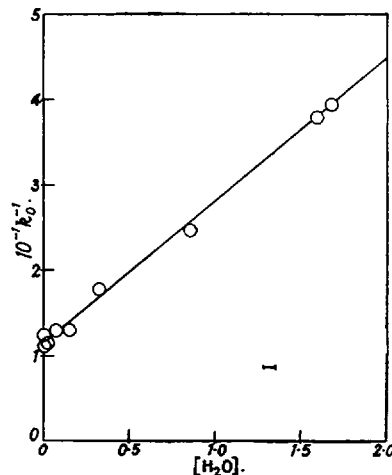


FIG. 12.

Effect of water on zeroth-order rate of nitration of toluene by 7M-nitric acid in nitromethane at -10.0°.



but the quantitative aspect of the effect is changed. Some data referring to first-order nitrations of nitrobenzene in nitric acid are given in Table XII.

TABLE XII.

Effect of added potassium nitrate on first-order rate constants (k_1 in sec^{-1}) for the nitration of nitrobenzene in nitric acid.

[H ₂ O] ₀ = 2.5M. [HNO ₂] = 0.02M. [C ₆ H ₅ O ₂ N] ₀ = 0.215M. Temp. = 0.0°.							
Expt.	[KNO ₃].	10 ² k ₁ .	Expt.	[KNO ₃].	10 ² k ₁ .	Expt.	[KNO ₃].
215	none	607	217	0.110	530	603	0.282
601	"	597	602	0.114	533	604	0.315
218	"	595	219	0.214	411		

In these experiments the influence of nitrous acid is negligible in comparison with that of potassium nitrate. This effect is, however, smaller by factors up to 80 than those shown in the preceding illustrations, a salt concentration of 0.31M. now being necessary in order to halve the first-order rate constant. Moreover, as Fig. 11 shows, the plot of the reciprocal of the rate constant against the concentration of potassium nitrate is far from linear in the low concentration range, although it seems to become asymptotically linear at the higher salt concentrations.

There are obvious resemblances between this reciprocal-rate curve for the anticatalytic effect of potassium nitrate, and the rate curve of Fig. 8 for the catalytic effect of sulphuric acid, on nitration in nitric acid. It is probably not accidental that the reciprocal-rate curve of Fig. 11 turns to meet the reciprocal-rate axis in the same concentration range as that in which the rate curve of Fig. 8 turns to meet the rate axis; that both curves converge towards straight lines through the origin in the higher concentration region; and that the concentration of

anticatalyst required to halve the rate of the anticatalysed reaction is nearly the same as the concentration of catalyst necessary to double the rate of the catalysed reaction.

In nitromethane solution also close similarities can be found between the effect of potassium nitrate on the reciprocal of the rate of nitration and that of sulphuric acid on the rate of nitration. Both effects apply to zeroth-order and first-order reactions alike, without disturbance to the reaction order; both effects have certain ranges of linearity; and both decrease in intensity with increasing concentration of nitric acid. At a given concentration of nitric acid, the concentration of potassium nitrate required to halve the rate of nitration is always of the same order of magnitude as the concentration of sulphuric acid needed to double the rate of the same nitration. Thus the necessary concentrations of potassium nitrate or of sulphuric acid increase by similar factors, each about 10^2 , as the concentration is increased from the lowest employed in these experiments, *viz.*, 7*M.*, up to that of pure nitric acid, *viz.*, 24*M.* These analogies will be discussed later [Section (2.4.2)].

(2.3) Observations on the Kinetic Effects of Water.

(2.3.1) *Effect of Added Water on Zeroth-order Rates of Nitration.*—Added water depresses the rates of zeroth-order nitrations, as is illustrated, for the nitration of toluene in nitromethane, in Table XIII. Even the largest of the investigated additions of water appeared to create no disturbance in the zeroth-order form of the reaction.

TABLE XIII.

Effect of added water on the zeroth-order rate constants (k_0 in $\text{sec.}^{-1}\text{g.}^{-1}\text{mol.}^{-1}$) of nitration of toluene in nitromethane.

$[\text{HNO}_3] = 7.0\text{M.}$ $[\text{HNO}_2] = 0.0013\text{—}0.0024\text{M.}$ (extreme values). $[\text{C}_6\text{H}_5]_0 = 0.09\text{M.}$ Temp. -10.0° .

Expt.	$[\text{H}_2\text{O}]_0$ *	10^5k_0	Expt.	$[\text{H}_2\text{O}]_0$ *	10^5k_0	Expt.	$[\text{H}_2\text{O}]_0$ *	10^5k_0
581	none	8.93	594	0.0809	7.76	597	0.8589	4.11
591	"	8.85	595	0.1633	7.72	598	1.586	2.61
592	"	7.97	596	0.3122	5.56	599	1.677	2.53
593	0.0179	8.61						

* $[\text{H}_2\text{O}]_0$ relates to initially added water: extra water is, of course, produced during the nitration.

In these experiments the influence of the nitrous acid is small in comparison with the effect under observation. This effect is exhibited in Fig. 12, in the form of a plot of the reciprocal of the rate against the initial concentration of water. The short horizontal line represents the approximate amount of extra water which is produced during the runs. If in the construction of the graph we had used average, instead of initial, water concentrations, all the points, and the line drawn through them, would have been shifted to the right by half this length. This would not affect the conclusion that the reciprocal of the rate is a linear function of the concentration of the water.

The anticatalytic effect of water is evidently very weak in comparison with that of nitrate ions. Thus a concentration of 0.6*M.* of added water is required to halve the rate of this reaction, whereas the same can be done by a concentration of only 0.004*M.* of added potassium nitrate. The line representing the water effect in Fig. 12 was reproduced on the appropriate scale in Fig. 9, for comparison with the graph there shown of the nitrate ion effect.

(2.3.2) *Effect of Added Water on First-order Rates of Nitration.*—Added water exerts a retarding influence also on first-order rates of nitration; and it does this without detectably disturbing the kinetic order of the reaction. This effect is illustrated with reference to the nitration of nitrobenzene in pure nitric acid, with and without added water, by the figures in Table XIV.

TABLE XIV.

Effect of added water on the first-order rate constants (k_1 in sec.^{-1}) of nitration of nitrobenzene in nitric acid.

$[\text{C}_6\text{H}_5\text{O}_2\text{N}]_0 = 0.07\text{—}0.12\text{M.}$ (extreme values). $[\text{HNO}_3] = 0.040\text{M.}$ Temp. $= -13.3^\circ$.

Expt.	$[\text{H}_2\text{O}]_0$ *	10^5k_1	Expt.	$[\text{H}_2\text{O}]_0$ *	10^5k_1	Expt.	$[\text{H}_2\text{O}]_0$ *	10^5k_1
400	none	468	401	0.891	276	406	2.42	125
405	0.396	354	403	1.48	204	407	3.19	77
402	0.557	341	404	2.10	157			

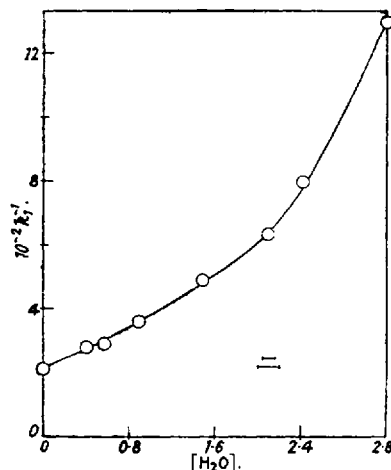
* $[\text{H}_2\text{O}]_0$ relates to water initially added to pure nitric acid, which at $T^\circ\text{C.}$ has the density 1.5300 $- 0.0014T$, and is therefore 24.58*M.* at -13.3° .

The kinetic influence of the nitrous acid present in these experiments is negligible in relation to the effect under observation. This effect of the water is shown graphically in Fig. 13, which exhibits a plot of the reciprocal of the rate constant against the concentration of added water. The amounts of extra water produced by nitration are indicated, as lower and upper limits, by the two short, horizontal lines on the diagram. In a corresponding graph relating to average, instead of to initial, water concentrations, the points would be shifted to the right of the points shown by distances within the range of the half-lengths of these two lines.

We have not been able to find any simple function of obvious chemical significance to fit this curve, which appears to steepen continuously as the water concentration increases. It does so especially rapidly at concentrations around 2.2M., which, as we shall notice later [Section (2.4.2)], is critical in another connexion.

The anticatalytic effect of water on nitration in nitric acid is evidently weak, a water concentration of 1.2M. being needed to halve the rate constant. The intensity of the effect is thus of the same order of magnitude as that of the retardation caused by potassium nitrate in the same medium. This similarity of magnitude forms a contrast to the quite different orders of magnitude of the retarding influences of water and nitrate ions, as they affect zeroth-order nitrations in nitromethane. We shall comment on this later [Section (2.4.2)].

FIG. 13.
Effect of water on first-order rate of nitration of nitrobenzene in nitric acid at -13.3° .



(2.4) Discussion (Part 2) : Effects of Some Solutes : Mode of Formation of the Nitronium Ion
(continued from p. 2412).

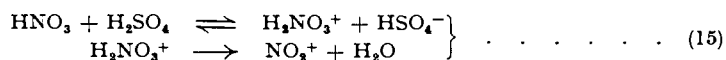
(2.4.1) Effects of Strong Acids, Nitrates, and Water : The Nitric Acidium Ion.—The following results require consideration. (1) Added very strong acids, such as sulphuric acid, accelerate both zeroth-order and first-order nitration, without changing the reaction order, the rate varying nearly linearly with the concentration of the added acid within certain ranges (cf. Figs. 7 and 8). The effect is strong for nitrations in nitromethane, but much weaker for nitrations in nitric acid; and in the latter case considerable deviations from linearity occur at low concentrations of added acid. (2) Added nitrates, such as potassium nitrate, retard both zeroth-order and first-order nitrations, without changing the kinetic form, the reciprocal of the rate varying nearly linearly with the concentration of the added nitrate within certain ranges (cf. Figs. 9, 10, and 11). The effect is strong for nitrations in nitromethane, but much weaker for nitrations in nitric acid. In the former case deviations from linearity set in at the higher concentrations of nitrate, whilst in the latter the chief deviations occur at the lower concentrations of added nitrate. (3) Added water retards both zeroth-order and first-order nitrations, without changing the reaction order, the reciprocal of the rate varying nearly linearly with the concentration of water, within certain ranges (cf. Figs. 12 and 13). In comparison with the strong effects already mentioned, the effect of water is weak, as well for zeroth-order nitrations in nitromethane as for first-order nitrations in nitric acid. In the latter case marked deviations from linearity appear.

From these results we first select for consideration the strong effects, which most plainly indicate the general character of the interpretation. These effects are the acceleration by very strong acids, and the retardation by nitrates, of nitrations in nitromethane, always without disturbance to the reaction order. The accelerations show that a proton uptake by nitric acid is necessary to the formation of the nitronium ion. The retardations show that a nitrate ion is eliminated in a reaction leading to the nitronium ion, and that the reaction in which it is eliminated can be driven backwards by added nitrate ion.

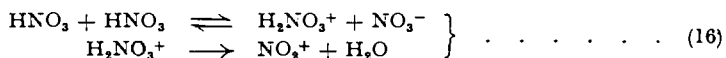
One of these strong effects is particularly significant : it is that zeroth-order nitration is strongly retarded by nitrate ion, without losing its zeroth-order character. This immediately shows that the formation of the nitronium ion, which is the rate-determining stage of zeroth-order nitration, itself consists of two stages; for some reaction-stage in the production of the nitronium ion, namely, the stage in which a nitrate ion is eliminated, must be reversible. But

another stage, namely, the final stage in the production of the nitronium ion must be effectively irreversible; for the essence of the interpretation of zeroth-order nitration is that none of the formed nitronium ion goes back into what it came from, all being consumed in the nitration of the aromatic compound. If we should try strongly to depress nitration rate by reversing the formation of the nitronium ion, we should inevitably convert a zeroth-order reaction into a first-order reaction.

These few facts thus determine the mechanisms written below for the formation of the nitronium ion, as measured in zeroth-order nitrations, with or without catalysis by such strong acids as sulphuric acid, and with or without anticatalysis by the nitrate ion. For the formation of the nitronium ion in zeroth-order nitrations catalysed by sulphuric acid, we have the following equations:



For the formation of the nitronium ion in the absence of a catalysing acid, we have a corresponding expression, which automatically "takes care" of the retardation by nitrate ion:



In each case, the second reaction-stage is expressed irreversibly, as is appropriate to zeroth-order nitration. For simplicity, the formed water is shown as free water, though we know that it becomes largely linked with nitric acid as the hydrate of nitric acid (cf. Gillespie and Millen, *loc. cit.*).

