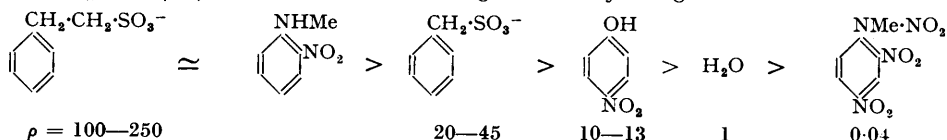




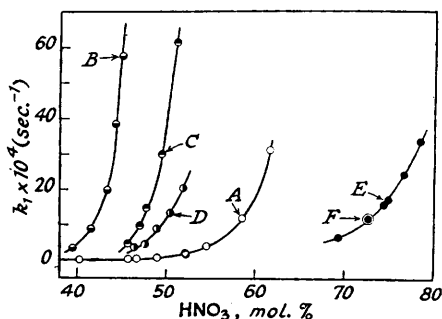
nitric acid concentration varies from one compound to another. The following approximate reactivities ( $\rho = k_1/k_w$ ) for our measurable range of acidity are given below:



The dependence of first-order rate coefficients on acidity is illustrated in Fig. 1.

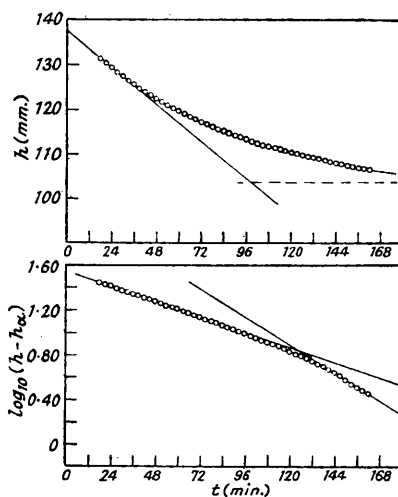
From a consideration of nitration products, Halberstadt, Hughes, and Ingold (*loc. cit.*) suggest that toluene- $\omega$ - and 2-phenylethane-sulphonic acids have similar reactivities to benzene and toluene, respectively. This allows our reactivity sequence to be correlated qualitatively with those observed in nitrations in non-aqueous solvents. In this sequence we have assumed the formation of *N*-methyl-*N*:2:4-trinitroaniline to be a true aromatic

FIG. 1. Variation of first-order rate coefficients with nitric acid concentration.



- A, Oxygen exchange  $K_1 = R/[\text{H}_2\text{O}]_2$ .  
 B, C-Nitration: Sodium 2-phenylethane-sulphonate.  
 C, ,, Sodium toluene- $\omega$ -sulphonate.  
 D, ,, *p*-Nitrophenol.  
 E, ,, *N*-Methyl-2:4-dinitroaniline.  
 F, ,, *N*-Methyl-*N*:2:4-trinitroaniline.

FIG. 2. Nitration of sodium 2-phenylethane-sulphonate.



$$\begin{aligned}
 [\text{HNO}_3]_0 &= 40.11 \text{ mol.-%} \\
 [\text{ArH}]_0 &= 0.763 \text{ mol.-%}
 \end{aligned}$$

nitration; this may not be true, and the reaction may involve a slow migration of the *N*-nitro-group to the aromatic ring, followed by a rapid *N*-nitration (Hughes and Ingold, *Quart. Reviews*, 1952, 6, 34). This possibility is at present under investigation.

*Evidence for Change in Kinetic Form.*—Exceptions to the simple first-order law discussed above were observed in the nitration of 2-phenylethanesulphonic acid present in concentrations  $>0.5\text{M}$ , a decrease of the order with respect to the aromatic compound being found (Fig. 2). This tendency towards zero-order kinetics should become more

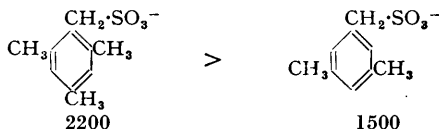
TABLE 1. Limiting first-order rate coefficients for mesitylene- $\alpha$ - and isodurene- $\alpha^2$ -sulphonic acids at 0°.

