494. Kinetics and Mechanism of Aromatic Nitration. Part III. Nitration in Acidified Aqueous Nitric Acid.
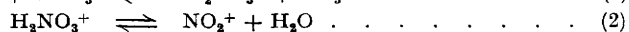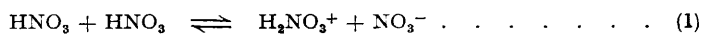
By E. S. HALBERSTADT, E. D. HUGHES, and C. K. INGOLD.

The nitration of 2-phenylethylsulphonic acid, and of benzylsulphonic acid, in aqueous solutions of nitric acid, containing some perchloric or sulphuric acid, has been kinetically studied. It is made plausible that the sulphonic acids are nitrated through their anions, which are comparable in reactivity to some of those aromatic compounds which exhibit zeroth-order nitration in organic solvents (cf. Part II, Section 1). With Millen, it is spectroscopically established that, in the aqueous media used, the perchloric acid is completely, and the sulphuric acid largely, ionised, whilst the nitric acid exists almost wholly in its non-dissociated form. It is shown that in these media the nitrations uniformly follow a first-order law. The effect of medium composition on the reaction rate is characterised by rather narrow thresholds, across which the nitrations pass, from being very slow, to very fast. An increase of the concentration either of nitric acid, or of the added strong acid, the concentration of the other being suitable, will lead to these thresholds of onset of nitration, which can arise in the presence of, *e.g.*, 75 mols. % of water. In the neighbourhood of such a threshold, added sodium perchlorate accelerates, whilst added sodium or ammonium nitrate retards, nitration.

The thresholds show that the nitrating agent in these aqueous nitrations is not the nitric acid molecule, the concentration of which changes relatively slowly with changing composition of the medium. It could be the nitric acidium ion, $H_2NO_3^+$, the equilibrium degree of formation of which is likely to exhibit thresholds, owing to a diversion of the proton, which is lost by the strong acid, from uptake by water towards uptake by nitric acid, as the activity of the water falls below a more or less critical value in consequence of a progressive involvement of the water in hydrates. The accelerating effect of sodium perchlorate is regarded as a general salt effect, operating by reduction of the water activity as the result of an increased formation of ion hydrates. The retarding effect of sodium or ammonium nitrate is considered to be the overall result of this accelerative general salt effect, and of a more powerful, specific, retarding effect of nitrate ions, which are assumed to act by deprotonating the nitric acidium ion (cf. Part II, Section 2). No evidence has been found that nitronium ions are effective in these solutions, in which they may not be able to exist in sufficient concentration, though the possibility of their intervention in such conditions is not excluded.

(1) Chemical Conditions in Aqueous Nitration.

(1.1) *Existence of the Nitric Acidium Ion.*—The kinetic observations reported in Part II provide the first definite proof of the existence of the nitric acidium ion, $H_2NO_3^+$, inasmuch as they show that its reversible production from nitric acid constitutes the first of the two steps by which the nitronium ion is formed in nitric acid :

$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental evidence was concerned with aromatic nitration by nitric acid in constant excess in organic solvents such as nitromethane and acetic acid. It could be shown by reference to the changes in kinetic order that, under these conditions, the nitrating agent was always the nitronium ion. There were two limiting kinetic types of nitration, the first-order and zeroth-order types the former applying to the less reactive aromatic compounds, such as di- and tri-halogenobenzenes, and the latter to the more reactive compounds, such as benzene and toluene. It was found that nitration, in both these kinetic forms, was strongly accelerated by the addition of small amounts of an acid stronger than nitric acid, and was strongly retarded by the addition of small concentrations of nitrate ions; and that both these effects on rate took place without disturbance to the reaction order, even when this was of zeroth order. Comparably small concentrations of added water had practically no effect on the rate.

These results show that the production of nitronium ion involves both the uptake by nitric acid of a proton, and the elimination from nitric acid of a nitrate ion. The effect of adding small amounts of an acid stronger than nitric acid is to increase the proton uptake by a generalised form (1*) of reaction (1) :

$$HNO_3 + HX \rightleftharpoons H_2NO_3^+ + X^- \quad . \quad . \quad . \quad . \quad . \quad (1*)$$
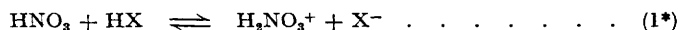
The effect of adding nitrate ions is to reverse the reaction stage (1) in which nitrate ion is produced. And since these effects, the second in particular, apply to zeroth-order nitrations, the stage reversed (1) cannot be that in which the nitronium ion is produced (2), because it is essential for zeroth-order nitration that nitronium ion production should not be appreciably reversed, *i.e.*, that substantially all the formed nitronium ion should combine with the aromatic

compound. This proves the two-stage nature of the process, and the intermediate formation of the nitric acidium ion.

(1.2) *Possible Nitrating Agents in Aqueous Nitric Acid.*—Water is in a different case from the nitrate ion. Water is not produced simultaneously with the nitric acidium ion in reaction-stage (1). It is consistent that in zeroth-order nitration its retarding action is trivial in comparison with that of the nitrate ion. On the other hand, water is produced simultaneouly with the nitronium ion in reaction-stage (2); and thus the addition of *enough* water should cause reversal of that reaction stage. Therefore, if we are observing a zeroth-order nitration of one of the more reactive aromatic compounds, the addition of sufficient water should retard the reaction, and should change the zeroth-order kinetics into first-order kinetics; for first-order nitration by nitronium ion results when nearly all the formed nitronium ion goes back into what it came from, only a small proportion combining with the aromatic compound.

This presupposes that, in the presence of much water, nitration continues to take place through the nitronium ion. However, it can be imagined that the water added might be sufficient completely to destroy the nitronium ion, leaving the possibility of nitration through the presumably less reactive nitric acidium ion. Any such nitration also should have a reduced speed, and should be kinetically of the first order. The latter conclusion follows because the nitric acidium ion can safely be assumed to be destroyed much more rapidly by the proton transfer which reverses the process of its formation (reaction 1 or 1*) than it will be by combination with an aromatic molecule.

It is difficult to distinguish between these two possible mechanisms, *viz.*, (*a*) nitration by the extremely minute amounts of nitronium ion that might survive in equilibrium with a great excess of water, and (*b*) nitration by larger equilibrium amounts of nitric acidium ion in these conditions. We have not succeeded in devising a critical experimental distinction. However, as has already been reported in a preliminary way (*Nature*, 1946, **158**, 514), we have studied the kinetics of aromatic nitration under conditions which are calculated very strongly to repress nitration by the nitronium ion, and to favour to the greatest possible extent nitration by the nitric acidium ion.