The observations cited thus provide the first definite demonstration of the formation of the *nitric acidium ion*, H_2NO_3^+ . They show at the same time that, side by side with the nitronium ion, this ion is ineffective for nitration in the conditions investigated.

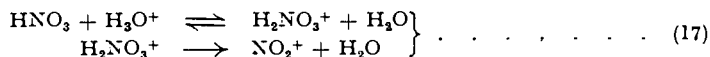
Equations (15) and (16) represent the rate of formation of the nitronium ion, *i.e.*, the zeroth-order nitration rate, as proportional to the equilibrium concentration of the nitric acidium ion. Thus the equations require, given certain simplifying conditions mentioned below, that sulphuric acid should produce a linear increase of rate, and that potassium nitrate should bring about a retardation corresponding to a linear increase in the reciprocal of the rate. The fact that we find such linear effects in certain ranges, and no signs of the corresponding quadratic effects, shows that only one proton is absorbed into, and only one nitrate ion is eliminated from, the system out of which the nitronium ion is directly generated. Thus the cation involved in the pre-equilibrium is H_2NO_3^+ , as represented, and is not $\text{H}_3\text{NO}_3^{++}$; for the formation of this bivalent ion would involve the intake of two protons and the elimination of two nitrate ions, and therefore should lead to quadratic, rather than the linear, catalytic and anticatalytic effects.

An obvious condition for linearity of the catalysis by sulphuric acid is that the process by which the nitronium ion is formed should essentially be that of equations (15) only, not a mixture of the processes of equations (15) and (16) in comparable proportions. This condition will be fulfilled if, as in our experiments on catalysed zeroth-order nitration, the catalysis is strong, *i.e.*, if the catalysed rate is many times larger than the uncatalysed rate. A necessary condition for the expected linear effect in the anticatalysis by potassium nitrate is that the salt should be fully dissociated into ions having the normal type of activity coefficient; and it is to the failure of this condition in nitromethane that we attribute the marked falling off in the specific anticatalytic effect of the salt at the higher concentrations investigated.

In the approximation to which the above treatment is carried, added water has no effect on zeroth-order nitrations; that is, it has no kinetic effect comparable in magnitude to the effects of strong proton-donors or of nitrates. This is consistent with equations (15) and (16), in which water appears only in the irreversible part of the process: nitrate ion is formed, but no water is formed, in the one reaction-stage which, in zeroth-order nitration, can be driven backwards.

However, when we begin to take account of the finer details of the experimental investigation, we have to deal with the position that added water does depress the rate, although its specific kinetic effect is some hundreds of times smaller than those of nitrates or strong acids. This effect is not due to a small reversibility of the second reaction-stage expressed in equations (16); for by adding enough water, we can reduce the rate considerably, *e.g.*, to one-third or one-quarter of its original value, without detectably disturbing the zeroth-order form of the reaction. Taking account of this, and also of the observation that the kinetic effect of water is essentially linear with respect to the reciprocal of the rate, we infer the existence of a second

process of destruction of the nitric acidium ion in a reversible reaction—one which is formally similar to, but much less important than, the reversible reaction-stage of equations (16). The chemical nature of this second reversible reaction is determined by the requirement that the products of the forward process must be nitric acidium ion and water. It may be represented as part of an alternative route to the nitronium ion, *viz.*, the following :



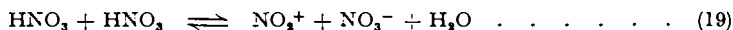
Here the equilibrium in the first reaction-stage must lie so far over to the right that the water normally formed in the reactions of equations (16) destroys very little of the nitric acidium ion, and thus produces only minute concentrations of hydroxonium ion. But when considerably more water is added to the system, then the reversible stage of process (17) retrogresses to a significant extent, reducing the stationary concentration of the nitric acidium ion, and therefore reducing the rate of formation of the nitronium ion. The linearity of the effect of water on the reciprocal of the rate is evidently accommodated by equations (17).

It will be obvious that, if we should add yet much more water, we must eventually produce a reversal of the second stage of these processes, with the result that zeroth-order kinetics will go over into first-order kinetics. Such a kinetic conversion has not been followed in detail,* though the results of a completed conversion of this type have been studied, as is reported in the next paper (Part III).

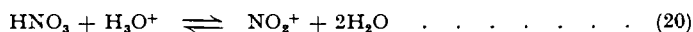
In first-order nitration, in contrast to zeroth-order nitration, the re-hydration of the nitronium ion has to be considered as rapid in relation to the reaction of nitronium ion with the aromatic compound. The discussion of these nitrations can therefore be based on a summarised representation of the processes leading to the nitronium ion. In this representation the two stages of each of the processes (15), (16), and (17) are combined, the total process being treated as reversible. Thus, for the reactions catalysed by sulphuric acid, we have the following equilibrium :



In the absence of a catalysing acid, the principal equilibrium will be the following, which takes account of the anticatalysis of first-order nitrations by nitrate ions :



There will be another reversible process of some importance in the presence of considerable quantities of water, namely, the following :



We are still representing the water as free for simplicity, although we know that in nearly pure nitric acid most of it is combined as a hydrate of the acid.

Since in first-order nitration the nitronium ion is maintained in a stationary concentration, to which the first-order rate constant is proportional, we must expect the first-order constant to be increased linearly by added sulphuric acid, and decreased so that its reciprocal is increased linearly by nitrate ions—always provided that certain simplifying conditions are satisfied. These conditions are the same as for zeroth-order nitration, with the additional requirement that, while the effect of nitrate ion is being studied, the water should be in constant excess. The expected influence of water is rather complicated, partly because an inverse quadratic effect is allowed by equation (20).

As with zeroth-order nitrations, so also with first-order nitrations, the conditions necessary for the production of the linear kinetic relations are most easily satisfied for nitrations in nitromethane. The special requirement for linear anticatalysis by nitrate, *viz.*, that the water should be in constant excess, can also be easily satisfied in this solvent, because such small concentrations of nitrate suffice to produce a substantial kinetic effect. An example showing the linear anticatalysis by potassium nitrate of a first-order nitration under such conditions has been given.

* Since this was written such a conversion has been followed through by Mr. M. H. Jones, with a practical object. He was concerned to compare the nitration rates of toluene and *tert.*-butylbenzene, and, since the use of the competition method would in this case involve a difficult analysis, he turned to the kinetic method, for which, with nitric acid in constant excess, first-order kinetics are essential in this type of experiment. It happens that, in the otherwise convenient solvent acetic acid, both these nitrations have zeroth-order kinetics. Therefore Mr. Jones added progressively increasing quantities of water, up to 5% by weight, to the acetic acid solvent, thereby driving the kinetics over from zeroth order to first order, in accordance with expectation.

Perhaps the main interest attaching to the experiments concerning solute effects on first-order nitrations relates to what happens when the conditions necessary for the linear relations are not fulfilled—as, generally, they are not for nitration in nitric acid itself. We proceed to consider this matter.

(2.4.2) *Further Effects of Acid, Nitrate, and Water: The Self-ionisation of Nitric Acid.*—Most of the non-linear effects which have been observed in connexion with the kinetic influence of these solutes on nitrations with nitric acid as both solvent and reagent can be understood on the basis that pure nitric acid is considerably self-ionised in the sense of equation (19). The self-ionisation is much greater than when the nitric acid is present in organic solvents. The effects to be expected from a substantial self-ionisation are readily deduced.

For example, when, by an addition of sulphuric acid, nitronium ion is produced by reaction (18), the new nitronium ion will destroy some of the old nitronium ion by repressing equilibrium (19): thus the two sources of nitronium ion will not behave additively, and the catalysis will not be linear. But if the added sulphuric acid has generated enough nitronium ion to suppress to insignificance its production in the original equilibrium (19), then the introduction of further quantities of sulphuric acid will yield nearly additive increments of nitronium ion, and so the catalysis will asymptotically become linear. Departures from linearity are marked up to a concentration of sulphuric acid of about 0.2M.; and hence we may conclude that the production of nitronium ion by equilibrium (19), in pure and nearly pure nitric acid, is of the order of 0.2M.

A similar effect arises in anticalysis by metallic nitrates. The immediate result of the introduction of an ionised nitrate will be to repress equilibrium (19), thus reducing the production of nitrate ions by the original method: hence the two sources of nitrate ions will not operate additively, and the total nitrate ion will not increase linearly with the amount of added nitrate. This means that, even if the water concentration is buffered, as it was in the relevant experiments, the reciprocal of the concentration of nitronium ion, and therefore the reciprocal of the first-order rate constant, will not increase linearly with the added metallic nitrate. Only when the amount of added nitrate is greater by several fold than the amount of nitrate ion originally produced by the self-ionisation, will further additions of nitrate linearly increase the total concentration of nitrate; and only then will the effect of the added nitrate on the reciprocal of the first-order rate constant asymptotically become linear. A consideration of the range of concentrations over which marked deviations from linearity occur in the anticalytic effect of added nitrate allows us to estimate that the concentration of nitrate ion originally produced by the self-ionisation of nitric acid is of the order of 0.2M. This estimate is consistent with that given above for the concentration of nitronium ion in self-ionised nitric acid, and also with the physical evidence concerning the self-ionisation of nitric acid which is presented in accompanying papers (*J.*, 1950, papers nos. 504, 505).

It seems possible to conclude from the kinetic results that potassium nitrate is fully ionised up to much greater concentrations in nitric acid than it is when nitromethane is the main constituent of the solvent.

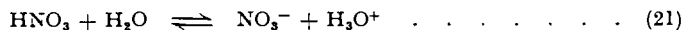
The reason for the much smaller sensitivity of nitration in nitric acid, than of nitration in nitromethane, to catalysis by sulphuric acid, and to anticalysis by metallic nitrates, will be clear. Pure nitric acid already contains so large a concentration of nitronium ion that a considerable addition of sulphuric acid is required to double it, and thus to double nitration rate; and a considerable addition of nitrate is required to halve it, and thus to halve nitration rate. The equilibrium concentration of nitronium ion in nitromethane solutions containing nitric acid is much smaller, and therefore proportionately considerable changes can be effected by means of much smaller additions of sulphuric acid or of nitrates. It can be estimated that the equilibrium concentration of nitronium ion in, for instance, 8.5M-nitric acid in nitromethane is of the order of 0.001M.

The reason why, in the various concentrations of nitric acid that have been used for nitrations in nitromethane, and also in nitric acid itself, the concentration of sulphuric acid required to double the rate is always of the same order of magnitude as the concentration of ionised nitrate needed to halve the rate will also be clear. It is simply that, in all conditions, apart from aqueous conditions which are the subject of another paper (Part III), comparable concentrations of nitronium ion and of nitrate ion are produced by the self-ionisation of nitric acid.

Comment may be made on the kinetic effect of water on first-order nitrations in nitric acid. The experimental result that the sensitivity of first-order nitrations towards anticalysis by water is of the same order of magnitude as their sensitivity to anticalysis by nitrates is in obvious agreement with the form of equation (19). However, there are several factors which

render consideration of the water effect quantitatively more complicated than that of the effect of nitrates.

For, first, except at quite low water concentrations, equilibrium (20) will probably have some importance, along with equilibrium (19), in fixing the stationary concentration of nitronium ion. Secondly, the concentration of nitrate ion is not only not buffered as the water concentration is varied: it will inevitably change with the water content, and will do so in a rather complicated way; for, on the one hand, water will destroy nitrate ion by equilibrium (19), and, on the other, it will produce nitrate ion by equilibrium (21); and thus, as water is progressively added, the concentration of nitrate ion must pass through a minimum—as, indeed, the electrical conductivity is known to do at a concentration about 2.2M. of water (Veley and Manley, *Proc. Roy. Soc.*, 1898, *A*, **191**, 365; Reed, unpublished work). The third source of complication is that much of what we call water is present in a bound form, as nitric acid hydrate.



It is difficult to assess the importance of the third of these effects, but on account of the first two we would expect the reciprocal of the first-order rate constant to increase with the water concentration according to a continually steepening curve. This is what is found, as Fig. 13 shows. It is probably significant that the steepening becomes sharp suddenly at water concentrations around 2.2M.; for this is the concentration which corresponds to the electrical conductivity minimum, and presumably corresponds approximately to the water concentration beyond which the content of nitrate ions begins to increase.

(Discussion continued on p. 2426.)

(3) MEDIUM EFFECTS ON NITRATION KINETICS: MODE OF ACTION OF THE NITRONIUM ION.

(3.0) *Significance of the Study of Solvent Effects.*—The observations to which attention will now be directed relate to solvent effects on rates of nitrations of different kinetic order, and on the kinetic order itself. The study of this subject is one of the ways in which we may discover the details of the last stage of the nitration process, *viz.*, the attack by the nitronium ion on the aromatic molecule.