Run no.	Compound	$[\text{HNO}_3]$ , mol. %	$[\text{ArH}]$ , mol. %	$10^4 k_1$ (sec. <sup>-1</sup> )	Reactivity ( $\rho = k_1/k_w$ )
60	Mesitylene- $\alpha$ -sulphonic acid	39.15	0.11	46.0	~1500
94	isoDurene- $\alpha^2$ -sulphonic acid	39.43	0.17	72.6	~2200

pronounced as the reactivity of the aromatic compound, or its concentration, is increased. More reactive compounds, prepared for this work, show this change of kinetic form at lower concentrations. With mesitylene- $\alpha$ - and isodurene- $\alpha^2$ -sulphonic acids we are unable to observe pure first-order kinetics throughout the run under any conditions, and the initial stages of the reactions approximate to a zero-order rate law (Fig. 3). However, at the end of runs, carried out with initially low concentrations of the aromatic compounds,

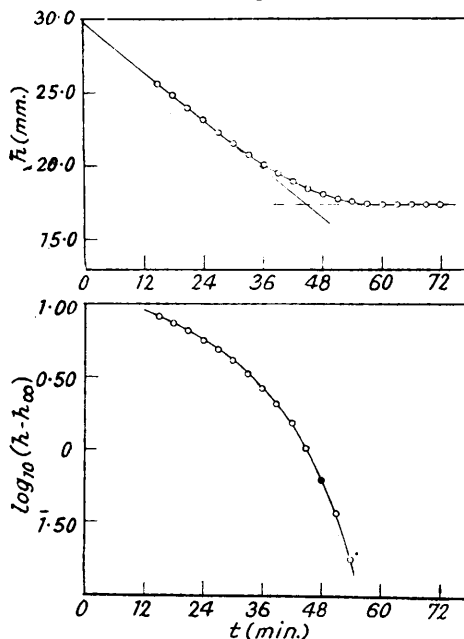
in a sensitive dilatometer, the residual first-order rate coefficients could be measured; a typical example is shown in Fig. 4, and the values are given in Table 1.

These measurements allow the assignment of reactivity values, relative to water, for the two sulphonic acids. In the region of 40 mole % nitric acid these were :



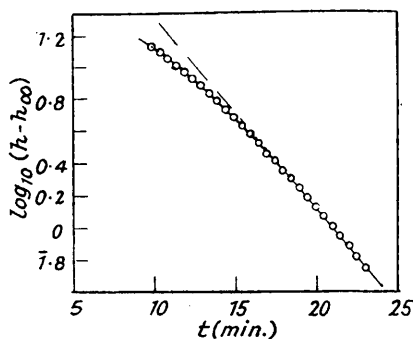
This change of kinetic form with increasing reactivity of the aromatic compound is similar to that observed in aromatic nitrations in nitromethane and acetic acid (Hughes,

FIG. 3. Nitration of sodium isodurene- $\alpha^2$ -sulphonate.



$$\begin{array}{l}
 [\text{HNO}_3]_0 = 37.97 \text{ mol.-%;} \\
 [\text{ArH}]_0 = 0.291 \text{ mol.-%.}
 \end{array}$$

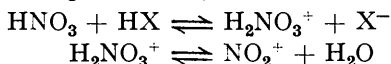
FIG. 4. Run No. 60. Nitration of sodium mesitylene- $\alpha$ -sulphonate.



$$\begin{array}{l}
 [\text{HNO}_3]_0 = 39.15 \text{ mol.-%;} \\
 [\text{ArH}]_0 = 0.11 \text{ mol.-%.}
 \end{array}$$

Ingold, and Reed, *J.*, 1950, 2400). We find for the nitration of these more reactive compounds that, as the reactivity or concentration increases, and the kinetic form tends from first to zero order, the nitration rates tend towards the rate of oxygen exchange, for a given acidity, although under our experimental conditions this value was never reached, nor was a pure zero-order form obtained. We consider this rate of oxygen exchange to be a limiting value for the rate of nitration in aqueous nitric acid.