(1.3) *Entities Present in the Nitrating Solutions.*—In this work, the organic solvent of the experiments of Part II has been replaced by water. This was done in order to destroy the nitronium ion as completely as possible. And the aqueous solutions have been acidified with a very strong acid, usually perchloric acid, in order to increase the production of nitric acidium ion. A typical composition of a nitrating solution would contain 70—75 mols. % of water, whilst of the remaining material usually more than half would be nitric acid and less than half perchloric acid. In some experiments a salt was added, such as sodium perchlorate, sodium hydrogen sulphate, sodium nitrate, or ammonium nitrate.

It is important to note that, in mixtures of this type, nitric acid is only slightly ionised as an acid. On the other hand, perchloric acid is completely dissociated. Its strong acidity is, no doubt, partly responsible for the relative lack of acidity of the nitric acid. Dr. D. J. Millen established for us the existence of these conditions by examining the Raman spectra of some typical nitrating mixtures. In illustration, one of his microphotometer records is reproduced in Fig. 1. It relates to the nitration solution which was made up for kinetic run No. 103, and which had the following molecular composition : H_2O, 72; HNO_3, 17; $HClO_4$, 11 mols. %.

The Raman spectrum shows that the perchloric acid is completely converted into perchlorate ion : the spectrum of this ion is prominent, even the diffuse line around 1115 cm.$^{-1}$ (cf. Millen, *J.*, 1950, paper no. 509) being well recorded, whereas the characteristic spectrum of the perchloric acid molecule is entirely absent. On the other hand, the spectrum of the nitric acid molecule is strongly developed, whilst the spectrum of the nitrate ion is quite weak. Intensity measurements show that only 4% of the total nitric acid, *i.e.*, only 0·68 mol. % of the whole mixture, is in the form of nitrate ion.

No trace of the easily detectable nitronium ion line can be found in the spectrum. What the spectrum cannot tell us is how much of the nitric acid is ionised as a base to form nitric acidium ion. The 11 mols. % of hydrogen ions, split off from the perchloric acid, must have added themselves either to water molecules to form hydroxonium ions, or to nitric acid molecules to give nitric acidium ions; but we can find neither in the Raman spectrum. This is a well-known difficulty : no simple or substituted hydroxonium ion has yet been induced to yield a Raman spectrum. The generally accepted explanation, due to Bauer, is that such ions exchange their protons too frequently to yield well-defined vibrational energy levels.

The spectrum nevertheless establishes that a large proportion of the introduced nitric acid is present as nitric acid molecules. The 11 mols. % of hydrogen ions derived from the added

perchloric acid must be distributed in some unknown ratio between the water and the nitric acid; and, even if all the hydrogen ions should have added themselves to nitric acid, there would still be 5 mols. %, calculated on the total mixture, of surviving molecular nitric acid, out of the 17 mols. % of added nitric acid, since less than 1 mol. % is present as nitrate ion. This is important, because we shall show later that small changes in the composition of the nitrating solution, *e.g.*, the use of a little more or a little less perchloric acid, can make large changes in the rate of nitration, whereas it could not, under any hypothesis as to how the hydrogen ion is distributed between water and nitric acid, make large changes in the concentration of molecular nitric acid. From this we shall conclude that nitration by molecular nitric acid is not under observation in the present experiments.

Fig. 1.
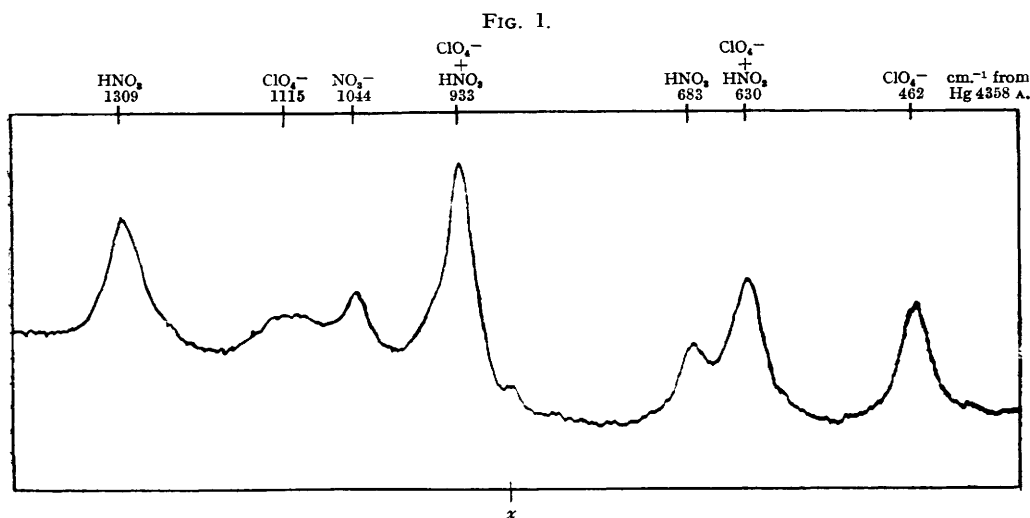
Microphotometer record of part of the Raman spectrum of the nitration solution of Run No. 103. *Stokes lines excited by* Hg 4358 A. (*The perchlorate ion frequency* 935 cm.$^{-1}$, *excited by* Hg 4347·5 A., *can be seen at* x.)—*By* D. J. MILLEN.

Another conclusion towards which the spectral evidence helps is that, if nitration is by the nitric acidium ion, then this must be present in comparatively small concentration : it cannot result from a nearly complete addition of the hydrogen ions, derived from perchloric acid, to nitric acid rather than to water. For if it did, the concentration of nitric acidium ions would not be a particularly sensitive function of the analytical composition of the nitration mixture : it would, over considerable ranges, change proportionately to the introduced perchloric acid, whereas we shall find that the rate of nitration changes much more steeply.

In some experiments an aqueous sulphuric acid medium, instead of aqueous perchloric acid, was employed. Qualitatively the situation was similar : the sulphuric acid was largely ionised, whilst the nitric acid was present mainly, but not wholly, in its molecular form. This again was established by Dr. Millen's examination of the Raman spectra. However, these Raman spectra were unsuitable for intensity measurements, owing to overlapping of the relevant lines.