The basis of the method is contained in the general theory of solvent effects on reaction rate (Hughes and Ingold, *J.*, 1935, 244; *idem et al.*, *J.*, 1948, 2043). A knowledge of the effect of solvent polarity, or ion-solvating power, on rate will tell us at once whether ions are formed or destroyed in the rate-controlling stage: polar solvents strongly accelerate reactions which generate ions and strongly retard those which consume ions. These are gross effects: if they are absent, a considerably weaker effect may sometimes be observed. It arises when an initially localised ionic charge becomes spread by mesomerism in the transition state of reaction; and it takes the form of a small retardation by polar solvents (for some illustrations, see Table III in the second of the papers cited above).

In the example of nitration, we can, by changing the reaction order, make rate-determining either the formation of the nitronium ion or its attack on the aromatic molecule. Hence, by studying solvent effects on nitrations of different orders, we can obtain the information indicated for each of the above stages, in particular, for the latter stage, which is now our main interest.

Our experiments on this part of the subject relate to the solvents acetic acid and nitromethane. But we shall be able to extend the conclusions thus derived to cover in a consistent way all that is known of medium effects on nitration in nitric acid and in sulphuric acid.

(3.1) *Observations on Medium Effects.*

(3.1.1) *Effect of Nitric Acid Concentration on Nitration Rate in Organic Solvents.*—Alike in Benford and Ingold's experiments on nitration in nitromethane, and in those now reported on nitration in this solvent and in acetic acid, the nitric acid has always been employed in a concentration sufficient to render it an important constituent of the solvent.

For nitration in nitromethane, Benford and Ingold found that the zeroth-order rate constants of benzene and more reactive aromatic hydrocarbons increased as the fifth or sixth power of the nitric acid concentration over the range of their observations. For the mixed-order reactions of the halogenobenzenes, no rate constants could be extracted from the kinetic observations, but the curvilinear rates themselves increased notably with the acid concentration. For the same solvent, nitromethane, we now find that the first-order rate constants of nitration

of *p*-dichlorobenzene, and other substituted benzenes of considerably reduced reactivity, also increase steeply with the concentration of nitric acid. Furthermore, we find all these effects repeating themselves in nitrations with acetic acid as the solvent. Some comparisons showing the effect of nitric acid concentration on zeroth-order and first-order rates in nitromethane, and in acetic acid, are given in Table XV. The experiments of each pair are so selected that the kinetic effect of nitrous acid, when not entirely negligible, is at least closely similar in the cases compared.

TABLE XV.

Effect of concentration of nitric acid on rate constants for nitration in organic solvents.

(Zeroth-order constants, k_0 , in sec.⁻¹ g.-mol. l.⁻¹; first order constants, k_1 , in sec.⁻¹.)

Expt.*	Order.	HAr.	Temp.	[HNO ₃].	[HNO ₂].	10 ⁵ k_0 .	10 ⁵ k_1 .
<i>Solvent: Nitromethane:</i>							
I 188 } I 294 }	Zeroth	C ₆ H ₆	0·0°	{ 5·0 7·0	{ 0·0089 0·0083	3·28 18·4	— —
150 } 156 }				First	<i>p</i> -C ₆ H ₄ Cl ₂	20·0	{ 8·5 11·5
<i>Solvent: 99·8% Acetic acid:</i>							
48 } 62 }	Zeroth	<i>p</i> -C ₆ H ₄ Me ₂	20·0	{ 5·0 7·0	{ 0·0096 0·0046	0·433 6·17	— —
281 } 310 }				First	<i>p</i> -C ₆ H ₄ Cl ₂	20·0	{ 10·5 12·2

* The numeral I distinguishes the experiments of Benford and Ingold's series (Part I, *loc. cit.*, from those of the present series.

(3.1.2) *Effect of Organic Solvents on Nitration Rate at a Constant Nitric Acid Concentration.*—Nitromethane is usually considered to be a more polar solvent than acetic acid. Nitromethane certainly has the larger dielectric constant and dipole moment. It is the better solvent for salts containing small ions. It is much the faster solvent for definitely ion-producing reactions, such as the formation of quaternary ammonium salts, and of sulphonium salts, from tertiary amines or alkyl sulphides and alkyl halides, sulphates, picrates, etc. Nitromethane is a much faster solvent than acetic acid for both zeroth-order and first-order nitration. This may be established by comparisons, with a fixed concentration of nitric acid, of rate constants for the nitration of any aromatic compound which reacts according to a common kinetic law in both solvents. Some examples are given in Table XVI.

TABLE XVI.

Effect of solvent polarity on rate constants for nitrations, with a fixed concentration of nitric acid, at 20·0°.

(Zeroth-order constants, k_0 , in sec.⁻¹ g.-mol. l.⁻¹; first-order constants, k_1 , in sec.⁻¹.)

Expt.	Order.	HAr.	[HNO ₃].	Solv.	[HNO ₂].	10 ⁵ k_0 .	10 ⁵ k_1 .
202 * } 60 }	Zeroth	C ₆ H ₅ Me	7·0	{ MeNO ₂ AcOH	{ 0·0046 0·0050	188 5·90	— —
156 † } 281, 164 ‡ }				First	<i>p</i> -C ₆ H ₄ Cl ₂	11·5	{ MeNO ₂ AcOH

* From the observed rate constant, $k_0 = 9·78 \times 10^{-5}$ sec.⁻¹ g.-mol. l.⁻¹ at $-10·0^\circ$, the quoted rate constant for 20·0° has been calculated by using Benford and Ingold's temperature coefficient (Part I, *loc. cit.*).

† From the observed rate constant, $k_1 = 2470 \times 10^{-5}$ sec.⁻¹ with [HNO₂] = 0·0269M., the quoted rate constant has been calculated to correspond with the lower nitrous acid concentration, 0·0030M., required for the comparison. The equation employed is $k_0^{-1} = a + b[\text{HNO}_2]^{1/2}$ with $b/a = 10$ (Benford and Ingold, Part I, *loc. cit.*).

‡ The quoted rate constant has been logarithmically interpolated between observed rate constants, $k_1 = 20·0 \times 10^{-5}$ sec.⁻¹ with [HNO₃] = 10·5M., and $k_1 = 165 \times 10^{-5}$ sec.⁻¹ with [HNO₂] = 12·0M., in order that it shall correspond to the nitric acid concentration, 11·5M., required for the comparison. The use of a power formula, instead of an exponential expression, gives practically the same result.

(3.1.3) *Effect of Nitric Acid Concentration on the Order of Reaction in an Organic Solvent.*—In certain cases it is possible to change the kinetic order of nitration in a given solvent by simply changing the concentration of nitric acid. The nitration of benzene in acetic acid provides an example. In 12·4M-nitric acid in this solvent, the nitration of benzene is very nearly of zeroth order; but in 7·0M-nitric acid in the same solvent the reaction is very nearly of first order. How

closely these approximations hold can be shown by means of the comparisons, set out in Table XVII, of the rate constants for nitration of benzene and toluene under identical conditions.

TABLE XVII.

Effect of nitric acid concentration on the kinetic order of nitration of benzene in 99.8% acetic acid.

(Zeroth-order constants, k_0 , in sec.^{-1} g.-mol. l.^{-1} ; first-order constant, k_1 , in sec.^{-1} .)

Expt.	HAr.	[HNO ₃].	Temp.	[HNO ₃].	[HAr] ₀ .	10 ⁶ k ₀ .	10 ⁶ k ₁ .
79	C ₆ H ₆	12.4	10.7°	{ 0.497	0.353	97	—
80	C ₆ H ₅ Me						
78	C ₆ H ₆	7.0	20.0	{ 0.0051	0.100	—	4.02
60	C ₆ H ₅ Me						

Toluene nitrates according to a zeroth-order kinetic law under the conditions of both the comparisons. If in either case the nitration of benzene followed a zeroth-order law exactly, it should in that case have identically the same rate-constant. Furthermore, the nitration of benzene could only follow a first-order law exactly if its absolute rate (not rate-constant) were indefinitely small in comparison with the zeroth-order rate of nitration of toluene.

From the figures given it appears that, in 12.4M-nitric acid, the zeroth-order rate of nitration of benzene is smaller by 6% than the zeroth-order rate of nitration of toluene under the same conditions. In competition experiments benzene is nitrated about 24 times more slowly than toluene. We conclude that the slightly smaller kinetic rate for benzene means that its nitration rate is not quite rigidly fixed by the rate of formation of the nitronium ion, but is being slightly restricted by the relatively low reactivity of the benzene molecule itself. Again, from figures given it appears also that, in 7.0M-nitric acid, the initial rate of nitration of benzene in 0.1M-concentration is smaller than what would be the steady rate if the reaction had followed a zeroth-order law by the factor $(4.02/5.90) \times 0.1 = 1/15$. We know what this steady rate would be, because it would be the same as the actually observed steady rate for the nitration of toluene in the same conditions. Thus the nitration of benzene starts with only 7% of its zeroth-order velocity, and, as the reaction proceeds, it becomes continually slower, both absolutely and relatively. These factors, 0.07 falling to zero, by which the actual reaction is slower than the zeroth-order reaction, measure the extent to which the existence of zeroth-order aromatic nitration must cause a deviation from strict first-order kinetics in the nitration of benzene in these conditions. This consideration of the deviations from integral reaction-orders only serves to emphasize that the change of order, produced by the change of nitric acid concentration, is very nearly integral.

(3.1.4) *Effect of Organic Solvents on the Order of Reaction at a Common Nitric Acid Concentration.*—As compared with nitration in nitromethane, nitrations in acetic acid show a generally smaller tendency towards zeroth-order kinetics and a greater towards first-order kinetics. This statement assumes that one compares the effect of the two solvents on reaction order at a common concentration of nitric acid. In illustration, we shall refer again to the nitration of benzene.

Benford and Ingold studied the nitration of benzene in nitromethane, with nitric acid at various concentrations extending over the range 3.0—7.0M.; and over the whole of this range they observed zeroth-order kinetics (Part I, *loc. cit.*). We have studied the nitration of benzene in acetic acid, with nitric acid in a series of concentrations extending over the range 7.0—12.4M.; and over this range, as we have just seen, the reaction order drops from first to zeroth.

TABLE XVIII.

Effect of solvent polarity on the kinetic order of the nitration of benzene with 7.0M-nitric acid.

(Rate constants: k_0 in sec.^{-1} g.-mol. l.^{-1} , and k_1 in sec.^{-1} .)

Expt.	Solvent.	Order.	Temp.	[HNO ₃].	[HAr] ₀ .	10 ⁶ k ₀ .	10 ⁶ k ₁ .
294—299 *	MeNO ₂	Zeroth	0.0°	0.0051	0.10	17.2	—
78	AcOH	First	20.0	0.0051	0.10	—	4.02

* Expts. nos. 294—299 of Part I (*loc. cit.*) covered the range of concentration of nitrous acid 0.0083M. to 0.1500M., and gave the rate formula $k_0^{-1} = 10^4(0.35 + 3.30[\text{HNO}_2]^{1/2})$. From this the quoted rate constant is calculated to correspond to the concentration of nitrous acid, 0.0051M., required for the comparison.

A comparison of the kinetic effects of the two solvents, nitric acid being at the common concentration 7.0M., is shown in Table XVIII. It appears that the effect on the reaction order of replacing acetic acid by nitromethane, with this fixed concentration of nitric acid, is much

like that of retaining acetic acid as the solvent, but substantially increasing the proportion of nitric acid dissolved in it. Each change presumably increases the polarity of the medium; and each change in fact produces a unit drop in the kinetic order of nitration.

(3.2) *Discussion (Part 3) : Medium Effects : Mode of Action of the Nitronium Ion*
(continued from p. 2423).

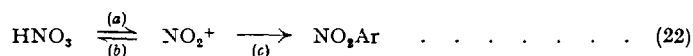
(3.2.1) *Molecularity of Aromatic Attack by the Nitronium Ion in Organic Solvents.*—In Part 1 of this Discussion we established the formation and effectiveness of the nitronium ion in nitration, essentially by means of a study of the variations in the kinetic order of reaction. We then set down (p. 2411) schemes (11) and (12), as representing in detail the reactions which produce the nitronium ion, in the presence, and in the absence, of acids stronger than nitric acid. We also set down (p. 2412) equations (13) and (14), expressing two alternative methods by which the nitronium ion might attack and nitrate an aromatic molecule. In Part 2 of the Discussion we were concerned to elucidate the reaction stages involved in the formation of the nitronium ion. Evidence on the matter was derived from a study of the kinetic effects of certain solutes. We thus established the correctness of schemes (11) and (12), which make the nitric acidium ion an essential precursor of the nitronium ion. Continuing our Discussion, we shall now attempt a decision between the alternative modes of action of the nitronium ion, as represented by equations (13) and (14), our evidence being derived from the study of medium effects on reaction rate and reaction order.