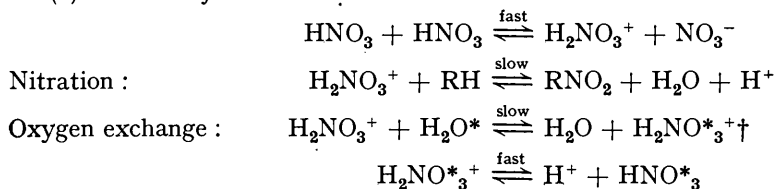
*Discussion.*—The probable mechanisms of nitration of the arylalkanesulphonic acids have been discussed by Halberstadt, Hughes, and Ingold (*loc. cit.*). The nitrating agents considered were the nitric acid molecule, the nitracidium ion,  $\text{H}_2\text{NO}_3^+$ , and the nitronium ion,  $\text{NO}_2^+$ , related by the following reactions (where HX is an acid) :



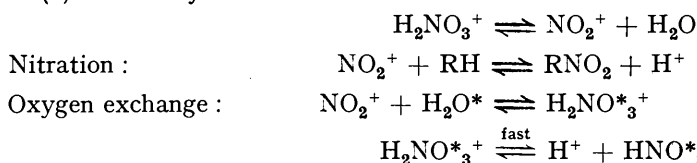
They excluded the nitric acid molecule as a probable nitrating agent and pointed out that the first-order rate law, which they observed, and the rapid increase in rate with increasing acidity, could be explained by (a) nitration by the nitracidium ion, or (b) formation of the nitronium ion in a very small equilibrium concentration followed by a

slow, rate-determining reaction between this ion and the aromatic compound. The kinetic evidence did not enable them to differentiate between these two mechanisms. A comparison of aromatic nitration and oxygen-exchange rates does, however, give evidence on the mechanism of both reactions. Following Halberstadt, Hughes, and Ingold (*loc. cit.*), we consider two possible reaction schemes for nitration, and compare these with analogous schemes for oxygen exchange in aqueous nitric acid:

(a) Reaction of the nitracidium ion:



or (b) Reaction of the nitronium ion:



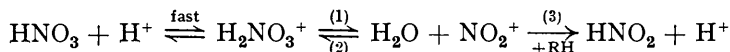
† By  $\text{HNO}_3^*$ ,  $\text{H}_2\text{NO}_3^{*+}$ , and  $\text{NO}_2^{*+}$  we imply all species containing one or more atoms of the tracer (see preceding paper).

For nitration, and oxygen exchange, by the nitracidium ion, we have a rapid pre-equilibrium proton transfer followed by a slow rate-determining reaction between the water molecule, or the aromatic compound, and the nitracidium ion. The rates of these reactions need bear no relation to each other, nor is there any reason why the rates of oxygen exchange should be limiting values for the rates of nitration.

The change of kinetics from first towards zero order indicates that the reaction between the nitrating entity and the aromatic compound is not, for reactive compounds, the only rate-determining stage. This second rate-determining stage (a process independent of the aromatic compound) can only be the formation of the nitracidium ion, which is a rapid proton transfer from one nitric acid molecule to another.

For oxygen exchange *via* the nitronium ion, the rate of exchange is the rate of formation, or destruction, of the nitronium ion, and as, in a given medium, the concentration of nitronium ion is constant, these rates are equal. The rate of oxygen exchange should therefore give a limiting value for the rate of nitration *via* the nitronium ion, as this rate cannot be greater than the rate of formation of the nitronium ion. So, because experimentally the rates of nitration are always lower than the rate of oxygen exchange, although they approach this figure for reactive aromatic compounds, which show approximately zero-order kinetics, we conclude that nitration and oxygen exchange both involve the formation and destruction of the nitronium ion.

The kinetics of these reactions can be considered in terms of a competition for the nitronium ion, between the aromatic compound and the water molecules:



For the less reactive compounds the rate of reaction between the water molecules and the nitronium ion, step (2), regenerating nitracidium ions, is much greater than the rate of capture of the nitronium ions by the aromatic compounds. We therefore have a small equilibrium concentration of nitronium ions, and observe first-order nitration kinetics. The more reactive aromatic compounds, in the initial stages of the reaction, capture virtually all the nitronium ions, and the rate-determining step of the reaction therefore approximates to the rate of formation of these ions. Towards the end of the reaction, the concentration of aromatic compound has so decreased that fewer of the nitronium ions

formed, are captured by the aromatic compound, and a decrease of rate is observed, together with a change of kinetic form towards first order.

*Quantitative Treatment of Mixed-order Reactions.*—A knowledge of the relative reactivities, towards nitric acid, of various aromatic compounds compared to water, allows the rate of any nitration to be predicted by consideration of the competition between a water molecule and an aromatic compound, for a nitronium ion.