(1.4) *Reactivity of the Aromatic Compounds Nitrated.*—Some explanation is necessary concerning the choice of aromatic compounds for nitration in the conditions described. We did not regard the well-known aqueous nitration of phenol as providing evidence concerning general mechanisms of aromatic nitration in aqueous solution, because special mechanisms of nitration operate in the nitration of phenol and aniline and their derivatives. We were concerned with general mechanisms of nitration : mechanisms applying to particular types of compound seemed to us to need separate consideration afterwards (Parts VI—VIII, *J.*, 1950, paper no. 512 *et seq.*).

It was necessary to employ water-soluble aromatic compounds ; we used 2-phenylethyl-sulphonic acid, and, to a smaller extent, benzylsulphonic acid. Ingold, Ingold, and Shaw have given evidence that the latter nitrates through its anion (*J.*, 1927, 813) ; and, having regard to the known effect of negative ionic charges in accelerating aromatic substitution, it seems highly probable that both these strong acids nitrate through their anions. (We always introduced

the acids as their sodium salts, supposing that in this form they would make the smallest initial disturbance to the concentration of hydrogen ions and of the other active components of the nitration medium.)

The rates of nitration of the two sulphonic acids have not yet been investigated by the competition method of Ingold and Shaw (*J.*, 1927, 2918) ; and therefore it is not known by direct observation where they stand, relatively to benzene itself and to other simple benzene derivatives, with respect to their reactivity in nitration. However, it is known that benzyl-sulphonic acid, on mononitration, gives 14% of the *m*-nitro-isomeride (Ingold, Ingold, and Shaw, *loc. cit.*), and that this proportion is not very different from those given by ethyl phenyl-acetate (11%) or benzyl chloride (15%) (Baker and Ingold, *J.*, 1927, 832; Flürscheim and Holmes, *J.*, 1928, 1611; Ingold and Shaw, *J.*, 1949, 575)—two compounds which have been investigated by the competition method. It has been shown that the former of the two compounds nitrates more quickly, and the latter more slowly, than benzene, but that both nitrate at rates which are the same as that of the nitration of benzene to within a factor of 4 (Ingold and Shaw, *J.*, 1949, 575).   Using our general theoretical ideas concerning the connexion of orientation with reactivity, we may infer with some assurance that the rate of nitration of ionising benzylsulphonic acid will be the same as that of benzene to within a small multiple. Again, taking account of our knowledge of the effect of side-chain homology on orientation, we may conclude, though with a somewhat larger margin for possible deviation, that the rate of nitration of 2-phenylethylsulphonic acid will be the same as that of toluene to within a small multiple.   A rough check on these conclusions may be derived from the fact that, whilst toluene has been shown by the competition method to nitrate 24 times faster than benzene (Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959), 2-phenylethylsulphonic acid has been found in the present kinetic investigation to nitrate 11—12 times faster than benzylsulphonic acid. A more exact numerical correspondence could not be expected. Therefore, with respect to their intrinsic reactivities in nitration, ionising benzylsulphonic and 2-phenylethylsulphonic acids may be regarded as approximately the equivalents of benzene and toluene, respectively, and hence as belonging to that more reactive group of aromatic compounds for which nitration in organic solvents can assume a zeroth-order form under the conditions of the experiments of Part II (*J.*, 1950, 2400).

<div align="center">(2) Kinetics of Aqueous Nitration.</div>

(2.1) *General Form of Kinetics.*—As in the work described in preceding papers of this series, dilatometry has been the principal means by which the reaction kinetics have been followed in the study of nitration here reported.   Chemical examination was used occasionally for checking the interpretation of the volume changes.

In the aqueous-acid solutions which have been employed for nitration in these experiments, the nitric acid was always present in constant excess over the aromatic compound.   Under these conditions, the nitrations of both 2-phenylethylsulphonic acid and benzylsulphonic acid obey a first-order rate law with considerable accuracy.   In illustration, Figs. 2—5 are given which show logarithmic plots of the variable part of the dilatometric height against time.   The examples are chosen to illustrate the use of both the aromatic sulphonic acids, of both the added strong acids, of medium compositions distributed over the range of compositions investigated, and of added salts.   First-order kinetics were invariably observed : a careful search was made for signs of the incursion of a zeroth-order process, but none could be found.

(2.2) *Effect of Medium Composition on Nitration Rate.*—The most salient feature of the connexion between the composition of the nitration medium, and the rate at which, at a fixed temperature, a given aromatic compound will be nitrated in it, is the existence of what may be called " thresholds " of reactivity in certain regions of composition.   For instance, one may study the rate of nitration of a particular substance, at a fixed temperature, in an aqueous nitric acid of given concentration, to which progressively increasing amounts of perchloric acid are added ; it is then found that no appreciable reactivity is developed until a certain stage is reached in the addition of the perchloric acid, but that, then, the reaction rate rises to very high values for quite small further increases in the content of perchloric acid.

Results are given in Table I for the first-order rate constants of nitration of 2-phenylethyl-sulphonic acid at 30·1° in a certain aqueous nitric acid (containing 18 mols. % of nitric acid and 82 mols. % of water), to which increasing proportions of perchloric acid were added.   From the graph of the results, which is shown in Fig. 6, one sees that there exists a fairly narrow band of concentrations of perchloric acid, running from about 8 to about 11 mols. %, below which the reaction was too slow to be measured, whilst above it the reaction was too fast to be measured.

FIGS. 2—5.

