1202. *Salt Effects on the Rate of Nitration of Benzenesulphonic Acid in Solvent Sulphuric Acid*

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The hydrogen sulphates of the alkali metals, ammonium, calcium, barium, *m*-nitrobenzoic acidium, and hexamine all produce a marked increase in the rate of nitration of benzenesulphonic acid in sulphuric acid, which is measured by a simple thermal method. In the presence of these substances, the non-electrolyte benzenesulphonic acid also depresses the freezing-point of sulphuric acid more than would be expected from the cryoscopic constant, and this is qualitatively consistent with an interpretation of the nitration results in terms of the Brønsted salt-effect theory. The effects on the reaction rate are, however, larger than expected, especially for calcium and barium, which may be acting in some special way through the formation of complexes. All reaction rates are determined under first-order conditions, with the aromatic compound in large excess over the nitronium ions, and the derived second-order constants vary markedly with the concentration of the aromatic compound itself.

BRØNSTED[1] successfully interpreted kinetic salt effects in dilute aqueous solutions by considering the ratio of the product of the activity coefficients of the reactants (A and B, say) to the activity coefficient of the activated complex (‡). According to his theory the specific rate constant, k, in any real solution is related to that at zero ionic strength, k_0, by the equation

$$k = k_0 f_A f_B / f_‡$$

where the f's are activity coefficients. Since the activated complex has an electrical charge equivalent to the sum of the charges of the two reactants, electrolyte theory makes it clear why a reaction involving an ion and a neutral molecule in aqueous solution is subject to very much smaller salt effects than one involving two ions; the most important contribution to the activity coefficient (the square-root term) depends on the electrical charge of the species, and so cancels out when f_A and $f_‡$ correspond to the same charge, leaving only a small linear effect on $\ln k$ determined by $\ln f_B$ and the difference in the linear residues of $\ln f_A$ and $\ln f_‡$. Accordingly, salt effects on reactions involving neutral molecules tend to be relatively unimportant in dilute aqueous solution.

Sulphuric acid is in many ways similar to water as a solvent, but a marked difference may exist in just this respect of the importance of the salt effects to be expected in reactions involving neutral molecules, simply because the activity coefficients of non-electrolytes seem to be much more sensitive to the presence of salts than those of the electrolytes themselves in this solvent. Cryoscopy[2] shows that cations of many different shapes and sizes all behave very similarly and almost ideally in sulphuric acid. The small differences which exist are regular and mostly attributable to solvation, and the regularities can be understood in terms of the interionic attraction theory.[3,4] The molecular depressions produced by non-electrolytes,[5] on the other hand, show quite marked and irregular fluctuations of the order of 10—20% in salt solutions up to 0·2 molal. In a reaction between an ion and a neutral molecule in sulphuric acid, therefore, the activity coefficients of the ion and the activated complex should approximately cancel, as in aqueous solution, leaving the non-electrolyte activity coefficient, f_B, as before, but this would now carry over the marked salt effects into kinetic phenomena. There might therefore be an

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[1] J. N. Brønsted, *Z. phys. Chem.*, 1922, **102**, 169.

[2] R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J.*, 1950, 2473—2551 (seven Papers).

[3] J. C. D. Brand, J. C. James, and A. Rutherford, *J.*, 1953, 2447.

[4] R. J. Gillespie and J. V. Oubridge, *J.*, 1956, 80; S. J. Bass, R. J. Gillespie, and J. V. Oubridge, *J.*, 1960, 837.

[5] P. A. H. Wyatt, *J.*, 1954, 2647; J. R. Brayford and P. A. H. Wyatt, *J.*, 1955, 3453.

interesting reversal of the roles of electrolytes and non-electrolyte in this solvent, whereby reactions involving only ionic species would exhibit small salt effects, and reactions involving neutral molecules large ones. (Compare the similar reversal in Liler's method [6] for the conductometric determination of equilibrium constants in sulphuric acid, in which the measurements are made not at high constant ionic strengths, but at high constant non-electrolyte concentrations.)

To test this idea we have investigated the effects of several metal and organic hydrogen sulphates upon the velocity of the reaction

$$C_6H_5{\cdot}SO_3H + NO_2^+ \longrightarrow O_2N{\cdot}C_6H_4{\cdot}SO_3H + H^+ \qquad (1)$$

Nitration was chosen as being a reaction of well-established mechanism,[7] the kinetics of which should be particularly simple in sulphuric acid, where the nitronium ion is formed quantitatively from the solute nitric acid.[2] Strictly speaking, the additives used are not salts since the hydrogen sulphate ion is, of course, the characteristic base in this solvent; but in view of the strong weight of opinion against the occurrence of base catalysis in this reaction [7] we assumed that the use of hydrogen sulphate simply as a convenient anion would not introduce any special complications.