Equation (13) represents what we call the "bimolecular" mechanism of nitronium ion attack. It implies that, very quickly after the nitronium ion becomes attached to the aromatic carbon atom, the aromatic proton is ejected into the solvent, without waiting to be extracted by a solute base, such as hydrogen sulphate or nitrate ion. In this case the proton transfer is too rapid to be kinetically significant, and the reaction is not base-accelerated.

Equation (14) expresses what we term the "termolecular" mechanism of nitronium ion attack. Here the picture is that, after the uptake of the nitronium ion, the proton remains in aromatic combination until it is found, and extracted, by a sufficiently powerful base. In this event the proton transfer is an important part of the rate-determining reaction-stage, and the reaction will be base-accelerated.

We shall first consider the effects to be expected from this distinction of mechanism in relation to the evidence concerning nitration in the absence of acids stronger than nitric acid. Accordingly we shall take equation (12) as expressing in detail the formation of the nitronium ion. Equations (13) and (14) are alternative representations of the mode of action of the nitronium ion.

It will simplify reference to the processes involved if we first express the combination of equation (12) with either equation (13) or equation (14) in the summarised form (22) :



This is done for the convenience of being able to use the labels (a), (b), and (c) for groups of associated reaction-stages. Process (a) signifies all the forward transformations involved in the conversion of a nitric acid molecule into a nitronium ion. Process (b) denotes the reversal of this group of transformations. Process (c) represents the final phase of nitration by the nitronium ion, *i.e.*, its actual attack on the aromatic molecule, together with the associated proton-transfer. We take equations (12) as the expressions of processes (a) and (b) together. At first we shall assume equation (13) to express process (c).

As can be seen from equations (12), process (a) converts three neutral molecules into one neutral molecule and two ions. This process will be much accelerated by the increased solvation forces of a more polar medium. For corresponding reasons the reverse process, (b), should be strongly retarded by an increase in the polarity of the medium. Process (c), as expressed by equation (13), neither creates nor destroys ionic charges in its rate-determining stage. In the first approximation in which we shall consider the gross kinetic effects, the rate of this reaction should be unaffected by the polarity of the medium.

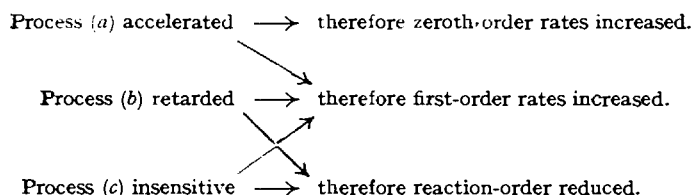
Putting these points together, we shall find that we can satisfactorily interpret all the main kinetic effects of solvent changes on the basis of the hypothesis that the bimolecular equation (13) really does express process (c). The argument is as follows.

The measured zeroth-order rates depend only on process (a). These zeroth-order reactions will therefore be strongly accelerated by increases in the polarity of the medium, such as might be produced by increase of nitric acid content, or a replacement of acetic acid by nitromethane.

The measured first-order rates are constituted as products of two factors. One factor is the stationary concentration of nitronium ion. This will closely approximate to an equilibrium concentration determined by the reversible conversion of three neutral molecules into one molecule and two ions. It follows that the stationary concentration of nitronium ion will be strongly increased by an increase in the polarity of the medium. The second factor is the specific rate of process (c). But, as we have already seen, this should, in our first approximation, be insensitive to changes in the medium. It follows that the complete first-order reactions must be strongly accelerated by increases in the polarity of the medium.

The kinetic order of nitration depends on what fate principally befalls the nitronium ion, and, in particular, on whether what is formed by process (a) is mostly destroyed by process (b) or by process (c). The former alternative leads to first-order kinetics, and the latter to zero-order kinetics; and thus the observed reaction order will depend on the ratio of the rates of processes (b) and (c). Since process (b) must be retarded by an increase in the polarity of the medium, whereas, in our present approximation, process (c) is insensitive to changes in the medium, it follows that the effect of a change to a more polar medium must be in the direction of replacing process (b) by process (c); that is, it must be in the direction of reducing the order of the over-all reaction from first order towards zeroth order.

We may assemble these deductions in the following summary of expected effects of increasing the polarity of the medium :



All these deductions have been experimentally verified.

The success of these deductions is definitely dependent on the choice of the "bimolecular" equation (13), rather than the "termolecular" equation (14), as representing process (c). Suppose that we allow equations (12) to represent processes (a) and (b) as before, but now assume that equation (14) expresses process (c). Then, since, according to equation (14), two ions disappear, becoming replaced by neutral molecules (cf. p. 2412), process (c) must be strongly retarded by an increase in the polarity of the medium. Indeed, process (c) should be retarded comparably to process (b); and hence we should not expect that first-order rates should be increased at least as sharply as zeroth-order rates, as media are made more polar; and we should not expect that reaction orders would be reduced in such circumstances. Thus our observations on medium effects provide a strong support for the bimolecular picture of nitronium ion attack, as expressed in equation (13).

(3.2.2) *Molecularity of Aromatic Attack by the Nitronium Ion in Nitric Acid.*—For the nitration of benzene in acetic acid, the reaction order is changed from first to zeroth when we replace a part of the acetic acid by nitric acid, as we do by increasing the nitric acid concentration from 7.0M. to 12.4M. According to our interpretation of medium effects, we should certainly expect the order of nitration of benzene to remain zeroth when we replace the rest of the acetic acid by nitric acid. However, all the kinetically observed nitrations in nitric acid are first-order reactions.

The reason for this is obviously to be sought in the changes that one has had to make in the nature of the aromatic compound in order to secure nitration rates low enough for measurement in pure nitric acid. A direct kinetic observation of the mononitration of benzene in nitric acid is scarcely possible, because of the very high speed of nitration of benzene in this medium. In order to obtain a measurable reaction rate, one has to introduce some strongly deactivating group, such as a nitro-group. It would not be unreasonable to estimate that a nitro-substituent reduces the specific rate of a nitrating attack on the benzene molecule by a factor of the order of 10^{-6} . Kharasch and Westheimer have suggested the more extreme value 10^{-7} . The precise value, however, is immaterial, for it is in any case intelligible that, when a constitutional change reduces the specific rate of process (c) by any factor such as either of these, process (b) will recover its position as the main mode of destruction of the nitronium ion, and we shall again observe a reaction of the first order.

These high speeds of nitration in pure nitric acid point to the conclusion that in this solvent,

as in organic solvents, the attack of the nitronium ion on the aromatic molecule follows the bimolecular mechanism represented in equation (13), and not the termolecular mechanism of equation (14). In order to illustrate the argument, let us take 10^{-5} as the factor by which a nitro-group reduces the rate of a nitrating attack on an aromatic molecule. We know that benzene may be nitrated at a measurable first-order rate by 7M-nitric acid in acetic acid, and that nitrobenzene may be nitrated at a measurable first-order rate by pure nitric acid. Employing our illustrative factor, we may assume that nitrobenzene is nitrated about 10^6 times faster in pure nitric acid than it would be by 7M-nitric acid in acetic acid. Again the exact ratio is immaterial; for clearly it would be impossible to understand an increase of rate by any such large factor on passing over from solvent acetic acid to solvent nitric acid, if any one of the stages of the forward reaction were required by theory to become continually and very markedly *slower* as the polarity of the medium is continually increased. And this is what the "termolecular" theory of nitronium ion attack does require of process (c). Accordingly, it seems that, by this simple argument, we may exclude the termolecular theory, with its implications that the reaction is base-accelerated, and that the extraction of the aromatic proton is kinetically important. The bimolecular theory, in its first approximation, requires that the specific rate of process (c) will not be greatly affected by the solvent, so that first-order nitration rates will follow, more or less closely, the stationary concentration of nitronium ion, which will increase strongly and continually as the medium increases in polarity. This inference is consistent with the general kinetic picture. We conclude that the nitronium ion attacks by the bimolecular mechanism, and that the aromatic proton is lost in a subsequent, fast reaction-stage.

(3.2.3) *Molecularity of Aromatic Attack by the Nitronium Ion in Sulphuric Acid.*—We shall continue to use the labels of scheme (22) in our discussion of the stages involved in nitration in sulphuric acid. But now, since sulphuric acid is a stronger acid than nitric acid, we have to regard processes (a) and (b) as interpreted in detail by equations (11) on p. 2411. The question for discussion is whether, in this solvent, process (c), the attack of the nitronium ion on the aromatic molecule, is to be identified with the bimolecular process of equation (13), or with the termolecular process of equation (14). We shall again conclude that the attack of the nitronium ion is bimolecular, the aromatic proton being lost in a subsequent, fast reaction-stage.

The broadest argument in favour of this view is on the lines of that just given in relation to nitration in nitric acid. For sulphuric acid, even more than nitric acid, is a highly polar solvent. And in sulphuric acid rates of nitration are very great in comparison with the rates observed in moderately polar organic solvents. This would be unintelligible if the nitration process contained any essential forward step which theory required to be strongly and continuously *retarded* as the medium is made more and more polar. This simple consideration appears to exclude the termolecular theory of nitronium ion attack, as represented in equation (14). On the other hand, the bimolecular theory, expressed by equation (13), is, as before, fully consistent with the general kinetic picture. It is implied that, for nitration in sulphuric acid, the elimination of the aromatic proton has no kinetic importance.

The contrary view, that for nitration in sulphuric acid the loss of the aromatic proton is kinetically significant, has been advocated by Bennett, Brand, James, Saunders, and Williams (*loc. cit.*), who first used a termolecular equation of the type of equation (14). Their object was to explain the fact, discovered by Martinsen (*loc. cit.*), and confirmed by many investigators since, that the addition of a few units per cent. of water to sulphuric acid increases nitration rate in that solvent (although the addition of much more water strongly decreases the rate). The explanation assumes a mass-law acceleration by hydrogen sulphate ions, acting as the base B^- of equation (14). In our view, this theory* envisages too small a range of observations, and neglects the general kinetic situation outlined above.

An effect of the type of that discovered by Martinsen should be expected on the basis of the bimolecular theory of process (c), as expressed in equation (13). For simplicity, let us suppose that, by keeping the added nitric acid in constant excess over the aromatic compound, we cause

* Some significance appears to have been attached to the expression of this theory in an algebraic equation by means of which the variation of nitration rate with the water content of the sulphuric acid can approximately be reproduced. We think, however, that the degree of agreement exhibited is largely a mathematical necessity, arising in part from the circumstance that the rate must follow the nitronium ion concentration when the latter is varying strongly, as it is in the more aqueous end of the solvent range, and in part from the method of choosing the disposable constants, which automatically secures a tolerable fit in the less aqueous end of the range, where the concentration of nitronium ion must always be close to its stoichiometric limit. A recent defence of the theory by Bennett (*Chem. and Ind.*, 1949, 235) lacks appreciation of this point.

the usual second-order nitration rates observed in sulphuric acid to degenerate into first-order rates, so that we can consider them collectively and continuously with the previously discussed first-order rates in less polar media, such as nitric acid, nitromethane, and acetic acid. We noted [Section (3.2.1)] that these first-order rates can be regarded as composed from products of a stationary concentration of nitronium ion and a specific rate of aromatic attack by the nitronium ion; and that, in the formation of the nitronium ion, ionic charges are created, whilst, in the aromatic attack of the nitronium ion, a previously concentrated ionic charge becomes spread into the aromatic ring. By using the solvent theory in its crudest form, which takes account only of the formation and destruction of charges, but not of their degree of distribution, we related the gross rate changes which accompany an increase of solvent polarity, from that of acetic acid in the direction of that of sulphuric acid, essentially to increases in the stationary concentration of nitronium ion, neglecting in comparison the changes in the specific rate of its attack upon the aromatic ring. Such neglect, however, will no longer be admissible when the stationary concentration of nitronium ion has increased to near its stoichiometric limit. And this happens in solvent sulphuric acid containing less than about 7% (or 30 mols. %) of water. The concentration of nitronium ion, now determined by its substantially quantitative formation, is buffered against further medium change; and therefore we have now to look more carefully at the second factor which enters into the determination of first-order nitration rates, *viz.*, the specific rate of attack by the nitronium ion on the aromatic nucleus. For this purpose, we must use the solvent theory in its second approximation which takes account of the degree of distribution of ionic charges.

Sulphuric acid is a highly polar solvent: its dielectric properties are much more extreme than are those of water (Gillespie, Hughes, and Ingold, *J.*, 1950, paper no. 497). Partly because, contrary to previously held opinion, water is not fully ionised in sulphuric acid (Gillespie, *J.*, 1950, paper no. 498), and partly because it is considerably ionised (the ionisation causing Debye "cavities" to occupy much of the medium), it seems certain that the first effect of adding water to sulphuric acid will be to reduce solvating power.