We assume  $R$ , the rate of oxygen exchange between water and nitric acid, to be the rate of formation of nitronium ions. The rate of nitration will be a fraction of  $R$ , determined by the relative reactivity ( $\rho$ ) of the aromatic compound and its concentration :

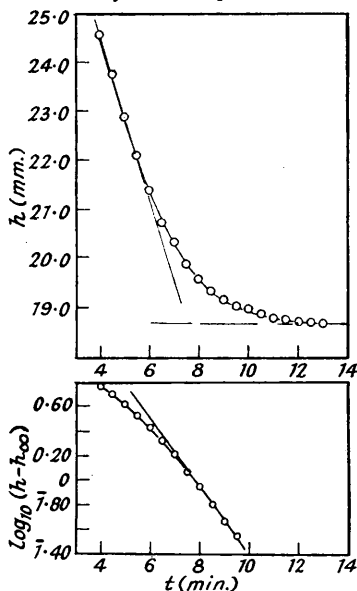
$$-d[\text{ArH}]/dt = (R\rho[\text{ArH}]) / (\rho[\text{ArH}] + [\text{H}_2\text{O}]) \quad \dots \quad (2)$$

or

$$= (Rk_1[\text{ArH}]) / (k_1[\text{ArH}] + R) \quad \dots \quad (2a)$$

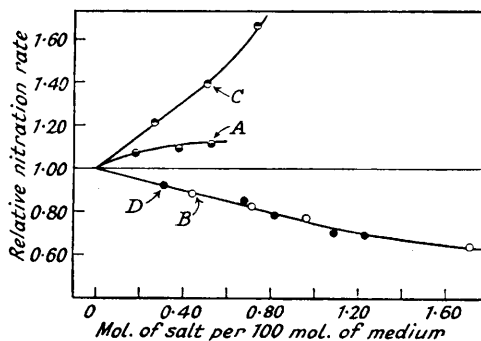
The instantaneous rate of nitration is simply the rate of nitronium-ion formation, multiplied by the probability of a nitronium ion's being destroyed selectively by the

FIG. 5. Nitration of sodium mesitylene- $\alpha$ -sulphonate.



$[\text{HNO}_3] = 21.20 \text{ mol.-%}$  ;  
 $[\text{HClO}_4] = 7.92 \text{ mol.-%}$  ;  
 $[\text{H}_2\text{O}] = 70.88 \text{ mol.-%}$  ;  
 $[\text{ArH}]_0 = 0.30 \text{ mol.-%}$  .

FIG. 6. Effect of added salts on zero- and first-order nitration rates.



Zero-order nitration of sodium isodurene- $\alpha^2$ -sulphonate :  
 A, Sodium perchlorate.  
 B, Potassium nitrate.  
 First-order nitration of sodium 2-phenylethane-sulphonate :  
 C, Sodium perchlorate.  
 D, Potassium nitrate.

aromatic compound rather than by water. With compounds of low reactivity,  $k_1[\text{ArH}]$  in (2a) is negligible relative to  $R$ , and the reaction is kinetically of the first order :

$$-d[\text{ArH}]/dt \cong k_1[\text{ArH}] \quad \dots \quad (3)$$

Conversely, when the reactivity is high,  $R$  may be neglected in the denominator of (2a), and the relation reduces to

$$-d[\text{ArH}]/dt \cong R \quad \dots \quad (4)$$

Equation (2) allows us to calculate the instantaneous rates of reactions that are intermediate between zero and first order. A comparison of experimentally observed rates of nitration, with those calculated from a knowledge of the rate of oxygen exchange and the reactivity of the aromatic compound, at any given nitric acid concentration, is given in Table 2.

In nitration in non-aqueous solvents (nitromethane and acetic acid), the concentration of water is comparable to that of the aromatic compounds, and it is therefore possible to

observe zero-order nitrations with compounds whose reactivity is only slightly greater than that of water, *e.g.*, benzene in nitromethane (Hughes, Ingold, and Reed, *loc. cit.*) and methyl alcohol in nitromethane (Blackall and Hughes, personal communication), but even in these solvents, when water becomes a bulk constituent, the order with reactive compounds is changed from zero to first, with considerable decrease in rate, as in the

TABLE 2. Initial nitration rates at 0° (tending to "zero"-order).