The results show that electrolytes do indeed have a marked effect on this reaction, in fact a larger effect than had been expected. For example, the reaction proceeds four times as fast in a 0·25 molal sodium sulphate solution as in the pure acid, and the presence of calcium and barium ions has a much larger effect still. Qualitatively this increase is compatible with the increase in activity coefficients indicated by supplementary cryoscopic measurements, but we feel that, at least with the bivalent ions, something more than a simple effect on the non-electrolyte activity coefficient is involved, and the matter is being further investigated.

RESULTS

The reaction (1) was found to be uncomplicated by side-reactions during the period of measurement and to have a velocity at 25° within the range of applicability of the simple thermal method,[8] which was adapted for use with the hygroscopic and corrosive solvent. (The requirements of this method are an appreciable heat of reaction and a half-life in the range 2 sec. to 2 min.) Preliminary attempts at the nitration of benzene itself confirmed that the rate of sulphonation was highly competitive in this case; [9] the benzene was sulphonated immediately and thereafter the rate of nitration corresponded to that of benzenesulphonic acid. Though somewhat too fast for the present technique and uncomfortably close to the rate of mixing, the first-order rate constant for the sulphonation of benzene at 25° was estimated at about 0·7 sec.$^{-1}$, which is concordant with a value extrapolated from data [10] published during the course of our work. Fortunately the uptake of a second sulphonic acid group is relatively slow, as shown by the fact that the molecular depression of freezing point of sulphuric acid caused by the solute benzenesulphonic acid does not change with time up to at least 20 hr. (It would increase three-fold for the complete formation of the disulphonic acid.) A slow increase of optical density was, however, observed when a solution of benzenesulphonic acid was kept at 70° for 3 days. For this reason stock solutions were always freshly prepared and never kept for more than 16 hr.

Similarly, the question of a second nitration did not arise, as confirmed by the fact that the freezing-point depressions of mixtures of the reactants in sulphuric acid correspond to the completion of reaction (1) only. Cryoscopic measurements also confirmed that benzenesulphonic acid is effectively unprotonated. Using sodium benzenesulphonate, Gillespie [11] originally deduced that the sulphonic acid itself was about 30% protonated; but at that time the effects of electrolytes on the apparent *i*-factors of non-electrolytes had not been investigated

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[6] M. Liler, *J.*, 1962, 4272.

[7] P. B. D. de la Mare and J. H. Ridd, " Aromatic Substitution: Nitration and Halogenation," Butterworths, London, 1959, p. 57.

[8] P. A. H. Wyatt, *J.*, 1960, 2299.

[9] H. Martinsen, *Z. phys. Chem.*, 1907, **59**, 605—634.

[10] M. Kilpatrick, M. W. Mayer, and M. L. Kilpatrick, *J. Phys. Chem.*, 1960, **64**, 1433.

[11] R. J. Gillespie, *J.*, 1950, 2542.

and we now show that the true *i*-value of the acid is much closer to unity. In any case the protonated form would nitrate more slowly, and its presence in amounts of the order of 5% would presumably make little difference to our results and conclusions.

The cell consists of a small platinum crucible, which rests in an insulating jacket of polystyrene foam within a water-tight container shaped like a large weighing-bottle, which is itself completely immersed in a thermostat apart from a B24 neck socket at the top. Into the latter fits a machined Polythene bung carrying a platinum/platinum–rhodium thermocouple, a small heater, a device for adding the second reagent, and a glass stirrer, all of which reach down into the liquid in the cell. The thermocouple indicates the temperature of the cell relative to the surrounding thermostat and so records the progress of the reaction. Its output is passed through a d.c. amplifier and followed visually on a galvanometer scale; the maximum temperature rise during a reaction was arranged to be about 0·2°.

To begin an experiment 10 ml. of a benzenesulphonic acid solution of the required strength, plus any added electrolyte, was transferred to the platinum crucible and its temperature adjusted with the heater. Temperature readings were then taken at 2 or 3 sec. intervals (with the help of a calibrated metronome) for several seconds before the addition of the second reactant, to fix the " base-line " for the subsequent changes. The nitronium ion was added in the form of a 16% solution of pure nitric acid in pure sulphuric acid, which was squirted from a fine glass tube at a noted time. Only about 0·01—0·02 g. of this solution was added, so that the initial molality of NO_2^+ ion was only 0·01—0·02 and the kinetics were always of first order. (The benzenesulphonic acid concentration was always large by comparison.) Readings were continued throughout the course of the reaction and for several seconds after the maximum temperature had been reached, to permit the small cooling correction to be made.[8]

All rate measurements were carried out at 25°.