Kinetic course of nitration by acid-aqueous nitric acid.
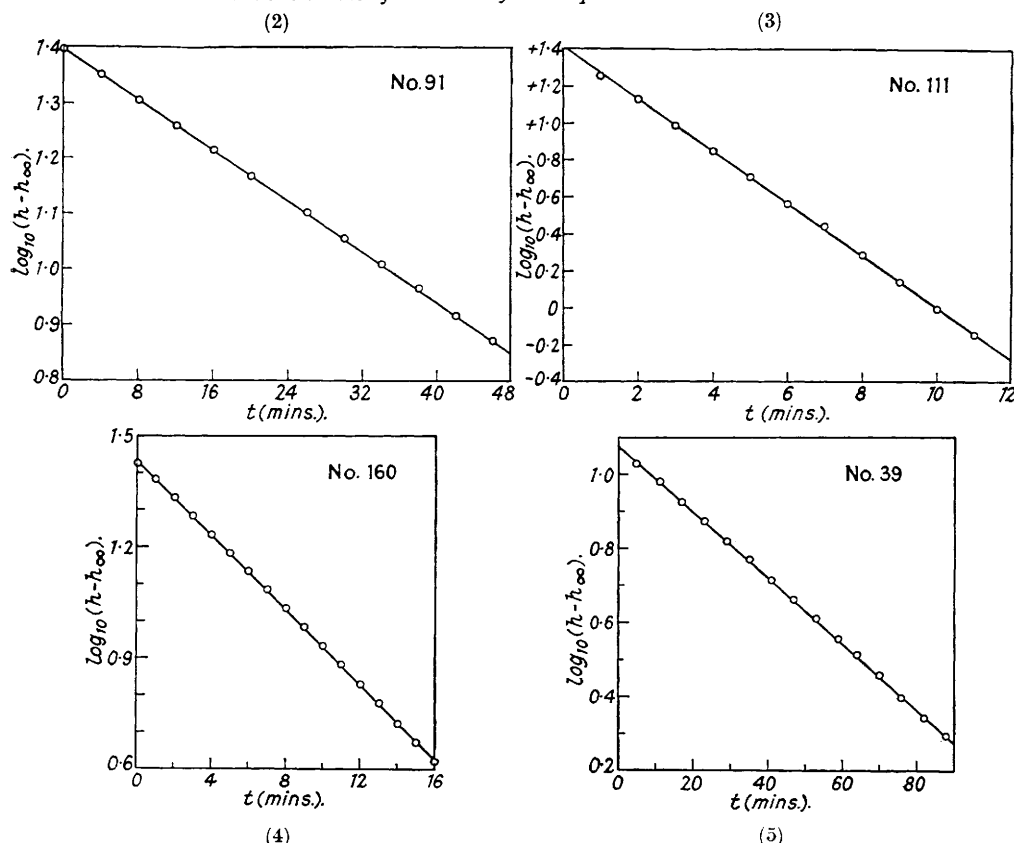
(2) Run No. 91. *Nitration of sodium 2-phenylethylsulphonate by nitric acid in aqueous perchloric acid. Medium :* H$_2$O, 76·5; HNO$_3$, 12·2; HClO$_4$, 11·3 mols. %. *Temp.* 30·10°. *Initially,* [C$_8$H$_9$·SO$_3$Na] = 0·169M. *From the graph* k$_1$ = 0·000445 *sec.*$^{-1}$. *By Guggenheim's method,* k$_1$ = 0·000432 *sec.*$^{-1}$.

(3) Run No. 111. *Nitration of sodium 2-phenylethylsulphonate by nitric acid in aqueous perchloric acid. Medium :* H$_2$O, 67·7; HNO$_3$, 25·5; HClO$_4$, 6·8 mols. %. *Temp.* 30·10°. *Initially,* [C$_8$H$_9$·SO$_3$Na] = 0·169M. *From the graph,* k$_1$ = 0·00530 *sec.*$^{-1}$. *By Guggenheim's method,* k$_1$ = 0·00537 *sec.*$^{-1}$.

(4) Run No. 160. *Nitration of sodium 2-phenylethylsulphonate by nitric acid in aqueous perchloric acid with added sodium nitrate. Medium :* H$_2$O, 72·6; HNO$_3$, 17·2; HClO$_4$, 10·2 mols. %. *Temp.* 30·10°. [NaNO$_3$] = 0·882M. *Initially,* [C$_8$H$_9$·SO$_3$Na] = 0·169M. *From the graph,* k$_1$ = 0·00190 *sec.*$^{-1}$. *By Guggenheim's method,* k$_1$ = 0·00187 *sec.*$^{-1}$.

(5) Run No. 39. *Nitration of sodium benzylsulphonate by nitric acid in aqueous sulphuric acid. Medium :* H$_2$O, 74·3; HNO$_3$, 7·0; H$_2$SO$_4$, 18·7 mols. %. *Temp.* 39·96°. *Initially,* [C$_7$H$_7$·SO$_3$Na] = 0·164M. *From the graph,* k$_1$ = 0·000342 *sec.*$^{-1}$. *By Guggenheim's method,* k$_1$ = 0·000333 *sec.*$^{-1}$.

(*We use ordinary logarithmic plots, such as are illustrated, for testing the degree of accuracy with which a first-order law is obeyed. But where the result of this test is satisfactory, we employ Guggenheim's method of plotting in order to derive the rate constant. Guggenheim's method was devised for the purpose of giving the best values of rate constants ; but it is not well suited for exhibiting small deviations from an integral reaction order.*)

A similar effect was encountered when, starting with an aqueous perchloric acid of fixed concentration, progressively increasing amounts of nitric acid were added. The left-hand part of Table II contains a set of rate constants for the nitration of 2-phenylethylsulphonic acid at 30·1° in an aqueous perchloric acid (containing 9 mols. % of perchloric acid and 91 mols. % of water), with various proportions of added nitric acid. The right-hand part of the Table contains a similar set of figures relating to another aqueous perchloric acid (containing 13 mols. % of perchloric acid and 87 mols. % of water), along with added nitric acid. The rate graphs for these two sets of mixtures are in Fig. 7. Their difference of position illustrates another general

TABLE I.

Effect of the concentration of perchloric acid, added to a given aqueous nitric acid, on the first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of 2-phenylethylsulphonic acid at 30·10°.

(Initially, $[C_8H_9SO_3Na] = 0.169$M., throughout.)

Run No.	H$_2$O.	HNO$_3$.	HClO$_4$.	$10^4 k_1$.	Run No.	H$_2$O.	HNO$_3$.	HClO$_4$.	$10^4 k_1$.
	Mols. %.					Mols. %.			

(Throughout, HNO$_3$: H$_2$O = 18·0 : 82·0 mols. %.)

Run No.	H$_2$O.	HNO$_3$.	HClO$_4$.	$10^4 k_1$.	Run No.	H$_2$O.	HNO$_3$.	HClO$_4$.	$10^4 k_1$.
79	75·5	16·7	7·8	1·16	82	73·4	16·3	10·3	14·5
80	75·1	16·6	8·3	2·68	84	73·2	16·2	10·6	21·7
78	74·0	16·4	9·6	7·48	83	73·1	16·2	10·7	27·0
81	73·7	16·3	10·0	11·3	77	73·0	16·1	10·9	30·0

FIG. 6.