Run no.	Sulphonic acid	[HNO <sub>3</sub> ] (mol. %)	[ArH] <sub>0</sub> (mol. %)	10 <sup>4</sup> R	10 <sup>4</sup> k <sub>0</sub> (mol. % sec. <sup>-1</sup> )	10 <sub>4</sub> k <sub>0</sub> (calc.)
49	2-Phenylethane-	39.95	0.53	2.37	1.07	1.12
51		40.11	0.75	2.51	1.26	1.39
59	Mesitylene-α-	39.72	0.23	2.16	1.81	1.85
63		38.89	0.32	1.66	1.47	1.47
100	<i>iso</i> Durene-α <sup>2</sup> -	39.37	0.27	1.93	1.60	1.75
103		37.39	0.29	1.26	1.09	1.15

nitrations of toluene and *tert.*-butylbenzene in aqueous acetic acid (observation by Jones, quoted by Hughes, Ingold, and Reed, *loc. cit.*). For nitrations in our range of aqueous nitric acid, we estimate that to observe sensibly zero-order kinetics for 90% of the reaction we require compounds of reactivity *ca.* 20,000 times that of water.

It would be expected that phenols or phenolic ethers would have this high reactivity. However, an examination of the nitrations of such compounds was complicated, in the case of the phenolic ethers, by concomitant side reactions, possibly nitrosation and demethylation. It was hoped that nitrophenol, which is highly reactive towards nitrosating agents, would be similarly reactive under our conditions. Its observed low reactivity, *ca.* 10 relative to the water molecule, suggests that it exists in our solutions as the uncharged molecule, and that its high reactivity to nitrosation and nitration in acetic acid is due to the existence of the nitrophenoxide ion in these solutions, and that the effects of the groups NO<sub>2</sub> and OH, on nitration, are opposite and (roughly) equal.

The experimental change of kinetic order from first towards zero, with increasing aromatic reactivity, or concentration, which we observe in aqueous nitric acid, was also found in nitrations in aqueous perchloric-nitric acid solutions, in the range studied by Halberstadt, Hughes, and Ingold (*loc. cit.*) (see Fig. 5). This change of kinetic form suggests that the nitronium ion is the nitrating agent in these solutions. Unfortunately, we were unable to measure the rates of oxygen exchange under these conditions, owing to the complicating presence of perchloric acid, and can therefore make no comparisons between oxygen exchange and nitration in the presence of perchloric acid.

In these solutions the variation of nitric acid, in the course of a kinetic run, was significant compared to the initial nitric acid concentration; this complicated the kinetic form of the nitration. A further indication of this change of order is shown by the decrease of initial first-order rate coefficients with increasing concentration of the aromatic compound (Table 3).

TABLE 3. Initial first-order nitration rates in aqueous nitric-perchloric acid media, at 24.85°.

Run no.	Sulphonic acid	Medium composition (mol. %)	[ArH] <sub>0</sub> (mol. %)	10 <sup>4</sup> k <sub>1</sub> (sec. <sup>-1</sup> )
		[HNO <sub>3</sub> ] [HClO <sub>4</sub> ] [H <sub>2</sub> O]		
54	2-Phenylethane-	16.36 9.75 73.89	0.081	4.53
55			0.84	2.30
61	Mesitylene-α-	17.58 6.56 75.88	0.070	5.92
62			0.19	3.84

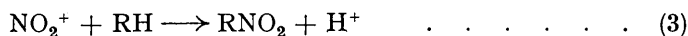
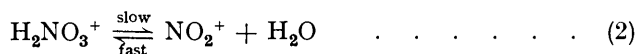
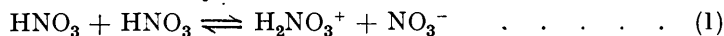
*Kinetic Salt Effects.*—The effect of added salts on the first-order rate coefficients of nitration of toluene-ω- and 2-phenylethane-sulphonic acid in aqueous perchloric-nitric acid was investigated by Halberstadt, Hughes, and Ingold (*loc. cit.*), who observed a strong acceleration by sodium perchlorate, and a weaker though well-marked, retardation by nitrates. In the present work the first-order nitration of 2-phenylethanesulphonic acid and the approximate zero-order nitration of *isodurene*-α<sup>2</sup>-sulphonic acid were carried out in the same medium, 39.3 mole % nitric acid, at 0°, in the presence of added sodium perchlorate and potassium nitrate. To minimise the effect of the fully ionised sodium

sulphonates, each group of measurements was carried out with a constant concentration of the given aromatic compound.