According to the bimolecular theory of aromatic attack by the nitronium ion, as expressed in equation (13), there is a spreading of charge in the formation of the transition state. Therefore the effect of a reduction of the solvating power of the solvent will be to increase the rate of the attack. Knowing the orders of magnitude of solvent effects due to charge distribution in other cases, it seems reasonable to assume that this particular charge-spreading would cause the rate of aromatic attack to increase by some quite small multiple (such as 2 or 4) as solvating power is reduced by adding water up to 30 mols. % to the solvent sulphuric acid. If it were not for a disturbance which is mentioned below, such a rate increase would appear with but slight modification in the observed nitration rates, because of the nearly stoichiometric formation of nitronium ion. (Of course, the addition of much more water will reduce nitration rate by reversing the reactions of equations (11), by which the nitronium ion is formed.)

Even if we could put this theory into a quantitative form, we should not expect it to agree with the published data for the dependence of nitration rate on the water content of solvent sulphuric acid; for, as Gillespie and Millen have pointed out (*Quart. Reviews*, 1948, **2**, 277; cf. Baddely, Graddon, and Kenner, *Nature*, 1947, **160**, 187), a complication enters in nearly all real cases. It is that most substances, whose nitration rates in sulphuric acid have been studied, combine with the acid to form unreactive salt-like complexes, which added water will partly break up, thereby facilitating nitration. This effect on rate is of the same qualitative form as the solvent effect deduced above, and therefore the observed result is in general a combination of both effects. In many cases, *e.g.*, for nitro-compounds, complex formation probably contributes appreciably to the total result, whilst in some examples, *e.g.*, benzoic acid, it probably plays a major rôle. These differences arise from differences in the basicity of the aromatic compounds (Gillespie, *J.*, 1950, paper no. 503); and they doubtless explain why the sensitivity of nitration rate in sulphuric acid to water content varies as much as it does from case to case.

Our conclusion is, then, that neither in solvent sulphuric acid, nor in any of the other solvents considered in this paper, has the loss of the aromatic proton any concern with the rate-determining stage of nitration. There is a simple way of confirming or disproving this proposition, by using the principle of the differing zero-point energies of the hydrogen isotopes. If the proton loss has no kinetic importance, as the bimolecular mechanism of equation (13) assumes, then identically situated aromatic protium and deuterium should be displaced by an entering nitro-group at identical rates; whereas if the proton loss is kinetically significant, as the termolecular mechanism of equation (14) demands, then we must expect protium to be displaced from 3 to more than 10 times faster than deuterium. We were engaged (jointly with Drs. Gillespie and

Millen) in trying these experiments, when we heard from Dr. L. Melander that he had completed some similar experiments, using tritium instead of deuterium as the heavier hydrogen isotope. His uniform result is that the rates of displacement of the isotopes are accurately identical.*

On all these grounds it seems clear that the attack of the nitronium ion on the aromatic molecule in the solvents we have considered is a two-stage bimolecular process, a slow uptake of the nitronium ion being succeeded by a rapid loss of the aromatic proton, in accordance with equation (13) on p. 2412. The establishment of this conclusion completes the central part of our kinetic analysis of the process of aromatic nitration by nitronium ions derived from nitric acid.

(Discussion continued on p. 2434.)

(4) EFFECT OF NITROUS ACID ON NITRATION KINETICS: CONDITION OF NITROUS ACID IN NITRIC ACID SOLVENTS.

(4.0) *Significance of the Kinetic Effects of Nitrous Acid.*—Here, as elsewhere in this paper, the term "nitrous acid" is used to include all those materials, present in nitric acid media, which in the water-diluted solution are together analytically determined as nitrous acid.

The original observation on the kinetic influence of nitrous acid was that of Benford and Ingold (Part I), who noted that the presence of this material caused a marked reduction in the rates of zeroth-order nitrations in nitromethane. There are two general causes of homogeneous anticatalysis, *viz.*, the breaking of reaction chains, and the retrogression of reversible reaction stages. Benford and Ingold adopted the former hypothesis as providing the more plausible explanation of their effect; for they could suppose that the nitrous acid was supplying nitrogen dioxide, or some other free-radical chain-breaker. Thus they were led to the inference that nitration under their conditions was a chain reaction. Our much wider kinetic investigation has, however, shown that nitration is not a chain reaction. Accordingly, the interpretation of the anticatalytic effect of nitrous acid needs reconsideration.

The solution of this problem is quite simple. In the course of our investigation of the kinetics of nitration, we encountered an anticatalytic effect which is more powerful than that of nitrous acid, *viz.*, the effect of nitrate ions; and we showed that this effect works by reversing a reaction stage. It will be established that nitrous acid, when present in nitric acid media, produces nitrate ions; and that it is these which are responsible for the observed anticatalytic effect of nitrous acid.

It follows from this interpretation that the kinetic study of the effect of nitrous acid on nitration provides a means of obtaining information about the molecular condition of nitrous acid in solvent nitric acid, *i.e.*, about the ionic and molecular species present in "yellow nitric acid." Complementary information has been yielded by the study of the physical properties of yellow nitric acid, notably of its spectroscopic and electrolytic properties, of which the former are described in an accompanying paper by Goulden and Millen (*J.*, 1950, paper no. 511), while the latter will be reported shortly. But before taking the physical evidence into account, we have to record some new extensions of the experimental study of the kinetic effects of nitrous acid on nitration.

(4.1) *Observations on the Kinetic Effects of Nitrous Acid.*

(4.1.1) *Constancy of the Concentrations of Nitrous Acid.*—Benford and Ingold commenced their study of the effect of nitrous acid on zeroth-order nitrations in nitromethane by showing that, under these conditions of nitration, nitrous acid is a true negative catalyst, *i.e.*, that, whilst affecting the rate of nitration, it is not itself either formed or destroyed in the nitration process. When extending the study of the effect of nitrous acid to first-order nitrations in nitromethane, and to zeroth- and first-order nitrations in other media, it was necessary to ascertain, for these cases also, whether the concentration of nitrous acid in a nitration solution does, or does not, remain undisturbed by the occurrence of nitration.

This was ascertained by determining the nitrous acid before and after nitration. The uniform result, obtained in a representative series of cases covering all the nitration media, types of aromatic compound, and kinetic forms of nitration, considered in this paper, was that the concentration of nitrous acid before and after nitration agreed to within the error of the analytical determination. A sample of such results is contained in Table XIX.

* Since this was written the work cited has been published in summary (Melander, *Nature*, 1949, **163**, 599; *Acta Chem. Scand.*, 1949, **3**, 95). Its agreement with our kinetic data has also been briefly pointed out (Gillespie, Hughes, Ingold, Millen, and Reed, *Nature*, 1949, **163**, 599). [*Added in proof.*] A full account has just appeared (*Arkiv Kemi*, 1950, **2**, 211).

Exceptions to the rule that nitrous acid is neither formed nor destroyed have been encountered in the nitration of certain (but by no means all) derivatives of phenol and aniline. Such nitrations display a somewhat complicated kinetic form, with nitrous acid functioning as a positive catalyst in certain conditions. These nitrations are not our present concern, since they involve special mechanisms. They are discussed in the accompanying papers, Parts VI and VII; *J.*, 1950, papers nos. 512, 513).

TABLE XIX.

Illustrating the constancy of the concentrations of nitrous acid during nitrations at 20°.

Expt.	Solvent.	HAr.	[HNO ₃].	[HNO ₂] _{initial} .	[HNO ₂] _{final} .
15	MeNO ₂	<i>p</i> -C ₆ H ₄ Cl ₂	8.5	0.00164	0.00170
16	"	"	"	0.00172	0.00174
18	AcOH	C ₆ H ₅ Me	6.0	0.00049	0.00049
11	"	C ₆ H ₆	9.5	0.495	0.505
12	"	"	—	0.503	0.500

(4.1.2) *Effect of Nitrous Acid on Nitrations in Nitromethane.*—The case of zeroth-order nitrations in this solvent was dealt with comprehensively by Benford and Ingold (Part I). They showed, in the examples of benzene and its homologues, that the rate of nitration was decreased by nitrous acid in such a way that the reciprocal of the rate increased linearly with the square-root of the concentration of nitrous acid. The formula $1/k_0 = a_0 + b_0[\text{HNO}_2]^{1/2}$ held over the whole of the investigated range of conditions, *viz.*, for nitric acid concentrations between 3*M.* and 7*M.*, and for nitrous acid concentrations up to about 0.1*M.* or rather more. All the observed retardations took place without sensible disturbance to the zeroth-order form of the reactions.

Some experiments have been carried out which extend the range of Benford and Ingold's observations to higher concentrations of nitrous acid. Here a disturbance is experienced: at concentrations well above 0.1*M.*, the anticatalytic effect increases with concentration considerably more steeply than corresponds to the equation written above. This is established by the rate constants quoted in Table XX. However, even the most strongly retarded reactions showed no detectable departure from the zeroth-order kinetic form.

TABLE XX.

Effect of nitrous acid on zeroth-order rate constants (k_0 in $\text{sec.}^{-1}\text{g.}^{-1}\text{mol.}^{-1}$) for the nitration of toluene in nitromethane (cf. Part I, Table II).

Expt.	[HNO ₂].	[HNO ₃] = 7.0 <i>M.</i> [HAr] ₀ = 0.09 <i>M.</i> Temp. = -6.0°.						
		10% <i>k</i> ₀ .	Expt.	[HNO ₂].	10% <i>k</i> ₀ .	Expt.	[HNO ₂].	10% <i>k</i> ₀ .
611	0.0038	7.78	617	0.0755	3.45	615	0.420	0.70
612	0.0253	4.93	614	0.170	1.84	616	0.448	0.64

This incursion of a specially strong anticatalysis at high nitrous acid concentrations appears to be a general phenomenon. It is illustrated for the zeroth-order nitrations in nitromethane in Fig. 14, where it appears as a deviation from a straight line representing the anticatalytic law established by Benford and Ingold for low concentrations of nitrous acid. The continuous line represents the approximate range of validity of their law.

Benford and Ingold showed (*loc. cit.*) that the mixed-order nitrations, which the four monohalogenobenzenes undergo in nitromethane, are also subject to anticatalysis by nitrous acid.

We now find that first-order nitrations in nitromethane are subject to a closely similar anticatalysis by nitrous acid. Some first-order rate constants for the nitration of *p*-dichlorobenzene in the presence of various amounts of nitrous acid are assembled in Table XXI. Even the strongest retardations are unaccompanied by any discernible disturbance to the first-order kinetic form of nitration.

TABLE XXI.

Effect of nitrous acid on first-order rate constants (k_1 in sec.^{-1}) for the nitration of *p*-dichlorobenzene in nitromethane.

[HNO ₃] = 8.5 <i>M.</i> [HAr] ₀ = 0.10 <i>M.</i> Temp. = 20.0°.											
Expt.	[HNO ₂].	10% <i>k</i> ₁ .	Expt.	[HNO ₂].	10% <i>k</i> ₁ .	Expt.	[HNO ₂].	10% <i>k</i> ₁ .	Expt.	[HNO ₂].	10% <i>k</i> ₁ .
301	0.0018	649	622	0.0350	276	623	0.0590	218	154	0.0829	187
150	0.0240	367	152	0.0365	298	153	0.0605	215	626	0.106	100
21	0.0240	360	151	0.0480	255	624	0.0676	194	628	0.174	45

If we temporarily leave aside the last two experiments, and plot the reciprocals of the rate constants against the square-roots of the nitrous acid concentrations, we obtain the linear relation shown in Fig. 15. Thus it appears that, for concentrations of nitrous acid which are not too high, the law obeyed by the anticatalysis is $1/k_1 = a_1 + b_1[\text{HNO}_2]^{1/2}$; that is, it is of the same form as for zeroth-order nitration, except, of course, that the constants, k_1 , a_1 , and b_1 , have not the same physical dimensions as the constants, k_0 , a_0 , and b_0 , which apply to the zeroth-order case.

FIG. 14.

Effect of nitrous acid on the zeroth-order rate of nitration of toluene by 7.0M-nitric acid in nitromethane at 6.0°.