Effect of perchloric acid concentration on the rate of nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous nitric acid.
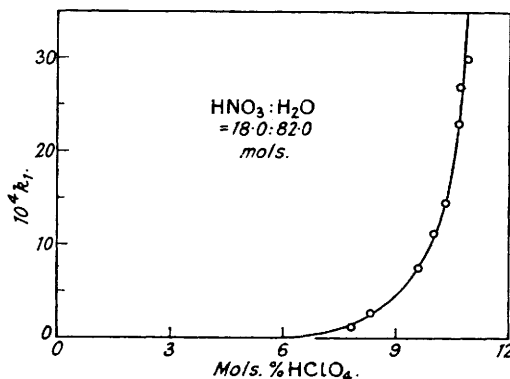

TABLE II.

Effect of the concentration of nitric acid, added to a given aqueous perchloric acid, on the first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of 2-phenylethylsulphonic acid at 30·10°.

(Initially, $[C_8H_9\cdot SO_3Na] = 0.169$M., throughout.)

Run No.	H$_2$O.	HNO$_3$.	HClO$_4$.	$10^4 k_1$.	Run No.	H$_2$O.	HNO$_3$.	HClO$_4$.	$10^4 k_1$.
	Mols. %.					Mols. %.			

|	(Throughout, HClO$_4$: H$_2$O = 9·2 : 90·8 mols. %.)					(Throughout, HClO$_4$: H$_2$O = 12·8 : 87·2 mols. %.)			
93	76·6	15·7	7·7	0·99	91	76·5	12·2	11·3	4·32
101	75·5	16·9	7·6	1·12	125	75·6	13·3	11·1	6·63
97	74·1	18·4	7·5	2·33	90	75·6	13·3	11·1	6·83
94	72·7	19·9	7·4	4·30	89	74·9	14·1	11·0	9·33
100	72·0	20·7	7·3	6·33	88	74·0	15·1	10·9	15·2
99	71·3	21·5	7·2	7·18	87	73·5	15·7	10·8	19·7
139	70·9	21·9	7·2	9·88	86	73·2	16·1	10·7	23·2
98	70·7	22·2	7·1	11·7	85	72·8	16·5	10·7	28·7
95	69·7	23·2	7·1	18·7	103	72·5	16·9	10·6	33·0
102	69·6	23·4	7·0	21·2					
96	67·8	25·4	6·8	48·0					
111	67·7	25·5	6·8	53·7					

point, *viz.*, that the threshold of reactivity, as developed by the progressive addition of nitric acid, appears at a higher content of nitric acid the lower the proportion of perchloric acid in the original aqueous perchloric acid.

Similar thresholds are found when we keep the nitric and perchloric acids in a fixed ratio and dilute with increasing amounts of water. In this case we descend a steep curve qualitatively like those shown in Figs. 6 and 7, thereby passing, for a relatively small change of composition, from reactions which were too fast to be measured to others which were too slow to be measured in our conditions.

Independently of which component of the medium is being added, the position of the rate threshold with respect to the concentration of the added compound depends on the proportions of the other components. The general relationship between reaction rate and medium composition may be expressed by means of a three-dimensional model, in which the rate is plotted vertically above a basal plane containing the two degrees of freedom of composition. Employing triangular co-ordinates of composition, such a model for the nitration of 2-phenyl-ethylsulphonic acid at 30·1° has been constructed from sections such as the curves of Figs. 6 and 7 constitute, together with a number of scattered observational points. It is represented in the form of a contour map in Fig. 8. This shows that, as we travel " south " from the water apex towards the contours, we remain at " sea-level " for a considerable distance, then come to a " shelving beach," and then, quite quickly, to a " steep cliff." As to the mechanism of nitration, it follows directly from these threshold phenomena that the nitrating agent cannot be the nitric acid molecule (Section 1.3).

FIG. 7.

Effect of nitric acid concentration on the rate of nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous perchloric acid.
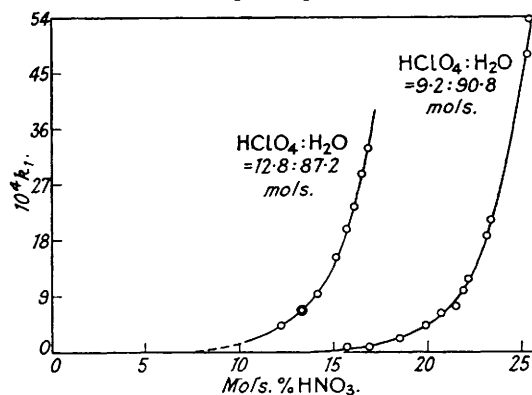

The same results have further implications. It follows from what was stated in Section 1.3 that, as we travel away from the water apex, towards the interior region of the composition–co-ordinate system, three main new species appear in the solutions, viz., solvated hydrogen ions, perchlorate ions, and nitric acid molecules. Now we know that cations and positively charged centres are in general much more strongly solvated by water than are anions and negative centres. Therefore, in comparison with other effects of which we have to take account, the effect of the perchlorate ion on the activity of the water may be neglected. However, the hydrogen ion and the nitric acid molecule form the stable monohydrates, H_3O^+ and $H_2O \ldots HO \cdot NO_2$, respectively; and both entities can probably combine more loosely with additional water to form higher hydrates. It will be evident that the continued production of these hydrates, as protons derived from perchloric acid and as nitric acid molecules are progressively supplied to a fixed amount of water, must lead to a stage at which a relatively sharp decrease in the activity of the water will occur because a high proportion of the originally available water has already become bound in the hydrates present in such solutions. We assume that, so long as free water is in excess, most of the protons derived from perchloric acid will combine with water, rather than with nitric acid; i.e., that, in these solutions, water will behave as a base which is at least as strong as nitric acid. We also adopt Gillespie and Millen's structure for nitric acid monohydrate (*Quart. Reviews*, 1948, **2**, 88) rather than Dalmon and Freymann's structure $HO \cdot NO_2 \ldots H_2O$: this is in accordance with the expectation that a moderately acidic molecule, such as nitric acid, should be hydrated mainly through its positive centre, viz., its ionisable proton. The implication is that hydration, by partly neutralising the positive centre, must increase the basic strength of nitric acid. Therefore, as the water becomes progressively bound, the nitric acid being largely hydrated, there must be a shift in the relative efficiencies with which the two entities, water and nitric acid, compete for protons; and thus the above-mentioned sharp decrease in water activity will be accompanied by a similarly sharp increase in the proportion in which protons, derived from perchloric acid, will be bound by nitric acid. It is to this sharp increase in the formation of nitric acidium ion that we ascribe the observed sharp increase in nitration rate in the relevant region of composition.