In order to make the approximately zero-order nitrations comparable, the rates quoted were measured over comparable parts of the runs. The experimental results are shown in Fig. 6. They show a retardation by nitrate ion in both kinetic forms, and an acceleration by sodium perchlorate, which is much more marked in the first-order than in the zero-order mechanism.

The retarding effect of nitrate ion is similar for both kinetic forms, and following the general theory of nitration (Hughes, Ingold, and Reed, *loc. cit.*), we consider that the nitrate ion decreases the standing concentration of the nitracidium ion, formed in the equilibrium  $\text{HNO}_3 + \text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^-$ . As this initial equilibrium is a component of the rate factors for both zero- and first-order nitrations, we expect a parallel effect of nitrate ion on both these rates. Owing to the high concentration of nitrate ion present in our nitrating solutions, we can draw no quantitative conclusions from the magnitude of this nitrate-ion effect, although, as we should expect, it is considerably smaller than the effect observed in nitrations in nitromethane and acetic acid (Hughes, Ingold, and Reed, *loc. cit.*) under conditions in which the concentration of nitrate ion initially present is small.

The acceleration of the first-order rates of nitration by sodium perchlorate, observed by Halberstadt, Hughes, and Ingold (*loc. cit.*), was considered by them to be due to the solvation of the cation by water molecules, decreasing the activity of the water. A detailed consideration of the mechanism of nitration suggests that such a solvation should affect the zero- and first-order reactions differently :



For a zero-order reaction, the rate-determining step is the heterolytic fission of the nitracidium ion (2), and because of the rapid capture of the nitronium ions by the aromatic compound, the reverse step of (2), the recombination of nitronium ions and water, which depends upon the activity of the water molecules, plays no part in the kinetics of the reaction. The comparatively small accelerating effect which we observe is probably due entirely to the enhanced selective protonation of the nitric acid.

The first-order reaction involves the equilibrium formation of the nitronium ion by steps (1) and (2), followed by the slow reaction of the nitronium ion and the aromatic compound. The standing concentration of nitronium ions will therefore be increased by a decrease in the activity of the water molecules, which will not only facilitate protonation of the nitric acid, but will also allow a higher standing concentration of nitronium ions in equilibrium (2).

This treatment ignores the effect of ionic strength on the actual nitration step. As this step involves, not a formation or destruction of charge, but merely the separation of an existing charge, such an effect should not be large. Any quantitative consideration of the effect of non-common ions is precluded by the necessity of adding the aromatic compounds as sodium salts.

#### EXPERIMENTAL

*Preparation of Materials.*—Nitric acid was purified by vacuum-distillation from sulphuric acid as described in Part I (*loc. cit.*). Perchloric acid, "AnalaR" 72% grade, was used without further purification. Inorganic salts, of "AnalaR" grade, were recrystallised from water and dried over phosphoric oxide in a desiccator. *N*-Methyl-2 : 4-dinitroaniline, kindly supplied by Dr. J. Glazer, was recrystallised from water; it then had m. p. 177°. *p*-Nitrophenol, recrystallised from water, had m. p. 113°.

Toluene- $\omega$ - and 2-phenylethane-sulphonic acids were prepared as sodium salts from the corresponding bromides by boiling aqueous sodium sulphite, recrystallised from water and dried over phosphoric oxide (Halberstadt, Hughes, and Ingold, *loc. cit.*). Mesitylene- $\alpha$ -sulphonic acid was similarly prepared from  $\alpha$ -bromomesitylene, obtained by direct bromination of

mesitylene (Kadesh, *J. Amer. Chem. Soc.*, 1947, **69**, 1211). Repeated micro-analyses for this and similar sodium sulphonates gave erratic results; the *sodium mesitylene- $\alpha$ -sulphonate* was therefore analysed directly for sodium (Found: Na, 10.4.  $C_9H_{11}O_3SNa$  requires Na, 10.4%), and further characterised by conversion into the *S-benzylthiuronium* derivative (Chambers and Watt, *J. Org. Chem.*, 1941, **6**, 376), m. p. 162° (Found: C, 56.6; H, 6.3; N, 7.2.  $C_{17}H_{22}O_3N_2S_2$  requires C, 56.8; H, 6.4; N, 7.4%).