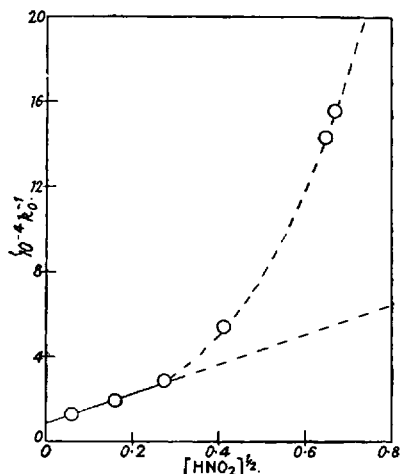
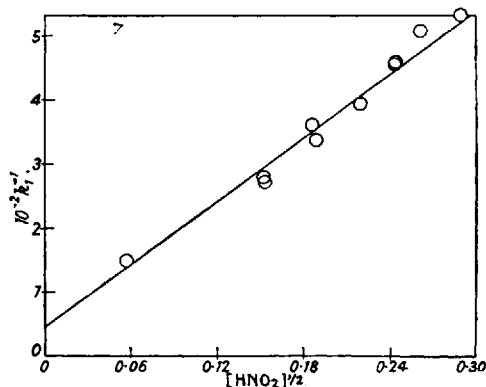


FIG. 15.

Effect of nitrous acid on the first-order rate of nitration of p-dichlorobenzene by 8.5M-nitric acid in nitromethane at 20.0°.



The last two experiments noted in Table XXI suffice to show, however, that this law is only a limiting law: the points representing these two experiments lie well above the projection of the straight line shown in Fig. 15. The complete graph is a straight line running into a rapidly steepening curve, such as in Fig. 14. We conclude that in first-order nitrations in nitromethane, just as in zeroth-order nitrations in this solvent, a specially powerful anticatalysis supervenes at the higher concentrations of nitrous acid.

(4.1.3) *Effect of Nitrous Acid on Nitrations in Acetic Acid.*—This has been investigated in the examples of the zeroth-order nitration of toluene in 7M- and in 12M-nitric acid, the zeroth-order nitration of benzene in 12M-nitric acid, the first-order nitration of benzene in 8M-nitric acid, and the first-order nitration of chlorobenzene in 10M-nitric acid. The kinetic phenomena observed in these cases are generally similar to those described in section (4.1.2).

In all cases nitrous acid reduces the reaction rate, without noticeably altering the kinetic form of the reaction: zeroth- and first-order reactions alike are retarded. The limiting form, for low concentrations of nitrous acid, of the law expressing the retardations appears to be the same for these nitrations in acetic acid as for nitrations in nitromethane, *viz.*, $k_0^{-1} = a_0 + b_0[\text{HNO}_2]^{1/2}$ for the zeroth-order reactions, and $k_1^{-1} = a_1 + b_1[\text{HNO}_2]^{1/2}$ for the first-order reactions. However, at concentrations of nitrous acid above about 0.1M., an anticatalytic effect supervenes which is much stronger than corresponds to the above limiting law. The results in Table XXII will serve to establish these points in the example of the nitration of chlorobenzene.

TABLE XXII.

Effect of nitrous acid on first-order rate constants (k_1 in sec^{-1}) for the nitration of chlorobenzene in 99.8% acetic acid.

		[HNO ₂] = 10.0M. [Har] ₀ = 0.10M. Temp. = 20.0°.						
Expt.	[HNO ₂].	10 ⁵ k ₁ .	Expt.	[HNO ₂].	10 ⁵ k ₁ .	Expt.	[HNO ₂].	10 ⁵ k ₁ .
291	0.0022	325	177	0.0450	182	174	0.146	43.8
170	0.0036	281	173	0.101	119	176	0.160	41.8
171	0.0128	241	175	0.135	61.4	178	0.203	15.0
172	0.0243	211						

A plot of the reciprocals of the rate-constants, given in Table XXII, against the square-roots of the nitrous acid concentration is shown in Fig. 16. From this graph it appears that the linear relationship representing the limiting law has approximate validity up to about 0.1M-nitrous acid, but that at higher concentrations than this the anticatalytic effect becomes intensified very rapidly.

(4.1.4) *Effect of Nitrous Acid on Nitrations in Nitric Acid.*—First-order nitrations with nitric acid as both solvent and reagent are also retarded by nitrous acid, the kinetic order of the reaction remaining undisturbed. This has been established in the examples of the nitration of nitrobenzene and of 1-nitroanthraquinone. Some data relating to the nitration of nitrobenzene in nitric acid containing nitrous acid are given in Table XXIII. It should be observed that, except for the nitrous acid (introduced as dinitrogen tetroxide), and the compound undergoing nitration, and its nitration products, the nitric acid used in these experiments was pure; for we

FIG. 16.

Effect of nitrous acid on first-order rate of nitration of chlorobenzene by 10.0M-nitric acid in acetic acid at 20.0°.

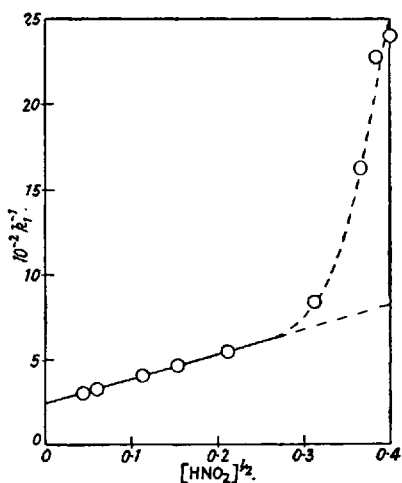
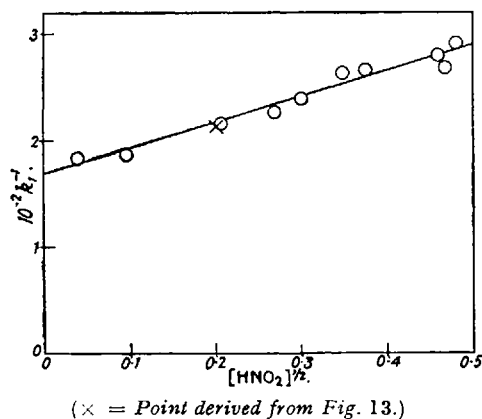


FIG. 17.

Effect of nitrous acid on first-order rate of nitration of nitrobenzene in anhydrous nitric acid at -13.3°.



shall note below that the kinetic effect of nitrous acid is very different when the employed nitric acid contains water.

TABLE XXIII.

Effect of nitrous acid on first-order rate constants (k_1 in sec.^{-1}) for the nitration of nitrobenzene in 100.0% nitric acid.

[HNO ₃] ₀ = 24.58M. * [H ₂ O] = 0.00M. [HAr] ₀ = 0.20M. Temp. = -13.3°.								
Expt.	[HNO ₂].	10 ⁵ k ₁ .	Expt.	[HNO ₂].	10 ⁵ k ₁ .	Expt.	[HNO ₂].	10 ⁵ k ₁ .
410	0.0015	547	417	0.0912	401	415	0.221	375
414	0.0094	536	419	0.121	378	421	0.211	357
416	0.0428	461	420	0.138	375	422	0.229	342
418	0.0734	426						

* Molarity before the introduction of nitrous acid or nitrobenzene (cf. p. 2418).

The retardations caused by nitrous acid in the speed of nitration are much smaller in pure nitric acid than they are in organic solvents: the largest of the nitrous acid concentrations used cut down the rate only by about one-third. Because of this, we are not able to establish the mathematical form of the effect with a chemically significant degree of precision. It is true that, as Fig. 17 shows, a plot of the reciprocals of the rate constants against the square-roots of the nitrous acid concentrations can be considered to indicate a straight line; but this is hardly significant because of the smallness of the effect. What Fig. 17 does show is that, up to nitrous acid concentrations of 0.23M., there are no signs of the incursion of a much more powerful anticatalysis of the type of that which, in organic solvents, supervenes at concentrations of nitrous acid above about 0.1M.

TABLE XXIV.

Effect of nitrous acid on first-order rate constants (k_1 in sec.^{-1}) for the nitration of nitrobenzene in nitric acid containing water.

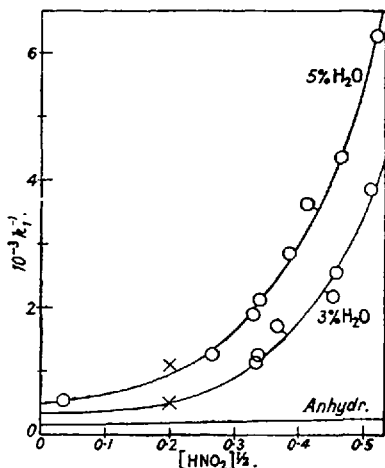
Expt.	$[\text{HNO}_2]$	$10^4 k_1$	Expt.	$[\text{HNO}_2]$	$10^4 k_1$	Expt.	$[\text{HNO}_2]$	$10^4 k_1$
Series A: $[\text{HNO}_3]_0 = 23.66\text{M.}^*$ $[\text{H}_2\text{O}]_0 = 1.65\text{M.}\dagger$ $[\text{HAr}]_0 = 0.21\text{M.}$ Temp. = -13.3° .								
631	0.110	88.2	633	0.132	57.8	635	0.210	39.4
632	0.113	79.5	634	0.207	46.6	636	0.259	25.8
Series B: $[\text{HNO}_3]_0 = 23.36\text{M.}^*$ $[\text{H}_2\text{O}]_0 = 2.93\text{M.}\dagger$ $[\text{HAr}]_0 = 0.20\text{M.}$ Temp. = -13.3° .								
425	0.00135	189	427	0.116	47.2	432	0.220	22.8
426	0.0702	78.6	429	0.148	34.9	430	0.273	15.9
428	0.109	53.1	431	0.166	27.2			

* Molarity before introduction of nitrous acid or nitrobenzene (cf. p. 2418).

† These figures relate to initially added water: extra water is produced during the nitrations.

The influence of added water on the kinetic effect of nitrous acid is illustrated by the two series of results in Table XXIV. They again relate to the nitration of nitrobenzene in nitric acid, at the same temperature as before; but in series A the nitric acid contained a uniform amount, about 3% by volume, of added water; and in Series B it contained another common amount, about 5% by volume, of water (the exact proportions are noted in the Table).

FIG. 18.
Effect of nitrous acid on first-order rate of nitration of nitrobenzene in slightly aqueous nitric acid at -13.3° .



(\times = Points derived from Fig. 13.)

evident that the general influence of added water is to make nitration much more sensitive to anticatalysis by nitrous acid; and that, in the presence of 3% or 5% of water, practically the whole of the observed anticatalysis is of that strong and rapidly steepening kind, which in other cases appears only at the higher concentrations of nitrous acid.

(4.2) Discussion (Part IV): Nitrous Acid Effects: Oxides of Nitrogen as Electrolytes

(continued from p. 2430).

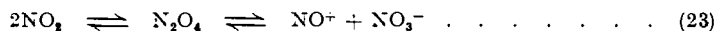
(4.2.1) Anticatalysis by Nitrous Acid in Low Concentration: Ionisation of Dinitrogen Tetroxide.—One of the more easily controlled ways of preparing solutions in nitric acid of what we call nitrous acid is to dissolve (below 0°) a known weight of pure dinitrogen tetroxide (redistilled in oxygen) in pure nitric acid (freed from nitrous acid and water by distillation from sulphuric acid at low pressure); water may be added if required. The solutions prepared from these pure, colourless, materials are yellow, and spectrally, and in other respects, are indistinguishable from "yellow nitric acid," containing the same analytical amount of nitrous acid and the same amount (if any) of water, obtained in other ways, e.g., by the thermal or photochemical decomposition of nitric acid (as in storage), or by the addition to nitric acid of nitrogen oxides lower than dinitrogen tetroxide. The state of oxidation of the species collectively regarded as nitrous acid, in whatever forms they may have been introduced, is

determined by the nitric acid medium, and, in nearly pure nitric acid, is essentially that of dinitrogen tetroxide. The problem of the nature of nitrous acid in solvent nitric acid can thus be simplified to that of determining the condition assumed by introduced, pure, dinitrogen tetroxide.

Although dinitrogen tetroxide is very soluble in anhydrous nitric acid, the solutions have a definite partial vapour pressure of the equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide. Hence one of the forms of change undergone by dinitrogen tetroxide in solvent nitric acid must certainly be partial homolytic dissociation to nitrogen dioxide. The yellow colour of the solutions suggests the presence, in small concentration, of nitrogen dioxide. It is true that the absorption of light by such solutions in the violet and near ultra-violet regions is not quite identical in spectral form with that of gaseous nitrogen dioxide; but the differences are probably not greater than could plausibly be explained by the polarising effect of solvation.