7 s

(2.3) *Effect of Added Salts on Nitration Rate.*—From the theory of the nitration process, it is to be expected that the addition of nitrate ions, in the form of sodium or ammonium nitrate, will reduce nitration rate; and that it will do this by reversing reaction (1) (cf. p. 2441), thereby diminishing the equilibrium concentration of nitric acidium ions.

<div align="center">Fig. 8.</div>

Contour-map of relief model showing the effect of medium composition on the rate of nitration of 2-phenyl-ethylsulphonic acid at 30·10°. (The significance of the points numbered 1—5 is explained in the text in connexion with Table III and Fig. 9—see pp. 2449 and 2450.)
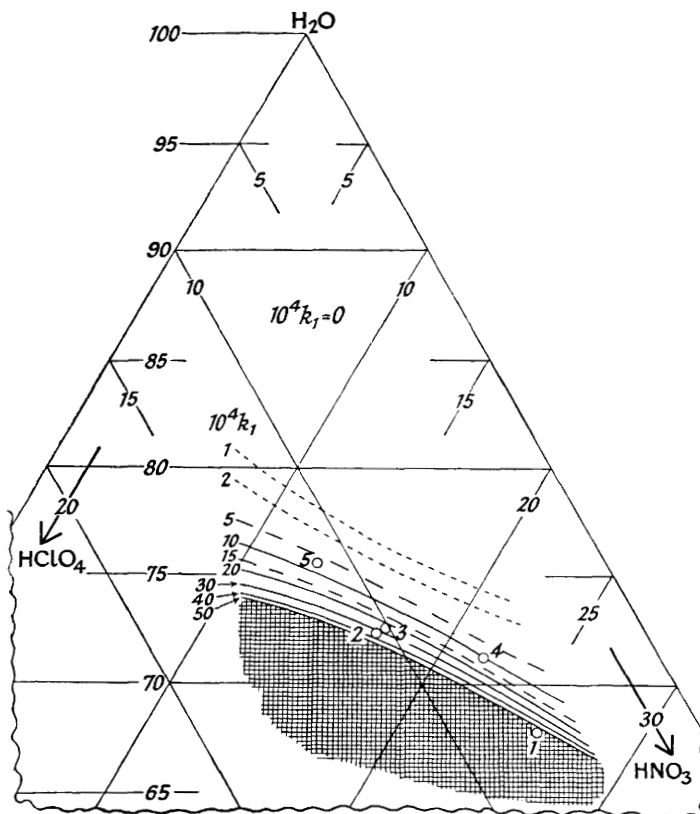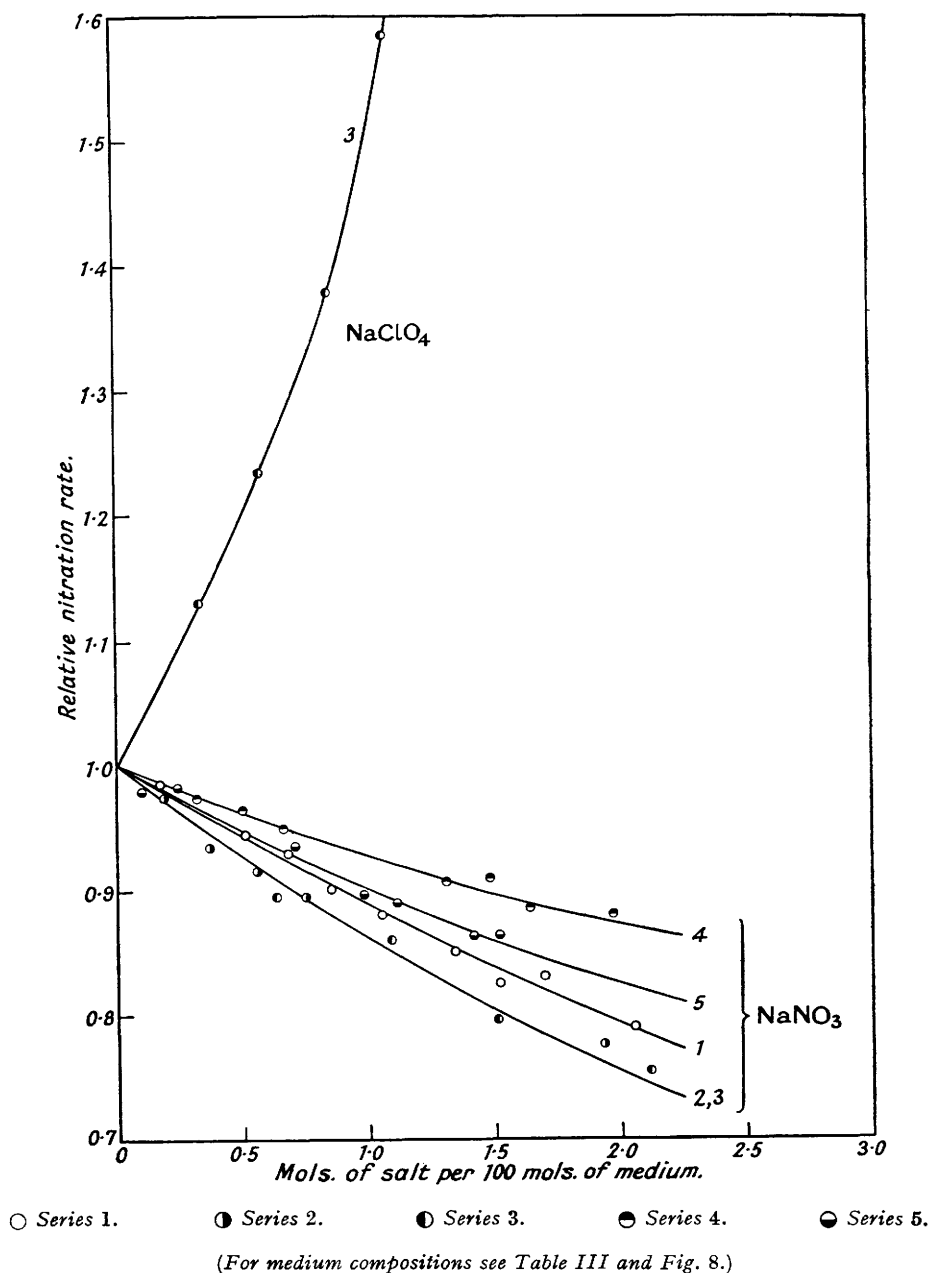