*isoDurene- $\alpha^2$ -sulphonic acid* was prepared, as the sodium salt, by chloromethylation of the corresponding hydrocarbon, followed by conversion into the iodide, and reaction of the iodide with sodium sulphite. It was purified by recrystallisation from water, and dried at 110° (Bunton and Halevi, forthcoming publication).

*Kinetic Measurements.*—The nitration of all the compounds was followed dilatometrically. Tap dilatometers, lubricated with silicone grease, were employed; their capillary bores in the range 0.4—1.1 mm., were chosen to accommodate the widely different initial concentrations of aromatic compound, otherwise they were of the design described by Halberstadt, Hughes, and Ingold (*loc. cit.*). The change in meniscus height with time was followed with a cathetometer. To allow a convenient comparison to be made with the results of oxygen exchange, the composition of the solution is expressed in mol. % of the initial components, and the concentrations of the compound being nitrated and of added salts are expressed as moles per 100 moles of the original medium.

The nitrations in aqueous nitric acid at 0° were carried out in an ice-water thermostat ( $\pm 0.001^\circ$ ); those in aqueous nitric-perchloric acid mixtures were carried out in a thermostat of conventional design, at  $24.85^\circ \pm 0.002^\circ$ . The nitrating solutions were kept overnight in the refrigerator after being made up, and it was then not necessary to carry out the degassing described by Halberstadt, Hughes, and Ingold (*loc. cit.*). For runs carried out at 0° it was necessary to allow 10 minutes, after filling the dilatometer, for temperature equilibrium to be reached. This, in the rapid runs, restricted the portion of the reaction which could be followed.

Nitrous acid was determined before each run, as described in Part I (*loc. cit.*). Its concentration varied from 1 to  $5 \times 10^{-3}$  mole %; such small concentrations had no noticeable effect on the rate.

*Analytical Control.*—Mononitration has been confirmed by Halberstadt, Hughes, and Ingold (*loc. cit.*), for toluene- $\omega$ - and 2-phenylethane-sulphonic acids, under conditions similar to those of the present investigation. In all other cases confirmation of mononitration was carried out by product isolation.

Nitration, under the conditions of the dilatometric runs, but on a somewhat larger scale, was allowed to proceed for 2—3 times the time required for complete dilatometer contraction, and the nitration product isolated and characterised or analysed.

*N-Methyl-2:4-dinitroaniline.* The nature of the two-stage nitration was deduced by Glazer (*loc. cit.*). In the present work it was impossible, owing to solubility difficulties, to obtain accurate kinetic data for the *N*-nitration, and therefore the control was repeated under our experimental conditions at 0°. After a period of time, deduced from approximate dilatometric rate measurements, the nitration mixture was poured on ice, and the product isolated and identified as *N*-methyl-*N*:2:4-trinitroaniline, m. p. 113—114° (Found: C, 34.8; H, 2.5; N, 23.4. Calc. for  $C_7H_8O_6N_4$ : C, 34.7; H, 2.5; N, 23.1%).

Under conditions of the *C*-nitration, this trinitro-compound was nitrated at a rate identical with that of the parent compound (Fig. 2).

*p-Nitrophenol.* The nitration product, isolated by pouring on ice and recrystallisation from water, had m. p. 114—115°. The sample did not depress the m. p. of an authentic sample of 2:4-dinitrophenol. 2:4-Dinitrophenol under these nitration conditions gave no dilatometric contraction.

*Mesitylene- $\alpha$ - and isodurene- $\alpha^2$ -sulphonic acids.* The nitrated mixture was poured into water, and the water and nitric acid were removed by hard pumping. The solid residue was recrystallised from a small amount of water, and finally washed with ice-water to remove traces of nitrate ion. The nitro-acids were analysed for nitrogen in their *sodium* salt (Found: N, 4.9, 5.2.  $C_9H_{10}O_3NSNa$  requires N, 5.2%) (Found: N, 5.1.  $C_{10}H_{12}O_3NSNa$  requires N, 5.0%).

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