Reed has studied the electrical conductivity of solutions of dinitrogen tetroxide in nitric acid solvents. His measurements show that dinitrogen tetroxide is a definite electrolyte in such solvents. In pure nitric acid it is quite a strong electrolyte. But in solutions of nitric acid in excess of nitromethane, dinitrogen tetroxide becomes a typical weak electrolyte, obeying Ostwald's dilution law, and thus showing itself to be a binary electrolyte. As to the nature of the formed ions, Goulden and Millen have made it clear that they are nitrosonium and nitrate ions. They have studied the Raman spectra of solutions of dinitrogen tetroxide in nitric acid, and also the transport phenomena and electrode processes associated with their electrolysis. They have also noticed that the addition of an alkali-metal nitrate to a solution of dinitrogen tetroxide in nitric acid produces a marked increase in the partial vapour pressure of nitrogen dioxide and dinitrogen tetroxide, and in some conditions leads to a visible evolution of these gases. The spectroscopic evidence is given by Goulden and Millen in an accompanying paper (*J.*, 1950, paper no. 511), but their electrochemical work and Reed's is being continued in various directions, the intention being to publish the whole of this branch of the general investigation later.

From this work it follows that we have to picture dinitrogen tetroxide as undergoing, not only a homolytic, but also a heterolytic, dissociation in nitric acid:

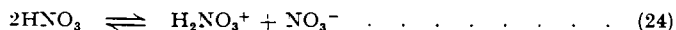


The total evidence strongly suggests that, in such conditions as are of present concern to us, the principal entity present is still the dinitrogen tetroxide molecule, although in nearly pure nitric acid large concentrations of the ions are produced.

In this respect, as in many others, we find solvent nitric acid exhibiting a character intermediate between that of sulphuric acid and that of relatively weakly polar or non-polar organic solvents. In two other papers of the present collection (*J.*, 1950, papers nos. 499, 508) it is shown, both cryoscopically and spectroscopically, that the splitting of dinitrogen tetroxide in sulphuric acid is entirely heterolytic. In non-polar solvents the fission is wholly homolytic. In nitric acid we observe both types of fission. Again, in sulphuric acid no molecular dinitrogen tetroxide survives, the heterolysis being complete. In organic solvents the heterolysis is vanishingly small. In nitric acid it is considerable, but still partial.

Turning to the kinetic findings, let us first consider Benford and Ingold's results (Part I) concerning zeroth-order nitrations in nitromethane. They observed that nitrous acid retarded these reactions in such a way that the reciprocal of the zeroth-order rate constant increased linearly with the square-root of the analytically determined concentration of nitrous acid. Now one molecule of nitrous acid is the analytical equivalent of one molecule of dinitrogen tetroxide. Since the principal solute species in Benford and Ingold's conditions was undoubtedly molecular dinitrogen tetroxide, we can take the concentration of this to be given, in sufficient approximation, by the analytically determined concentration of nitrous acid. Provided that, as the physical evidence indicates, the amount of nitrate ion formed by heterolysis of this dinitrogen tetroxide is considerably greater than the amount arising by self-ionisation of the nitric acid contained in the nitromethane solvent, equilibrium (23) will require the *total* concentration of nitrate ions to be approximately proportional to the square-root of the concentration of molecular dinitrogen tetroxide, and therefore approximately proportional to the square-root of the analytically determined concentration of nitrous acid. But we have already seen [Section (2.2.2)] that, within appropriate ranges of concentration, added nitrate ions retard zeroth-order nitrations in such a way that the reciprocal of the rate constant increases linearly with the first power of the concentration of nitrate ions. And we have seen also [Section (2.4.1)] that this can be understood on the basis that the effect of the nitrate ion is to deprotonate the nitric acidium ion in accordance with the reversible equation

(24), thus reducing the equilibrium concentration of nitric acidium ion, to which the rate of formation of nitronium ion, and hence the zeroth-order rate of nitration, is proportional :



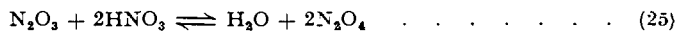
Combining these points, we see that nitrous acid should retard nitration in such a way that the reciprocal of the zeroth-order rate constant increases linearly with the square-root of the analytically determined concentration of nitrous acid. Thus, Benford and Ingold's law for the anticatalysis by nitrous acid of zeroth-order nitrations in nitromethane becomes explicable on the simple ground that "nitrous acid" exerts its effect by supplying nitrate ions as represented in equation (23), and that the nitrate ions act, as we have other reasons for believing they do, by deprotonating the nitric acidium ion in accordance with equation (24).

The analogous reciprocal-square-root law, which we have observed for the effect of nitrous acid on first-order nitrations, can evidently be explained on similar lines : the difference is only that the equilibrium concentration of nitric acidium ion now determines the stationary concentration of the nitronium ion, to which the first-order rate constant is proportional.

For first-order nitrations in anhydrous nitric acid as solvent the anticatalysis by nitrous acid is relatively weak : it is too weak to enable a chemically significant law for the effect to be critically derived from the data. The comparative weakness of the effect undoubtedly arises from a less favourable relation in nitric acid alone than in solutions of nitric acid in organic solvents, between the amounts of nitrate ion supplied by heterolysis of the dinitrogen tetroxide and the quantities furnished by self-ionisation of the nitric acid. For this reason, the law obeyed by the effect is not expected to have any simple mathematical form.

(4.2.2) *Anticatalysis by Nitrous Acid in Higher Concentration and in the Presence of Water : Ionisation of Dinitrogen Trioxide.*—The substance of our theory of the specially strong anticatalysis of nitration by nitrous acid in the higher range of concentrations investigated, and by nitrous acid at all concentrations in the presence of suitable amounts of water, is that these effects arise from the formation of dinitrogen trioxide, which, although in smaller concentration than the dinitrogen tetroxide, is specifically a much more powerful anticatalyst.

When pure dinitrogen trioxide (redistilled in nitric oxide) is added to a large excess of absolute nitric acid at -40° , the blue colour of the former substance is instantly destroyed, and a yellow solution results which is quite similar to the solutions which one prepares by the use of dinitrogen tetroxide. The oxidation-reduction which this colour change indicates must in principle be a balanced reaction :



It is undoubtedly true for the conditions of main concern to us that, of all the species collectively estimated as nitrous acid, the preponderating species is molecular dinitrogen tetroxide. This being so, it follows from an application of the mass law to equation (25) that the proportion of so-called nitrous acid which exists in the form of dinitrogen trioxide must increase with the total concentration of dinitrogen tetroxide, *i.e.*, of analytical nitrous acid, and also with the concentration of water. Up to the highest concentrations of nitrous acid, and of water, with which we deal in this paper, say, $M/3$ for nitrous acid and $3M$. for water, the proportion of dinitrogen trioxide in the nitric acid solvents seems to be too small to permit estimation of the trioxide, in the presence of accompanying substances, by means of its colour, *i.e.*, by its absorption of light in the red and the near infra-red regions. However, when much more water is introduced into these solutions, they become blue. There can be no reasonable doubt that in such conditions important quantities of dinitrogen trioxide are formed, illustrating the reversibility of reaction (25).*

Let us now consider how dinitrogen trioxide might retard nitration with such specific strength that it can become effective as an anticatalyst at some quite low threshold of concentration.

We know many close analogies of chemical behaviour between dinitrogen trioxide and dinitrogen tetroxide. In the gas phase, and in non-polar or weakly polar organic solvents, dinitrogen trioxide is partly homolysed into nitric oxide and nitrogen dioxide, just as dinitrogen

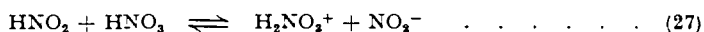
* It is often assumed that molecular nitrous acid, HNO_2 , is blue, but we doubt this : molecular nitrous acid should be pale yellow. We think that the blue colour attributed to nitrous acid is the property of its anhydride, with which the acid enters into equilibrium, even in the presence of much water. It is also stated that methyl nitrite is blue, but it should not be, having no suitable chromophore. And, in fact, it is not : prepared in these laboratories by Dr. A. T. Austin, it is pale yellow (and, according to his observation, it boils at -18.5° , not -12° as is recorded in the literature). The blue colour observed by other workers is undoubtedly due to contamination by dinitrogen trioxide.

tetroxide in such conditions is partly dissociated into two molecules of nitrogen dioxide. Again, as is shown in two of the accompanying papers (*J.*, 1950, papers nos. 499, 508), dinitrogen trioxide, like dinitrogen tetroxide, is heterolytically dissociated in solvent sulphuric acid. The products of heterolysis in the two cases are strictly analogous, and for both oxides the heterolysis is complete. We shall now assume that analogies, such as we observe in non-polar and weakly polar solvents, on the one hand, and in highly polar sulphuric acid, on the other, will continue to hold in the solvent of intermediate character, nitric acid. In particular, we shall assume that, in solvent nitric acid, dinitrogen trioxide, just like dinitrogen tetroxide, will undergo partial homolysis and partial heterolysis side by side. This is expressed in equations (26), which are to be compared with equations (23) :



The products of the heterolysis will be the nitrosonium ion and the nitrite ion, and it is with the latter that we shall now be especially concerned.

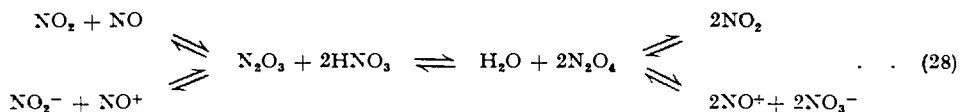
Our theory is that, just as the anticatalytic behaviour of dinitrogen tetroxide is dependent on its heterolysis to the nitrate ion, so the retarding effect of dinitrogen trioxide arises from its heterolysis to the nitrite ion; and that the nitrite ion exerts its action, exactly as the nitrate ion does, namely, by deprotonating the nitric acidium ion. Accordingly, in the presence of dinitrogen trioxide, and therefore of nitrite ion, the stationary concentration of nitric acidium ion is limited by equilibrium (27) :



This equilibrium will therefore limit zeroth-order and first-order nitration rates, both of which are proportional to the stationary concentration of nitric acidium ion.

Equation (27) is to be compared with equation (24), which expresses the analogous reaction of the nitrate ion. However, the nitrite ion, as the anion of a weak acid, will be a much stronger base than is the nitrate ion. Consequently, we must expect a low concentration of nitrite ion to be as effective as a much higher concentration of nitrate ion for the destruction of the nitric acidium ion, and hence for the anticatalysis of nitration.

Let us now combine equations (23), (25), and (26) in the following scheme :



It has to be emphasized that, under the conditions of our kinetic experiments, the equilibria of system (28) lie in the direction of dinitrogen tetroxide rather than dinitrogen trioxide, and of nitrate ions rather than nitrite ions. Obviously the ratio of nitrite ions to nitrate ions in a large excess of nitric acid must always be small. But the points of kinetic importance are, first, that, because of the superior specific effectiveness of the nitrite ion, a small ratio of nitrite to nitrate may well be large enough to give to the nitrite ion a practical kinetic importance; and secondly, that the ratio can be substantially increased by increasing either the concentration of the dinitrogen tetroxide (*i.e.*, of the nitrous acid as measured analytically) or the concentration of the water.

Therefore we can understand what happens to the total anticatalytic effect of nitrous acid as the concentration of analytical nitrous acid, or the concentration of water, is progressively increased. We deduce that, as the rising proportion of nitrite ion reaches some quite low threshold, this ion will begin to take a part in the anticatalysis quantitatively comparable to the part taken by the nitrate ion, which up to that stage had been the sole effective agent; and that, if the concentration of the analytical nitrous acid, or of the water, is further increased, so that the proportion of nitrite ion continues to rise, then this ion will rapidly assume a dominating rôle, with the result that the total anticatalytic effect will increase steeply. This is what we observe. It should apply alike to zeroth- and first-order nitrations, and, as far as our observations extend, it does so.

The confirmation of this interpretation on quantitative lines can readily be carried to a semi-quantitative stage, but hardly beyond that on the basis of our results. With the help of the mass-law, it is easy to derive mathematical expressions for the anticatalysis, which should have approximate validity over a considerable part of the investigated range of concentration. Thus we can deduce the equation $1/k_0 = a_0 + b_0[\text{HNO}_2]^{1/2} + c_0[\text{HNO}_2]^{3/2}$ for zeroth-order

nitration, and a similar formula for first-order nitration. In these equations the interesting term is the last, since it expresses the presumed effect of the nitrite ions.*

Equations of the type indicated have been found to have a considerable measure of validity when applied to our data. Thus in Fig. 18 (p. 2434), the curve labelled "5% H₂O," although it is scarcely distinguishable from the best smooth curve through the observational points, was actually drawn as the graph of the equation $10^{-3}k_1^{-1} = 0.5 + 40[\text{HNO}_2]^{3/2}$. Similarly the curve labelled "3% H₂O," though it appears to be drawn to fit the points, is, in fact the graph of the equation $10^{-3}k_1^{-1} = 0.3 + 25[\text{HNO}_2]^{3/2}$. It will be noticed that the ratio of the coefficients, 40 and 25, of the main terms in these equations is approximately equal to the ratio of the corresponding water concentrations—as one might expect from elementary theory.† We do not wish to over-emphasize such comparisons with experiment, because experimental error, the number of disposable constants, and the neglect of activity corrections, all limit their quantitative significance. However, considered as a semi-quantitative check, the above comparison is clearly satisfactory.