The same expectation follows, if we use our empirical knowledge (*a*) that, in the range of media investigated, the perchloric acid is completely dissociated, whilst the nitric acid is nearly completely undissociated; and (*b*) that the rate contours, over this range of media, lie, as Fig. 8 shows, more nearly normal to the co-ordinates of perchloric acid concentration than to the co-ordinates of nitric acid concentration. For the addition of, say, sodium nitrate must be the approximate equivalent, apart from any effect due to sodium perchlorate, of replacing an equimolecular amount of ionised perchloric acid by a corresponding quantity of non-ionised nitric acid; and this replacement is represented by a shift from left to right in Fig. 8; and therefore it must lead to a descent through the rate contours.

We have examined the effect of adding sodium or ammonium nitrate on the rates of nitration of 2-phenylethylsulphonic acid in a number of aqueous nitric acids containing either perchloric or sulphuric acid. In all cases the rates are decreased by the added nitrate. Some results concerning the effect of sodium nitrate on the first-order rate constants, measured at 30·10° in five aqueous solutions of nitric and perchloric acids, are given in Table III. The effect is illustrated by the graphs in the lower part of Fig. 9. Here, the rate constants for each group of experiments involving the same medium with different amounts of added salt, are expressed in terms of the rate in the salt-free medium as the unit.

The five groups of experiments are numbered 1—5 in Table III and Fig. 9, and the

Fig. 9.

Effect of added sodium nitrate and of added sodium perchlorate on the rate of nitration of 2-phenylethyl-sulphonic acid at 30·10° in aqueous solutions of nitric and perchloric acids.

○ *Series* 1.   ◑ *Series* 2.   ◐ *Series* 3.   ⊖ *Series* 4.   ⊖ *Series* 5.

(For medium compositions see Table III and Fig. 8.)

compositions of the media, which were employed in them, are indicated by correspondingly numbered points in Fig. 8. It can be seen from Fig. 9 that the rate depressions caused by sodium nitrate vary with the medium, but lie within the range 6—14% for each 1 mol. % of added salt. These depressions are several times smaller than would be reckoned from the left-to-right rate-gradients of the relief model at the marked points in Fig. 8. This fact indicates the existence of a large positive salt effect due to sodium perchlorate.

TABLE III.

Effect of added sodium nitrate on the first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous solutions of nitric and perchloric acids.

(Initially, $[C_8H_9 \cdot SO_3Na] = 0.169$M., throughout.)

Run No.	Mols. NaNO$_3$ per 100 medium.	$10^4 k_1$.	Run No.	Mols. NaNO$_3$ per 100 medium.	$10^4 k_1$.
Series 1 :—Medium composition : H_2O, 67·8; HNO_3, 25·7; $HClO_4$, 6·5 mols. %.					
124	0·00	52·2	115	1·05	45·3
122	0·17	51·5	116	1·34	44·5
118	0·51	49·2	119	1·52	43·0
113	0·68	48·7	114	1·70	43·3
120	0·85	47·0	117	2·06	41·0
Series 2 :—Medium composition : H_2O, 72·4; HNO_3, 17·0; $HClO_4$, 10·6 mols. %.					
103	0·00	33·0	109	0·56	30·2
108	0·19	32·3	105	0·75	29·5
104	0·37	30·8	107	1·94	25·7
Series 3 :—Medium composition : H_2O, 72·6; HNO_3, 17·2; $HClO_4$, 10·2 mols. %.					
152	0·00	24·8	159	1·52	19·7
158	0·63	22·2	160	2·12	18·7
157	1·09	21·3			
Series 4 :—Medium composition : H_2O, 71·2; HNO_3, 21·8; $HClO_4$, 7·0 mols. %.					
139	0·00	9·88	141	1·31	8·95
150	0·24	9·72	147	1·48	9·03
143	0·32	9·73	140	1·64	8·73
146	0·49	9·62	148	1·97	8·68
144	0·66	9·38			
Series 5 :—Medium composition : H_2O, 75·6; HNO_3, 13·0; $HClO_4$, 11·4 mols. %.					
125	0·00	6·63	127	1·11	5·92
134	0·24	6·58	136	1·22	5·72
137	0·71	6·23	135	1·42	5·74
129	0·98	5·59	130	1·52	5·72

TABLE IV.

Effect of added sodium perchlorate on first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of 2-phenylethylsulphonic acid at 30·10° in aqueous solutions of nitric and perchloric acids.

(Initially, $[C_8H_9 \cdot SO_3Na] = 0.169$M., throughout.)

Run No.	Mols. NaClO$_4$ per 100 of medium.	$10^4 k_1$.	Run No.	Mols. NaClO$_4$ per 100 of medium.	$10^4 k_1$.
Series 3 :—Medium composition as for Series 3 in Table III.					
152	0·00	24·8	156	0·84	34·3
154	0·32	28·0	155	1·06	39·3
153	0·57	31·5			

This effect of sodium perchlorate on the rate of nitration was directly confirmed by experiments such as those of the series recorded in Table IV. In this series, 2-phenylethyl-sulphonic acid was nitrated at 30·10° in solutions prepared by adding successively increasing amounts of sodium perchlorate to a medium of the same composition as was used for one of the groups of experiments on the effect of added sodium nitrate (Series 3 of Table III). Sodium perchlorate was thereby shown to have a marked accelerative effect on nitration in aqueous nitric and perchloric acids. This is illustrated by the uppermost curve in Fig. 9. A positive kinetic effect of salts on nitration in this type of medium is probably general for salts of very strong acids, since we have observed it again with sodium hydrogen sulphate as the added salt. (It is on this account that standard concentrations of sodium 2-phenylethylsulphonate or sodium benzylsulphonate were used in nearly all the present experiments.)