(5) EXPERIMENTAL METHODS.

(5.1) Purification of Materials.

(5.1.1) *Nitric Acid*.—This was purified as described by Benford and Ingold (Part I), except that the two distillations from excess sulphuric acid were, by the use of a rotary oil-pump, conducted at lower pressures than they employed, and at temperatures below 0°. The second distillation was accomplished without permitting visible boiling. The colourless crystalline distillate was collected at -80°. It could be preserved in sealed tubes in the dark at -80°. It melted to give a colourless liquid, which had the theoretical acid equivalent of nitric acid to within the error of measurement. Its content of nitrous acid was often undetectably small, and was normally less than 0.001M. At temperatures above 0° the material developed nitrous acid rapidly.

(5.1.2) *Organic Solvents*.—Specimens of nitromethane obtained from several commercial sources, and also samples prepared in the laboratory, were dried (CaCl₂), and distilled through an efficient fractionating column, the constant-boiling fraction (*e.g.*, of b. p. 101.2°/762.0 mm.) being collected for use.

Acetic acid ("AnalaR" supplied by British Drug Houses Ltd.) was boiled for several hours under reflux with chromium trioxide, and recovered by distillation. It was then rectified with the aid of a fractionating column, a fraction of b. p. 117.8–118.2° being collected for further purification. This was fractionally frozen until the m. p. 16.65° was obtained. The correct weight of water was then added in order to produce the 99.8% acetic acid used as solvent.

(5.1.3) *Nitrates and Other Salts*.—All the salts employed, *viz.*, lithium, sodium, potassium, ammonium and urea nitrates, potassium perchlorate, and potassium hydrogen sulphate, were purified by crystallising them several times from water, and drying them at temperatures between 110° and 200° in a vacuum over phosphoric oxide.

(5.1.4) *Dinitrogen Tetroxide and Dinitrogen Trioxide*.—The procedures used for the preparation and purification of these substances were as described in an accompanying paper (*J.*, 1950, paper no. 499).

(5.1.5) *Aromatic Compounds*.—All the compounds employed for nitration, *viz.*, benzene, toluene, ethylbenzene, *p*-xylene, mesitylene, fluoro-, chloro-, bromo-, and iodo-benzene, *o*-, *m*-, and *p*-dichlorobenzene, 1:2:4-trichlorobenzene, ethyl benzoate, nitrobenzene, *p*-chloronitrobenzene, and 1-nitro-anthraquinone, were purified by the standard methods of fractional freezing, crystallisation from solvents, sublimation, or distillation through an efficient fractionating column. Some of the substances were given additional special treatments. For instance, benzene was shaken with sulphuric acid until the latter ceased to become coloured, and toluene was shaken with mercury.

(5.2) Methods for following the Kinetics of Nitration.

(5.2.1) *The Dilatometric Technique*.—The technique used was essentially that worked out by Benford and Ingold (Part I). The instruments employed, *viz.*, the precision thermostats, including one for temperatures below 0°, and the tapless dilatometers, were as described by them.‡ Difficulty with

* The power 3/2, characterising this term, arises as follows. The use of the mass law, with reference to equations (28), yields the conclusion that the product $[\text{NO}^+][\text{NO}_2^-]$ is proportional to $[\text{N}_2\text{O}_4]^2$; and that $[\text{NO}^+]$, which is approximately equal to $[\text{NO}_2^-]$, is therefore proportional to $[\text{N}_2\text{O}_4]^{1/2}$. Thus $[\text{NO}_2^-]$ becomes proportional to $[\text{N}_2\text{O}_4]^{3/2}$, that is, to $[\text{HNO}_2]^{3/2}$, where HNO₂ signifies the analytical nitrous acid.

† The theory is as follows. With reference to equations (28), the mass law indicates that the product $[\text{NO}^+][\text{NO}_2^-]$ is proportional to $[\text{H}_2\text{O}]$, and that the product $[\text{NO}^+][\text{NO}_2^-]$, and hence also each of its nearly equal factors, are independent of $[\text{H}_2\text{O}]$. Thus $[\text{NO}_2^-]$ becomes proportional to $[\text{H}_2\text{O}]$, justifying the statement in the text. Of course, this applies only so long as there is too little water to produce important amounts of $[\text{NO}_2^-]$ by the ordinary aqueous ionisation of nitric acid.

‡ The most suitable of Benford and Ingold's dilatometers for use with rapid reactions is their "Type C," one limb of which is bent over for convenience in filling. However, occasionally during a run, a small droplet, formed by drainage of the capillary walls, gets into the down-facing end, thereby creating a pressure change which interferes with the hydrostatic equilibrium governing the relation between the heights of the two menisci in the body of the dilatometer. The possibility of this occurrence is excluded by making the bent-over part of the capillary tube detachable, through the provision, near the top, of a very small, ground-glass joint: then, as soon as the dilatometer is filled, the bend can be taken off.

maintenance of accurately constant temperatures over long periods was reduced by the use of thermostat regulators having closed heads filled with hydrogen. A cathetometer was employed for reading the dilatometers, greater accuracy being thus obtainable than could be secured by the use of a scale attached to the dilatometer.

Benford and Ingold's procedure for starting runs was slightly modified. The aromatic compound was weighed into a measuring flask, which was immersed in the thermostat. The nitrating medium contained in another flask was also placed in the thermostat, and was there allowed to come to thermal equilibrium. It was then added to the aromatic compound up to the marked volume (10 c.c.), and simultaneously the stop-watch was started. The mixture was immediately shaken until homogeneous; it was then transferred, with the aid of a suction pump, to the dilatometer, likewise immersed in the thermostat.

In a few cases the thermal effect of dissolving the aromatic compound in the nitrating medium was investigated with the aid of a thermocouple. Increases of temperature, extending to 2.4° in the more concentrated solutions, were observed; but in the dilatometers all these disturbances disappeared in less than 5 minutes.

(5) 22. *Chemical Control of Dilatometric Runs.*—When following reaction kinetics by the variation of a physical property, it is important to identify the reaction measured. In the present work, this was done, for each aromatic compound and each nitrating medium, by at least one of the following four methods, *viz.*, (1) by determining aromatic nitroxy in the product after the dilatometric contraction ceases; (2) by isolating, and obtaining an ultimate analysis of, the nitration product after the contraction ceases; (3) by ascertaining that the mononitro-derivative of the aromatic compound used (or at least one of the nitro-isomerides, when there are several) does not give any dilatometric or other indication of reaction when placed for the same length of time under the same conditions; and (4) by following the kinetics of the reaction completely by chemical analysis.

Method (1) was used in every case. We do not quote the results, because they are numerous and quite uniform: always the percentage of nitroxy corresponded to mononitration to within $\pm 0.2\%$. Method (2) was employed occasionally as an additional check. Thus the product from 1:2:4-trichlorobenzene on analysis (Drs. Weiler and Strauss) gave the following figures: C, 32.4; H, 1.2; N, 6.3 (Calc. for $C_6H_3Cl_3O_2N$: C, 31.8; H, 0.9; N, 6.2%). Method (3) was often used as a further check, especially in cases of mixed-order kinetics, since it was then particularly necessary to be certain that the kinetic complications did not arise from consecutive reactions. Thus it was ascertained that, under the conditions used for the nitration of chlorobenzene, *p*-chloronitrobenzene undergoes no change. Method (4) was employed only as an approximate check on the dilatometric results for some fast nitrations of nitrobenzene in absolute nitric acid. These runs involved the difficulty that the dilatometric rate constant depended on observation only over the latter part of the reaction, a good deal of reaction having occurred during the few minutes in which the thermal effect of mixing precludes dilatometric readings of the reaction rate. However, the heat of mixing has a much less serious effect on the reaction rate itself than on its dilatometric indication, and thus in principle the rate can be measured in other ways, at least approximately, during much of the period of the thermal disturbance. We stopped the nitrations by delivering samples into water about once a minute, and then determined the dinitrobenzene in the diluted samples by a method involving the use of dimethylaniline, as described below.

(5.3) Methods of Chemical Analysis.

(5.3.1) *Determination of Nitroxy.*—For the routine control of dilatometric runs by method (1) above, nitroxy in the isolated aromatic nitration product was determined by the method of Kolthoff and Robinson (*Rec. Trav. chim.*, 1926, **45**, 169), 30% aqueous sodium nitrate being employed as buffer, and aqueous potassium thiocyanate as the indicator. The method was tested by its application to a considerable variety of pure nitro-compounds, including at least one isomeric form of all those which were expected to be produced by nitration. In almost all cases the results were correct to within 0.2%. The one exception was *m*-nitroanisole which, because of an impurity, persistently gave results 0.4% high.

In the chemically followed kinetic runs on the nitration of nitrobenzene in absolute nitric acid, noted under method (4) above, we traced the production of the dinitrobenzenes by utilising the coloured molecular compounds which nitrobenzene and the dinitrobenzenes yield on combination with dimethylaniline (Biron and Morguleva, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1598). The intensity of the colour given by any of these nitro-compounds in a large excess of dimethylaniline is proportional to the concentration of the nitro-compound. The colour produced by nitrobenzene is pale yellow, whilst that given by the dinitrobenzenes is an intense red; and thus, by measuring the intensity of the red colour, it is possible to determine the dinitrobenzenes. Though the accuracy of the method is low, it was sufficient for the purpose we had in view, which was to confirm, in the case of these rapid nitrations, that the part of the reaction which could be followed dilatometrically was indeed a part of the mononitration process. Our method was to make the diluted samples alkaline and extract them with ether; and then, after drying and evaporating the ether, to make up to a fixed volume with dimethylaniline, and measure the intensity of the colour. This was done with the aid of a Spekker absorptiometer, employing green filters, which transmit only light which is not absorbed by the nitrobenzene compound but is absorbed by the dinitrobenzene compounds.

(5.3.2) *Determination of Nitrous Acid.*—Benford and Ingold (Part I, *loc. cit.*) developed a method for the determination of nitrous acid, which is based on an earlier method due to Lunge and Lwoff, and

consists in employing the nitrous acid for a diazotisation, and thence for the production of an azo-dye, which can be estimated colorimetrically. At first we used exactly Benford and Ingold's procedure, which involves, first, comparing in a colorimeter, against a permanent colour standard, the azo-colour developed from a series of nitrite solutions of known concentrations, and then, comparing the azo-colour developed from the solution to be analysed, in the same way, and against the same permanent colour standard.

With the higher colour intensities involved in some of these analyses we found difficulty in matching the colours. Our first reply to this was to go over to the volumetric method described below, but only for the determination of the higher nitrous acid concentrations, for which alone this method was satisfactory. The method of Benford and Ingold was retained for the determination of low concentrations.

The volumetric method is based on the oxidation of nitrous acid by chloramine- τ . A measured amount of the solution to be analysed was made up to a known volume with water, and measured samples of the diluted solution were delivered into stoppered bottles, there to be mixed with more water, some glacial acetic acid, and measured amounts of a standard solution of chloramine- τ . The mixtures were shaken, and, after 15–20 minutes, were treated with an excess of potassium iodide and titrated against standard thiosulphate, with starch as indicator. Blank experiments showed that no sensible error was caused by the presence of the aromatic compounds in some of the solutions analysed. The only serious disadvantage of this method is that, for low nitrous acid concentrations, the titre-differences are small, and the determinations correspondingly inaccurate.

At a later stage, we found it convenient to return to the colorimetric method, but in a modified form, which overcame the above-mentioned difficulty of colour matching at high colour intensities, and enabled both high and low concentrations of nitrous acid to be determined satisfactorily by a common procedure. The new method consisted in developing the azo-colours from the nitrous acid solutions just as before, and then measuring the colour intensity by means of a Spekker absorptiometer, without the employment of any permanent colour standard.

Green filters were used in order to secure strong absorption. The left-hand cell and one right-hand cell of the absorptiometer were filled with water, and the other right-hand cell with a solution containing the azo-compound. The diaphragm was closed, and the drum set to zero, with the two water cells in line; and the sensitivity of the galvanometer was then adjusted to give a full scale deflection. The cell containing the azo-colour was now substituted for the water cell on the right-hand side of the instrument, and the diaphragm was opened until the galvanometer showed no deflection. Then the water cell on the right-hand side was restored to its original position, and the resulting galvanometer deflection was reduced to zero by rotation of the calibrated drum. The instrument was first calibrated by this means, a number of nitrite solutions of known concentration being used for the purpose; and a curve was constructed connecting the drum reading with the concentration of nitrous acid. It was then necessary only to repeat the procedure with the solution to be analysed, note the drum reading, and apply the calibration curve.

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