It need hardly be said that the kinetic behaviour of ionised salts in media already very concentrated with respect to ions cannot be treated on the basis of the theory of salt effects at low ionic strengths. A simple (and probably over-simplified) way of regarding the effect of non-reacting salts, such as sodium perchlorate, on nitration rates in aqueous nitric acid containing a strong acid, such as perchloric acid, is to suppose that the salt, presumably acting mainly through its cation, binds water, thereby making water less available for the binding of protons,

which accordingly combine to a greater extent with nitric acid, thus forming increased equilibrium concentrations of nitric acidium ion. The degrees of solvation which it is necessary to assume in order to account on this simple basis for the observed kinetic effects are not excessive. Thus, as one can find by measurements on the model represented by Fig. 8, the gradient of the sodium perchlorate curve shown in Fig. 9 would be given correctly if we should assume that each sodium perchlorate molecule leads to the binding of an average of about 0·5 molecule of water. Our picture of the nitration process does not require us to allow for any gross kinetic salt effect arising from the mechanism of the nitration itself. For the positive charge in the transition state of nitration pre-existed in the nitration medium as the charge on a hydroxonium ion; from which it was transferred, by way of nitric acid, to the aromatic ring, only to become the charge on a hydroxonium ion again at the end of the reaction. In short, the nitration process displaces ionic charges but does not create or destroy them.

(2.4) *Effect of Temperature on Nitration Rate.*—This has been cursorily investigated both for the nitration of 2-phenylethylsulphonic acid in aqueous solutions of nitric and perchloric acids, and for the nitration of benzylsulphonic acid in aqueous solutions of nitric and sulphuric acids, in each case over temperature ranges of only about 20°, no special attempt having been made to secure high accuracy in the measurement of the temperature coefficients. In the conditions used, the apparent energies of activation, E, in the equation $k_1 = Be^{-E/RT}$, lay within the interval 17—20 kcals. g.-mol.$^{-1}$, whilst the frequency factors, B, lay in the range $10^{9\cdot5}$ to $10^{11\cdot5}$ sec.$^{-1}$. An illustrative series of measurements is recorded in Table V.

TABLE V.

Effect of temperature on the first-order rate constants (k_1 in sec.$^{-1}$) for the nitration of 2-phenylethylsulphonic acid in an aqueous solution of nitric and perchloric acids.

(Initially, $[C_8H_9 \cdot SO_3Na] = 0\cdot169$M. throughout.)

Medium : H_2O, 72·6; HNO_3, 17·2; $HClO_4$, 10·2 mols.%.

Run No.	Temp. (°K.).	$10^4 k_1$ (obs.).	$10^4 k_1$ (calc.).*	Run No.	Temp. (°K.).	$10^4 k_1$ (obs.).	$10^4 k_1$ (calc.).*
166	293·1	8·15	8·7	165	308·2	35·5	38·0
152	303·2	24·8	23·4	163	313·0	62·2	57·5

* Calculated from the equation $k_1 = 7\cdot5 \times 10^9 \times e^{-17,350/RT}$.

(3) *Experimental Methods.*

(3.1) *Materials.*—Sodium benzylsulphonate was prepared by the standard method from fractionated benzyl chloride and sodium sulphite. It was purified by crystallising it several times from ethyl alcohol (Found : C, 43·6; H, 4·2; S, 16·4; Na, 11·7. Calc. : C, 43·3; H, 3·6; S, 16·5; Na, 11·8%).

Sodium 2-phenylethylsulphonate was prepared from fractionated 2-phenylethyl alcohol, by conversion of the latter, with the aid of phosphorus tribromide, into 2-phenylethyl bromide, and treatment of the crude bromide, still containing some unconverted alcohol, with a solution of sodium sulphite (cf. Rupe, *Annalen*, 1913, **395**, 114; Evans, Mabbott, and Turner, *J.*, 1927, 1161). The salt was purified by alternately washing it with ethyl alcohol and crystallising it from water several times (Found : Na, 11·0, 11·05. Calc. : Na, 11·05%).

(3.2) *Dilatometric Methods.*—The tapless dilatometers of Benford and Ingold did not work well with the aqueous solutions involved in these experiments, owing to small, uncontrolled movements of the two meniscuses. On the other hand, these aqueous nitration media attacked the better kinds of tap-grease sufficiently slowly to permit the use of a tap. The dilatometers actually employed were similar in form to Benford and Ingold's dilatometer of "type C" (*J.*, 1938, 932), except that the bent capillary was supplied with a tap above the level of the bulb, and was made of wider bore than the straight capillary, in order to increase the speed with which the dilatometer could be filled. The tap, which was of the oblique-bore type with a blown key, was lubricated with Apiezon L grease. The level of the meniscus, which falls during the course of a nitration, was read with a cathetometer.

Nitration media were made up from sulphuric acid, or from aqueous perchloric acid, each purchased as pure, from nitric acid, free from nitrous acid, prepared as described in Part II (*J.*, 1950, 2400), and from water. When measurements of volume were involved, densities also were measured by the use of a density bottle, in order to permit the expression of compositions as mol.-fractions, or in any other desired form. The inorganic salts, sodium nitrate, ammonium nitrate, sodium hydrogen sulphate, and sodium perchlorate, all crystallised several times from water, and well-dried over phosphoric oxide, were added by weight to a known weight of salt-free medium.

The required weight of the sodium salt of the aromatic sulphonic acid was placed in a graduated flask, and there dissolved in the nitration medium by shaking at 0°. The solution was made up to the mark at 0°, and was then transferred to a bulb in which it was quickly cooled to about −25°, while the gas in the apparatus was pumped out for some minutes with a rotary oil pump. The object of this treatment was to avoid the subsequent formation of bubbles of gas in the dilatometer. A portion of the de-gassed solution was then brought more nearly to the temperature, usually between 20° and 40°, at which the kinetic run was to be conducted, and was transferred by suction into the dilatometer already immersed in the thermostat.

(3.3) *Analytical Control.*—An approximate method for the analytical control of completed dilatometric runs was devised. It involved diluting the solution from the dilatometer with water, reducing the nitro-compounds by the addition of zinc dust, diazotising the resulting amino-compounds, and developing an azo-colour with alkaline β-naphthol. A standard was provided by nitrating the sulphonic acid with aqueous nitric acid in the absence of perchloric or sulphuric acid. In this case the unconsumed nitric acid could be evaporated by hard pumping at a relatively low temperature, leaving the total product as a residue, which was shown by determination of its nitrogen content to be mononitrated (Found, for the nitration product of sodium 2-phenylethylsulphonate : N, 5·35. Calc., for a mixture of mononitro-derivatives : N, 5·53%).

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