Dependence of the Reaction Rate on the Molality of Benzenesulphonic Acid in the Absence of Added Electrolytes.—If reaction (1) proceeds by a simple bimolecular mechanism, the observed first-order rate constant, k_1, should be the product of the true second-order constant (k_2) and m_2, the concentration of the reactant in excess, *i.e.*, the benzenesulphonic acid. (Because of the convenience of making up the solutions by weight, all " concentrations " are expressed as molalities in this Paper.) Table 1 shows the first-order constants obtained in 100% sulphuric acid. It is clear that even in the absence of electrolytes the value of k_1/m_2 is not constant, which implies that the non-electrolyte itself has a marked effect upon the kinetic activity factor. This is not entirely unexpected since it is known that non-electrolytes interfere with the solvent in some way which shows up, for example, in the electrical conductance of the hydrogen sulphate ion.[12]

TABLE 1

First- and second-order rate constants for the nitration of benzenesulphonic acid in pure sulphuric acid

Molality of $C_6H_5\cdot SO_3H$ ($=m_2$)	0·075	0·150	0·250	0·350	0·425	0·500	0·600	0·750
$100k_1$ (sec.$^{-1}$)	1·37	1·62	1·96	3·55	4·52	6·90	8·95	12·45
k_1/m_2 ($=k_2$)	0·183	0·108	0·078	0·101	0·106	0·138	0·149	0·166

Dependence of the Reaction Rate on the Presence of Water in the Solvent.—It is well known that the rate of nitration of aromatic compounds passes through a maximum near 90% sulphuric acid. In fact, the rate of nitration of benzenesulphonic acid proved too fast for our technique in the 92 and 98% acid, but Table 2 shows the first-order constants obtained at some other concentrations, using a fixed molality (0·25) throughout. The most important feature from the present point of view is that the rate constant only increases by about 60% between the 100 and 99·5% acid (which corresponds to a water molality of 0·28) and, since the solvent composition can be controlled by freezing point and conductance to at least two orders of magnitude

TABLE 2

Rate constants for the nitration of 0·25 molal benzenesulphonic acid in the presence of water

Wt. % H_2SO_4	100	99·5	99·0	98·5	85	82
$100k_1$ (sec.$^{-1}$)	1·96	3·20	4·10	17·0	27·0	1·25

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[12] R. J. Gillespie and C. Solomons, *J.*, 1957, 1796.

better than this, there is consequently no fear of significant errors in the latter results caused by the presence of extraneous water.

Rate of Nitration of Benzenesulphonic Acid when added as its Salts.—The addition of alkali and alkaline-earth benzenesulphonates to sulphuric acid produces hydrogen sulphate ions and free benzenesulphonic acid in equal amounts:

$$C_6H_5{\cdot}SO_3Na + H_2SO_4 \longrightarrow Na^+ + C_6H_5{\cdot}SO_3H + HSO_4^- \qquad (2)$$

$$(C_6H_5{\cdot}SO_3)_2Ca + 2H_2SO_4 \longrightarrow Ca^{2+} + 2C_6H_5{\cdot}SO_3H + 2HSO_4^- \qquad (3)$$

Some reactions were carried out in this way because of convenience in investigating the effects of the alkaline-earth ions, which are otherwise not easy to get into solution, and because it provided a cross-check on the chemical reactants and the rate constants.

Preliminary work with benzenesulphonic acid and its salts raised doubts about techniques of preparation, methods of freeing the acid from diphenyl sulphone, etc., and it was therefore useful to have two ways of preparing solutions containing the alkali metals. They were made up both from the dried benzenesulphonates themselves (method A) and from the purified benzenesulphonic acid with the alkali-metal sulphate added separately (method B). The results obtained by the two methods are compared in Table 3. They are sufficient to confirm that the methods of preparation are satisfactory, but also indicate that the actual values of k_1 are not reliable to better than 10%. For this reason all the subsequent results are presented with sufficient accuracy in graphical form.

TABLE 3

Values of $100k_1$ (sec.$^{-1}$) with sodium and potassium benzenesulphonate solutions prepared by two different methods

	Sodium salt		Potassium salt	
Salt molality	Method A	Method B	Method A	Method B
0·15	—	—	1·8	—
0·25	4·1	3·6	4·4	4·2
0·35	7·5	7·8	8·6	8·0
0·50	19·8	22·0	23·1	21·4

Figure 1 shows how much faster the reaction proceeds in the presence of calcium and barium than of sodium and potassium ions, when the first-order constants are compared at the same molality of hydrogen sulphate ion and benzenesulphonic acid, produced according to equations (2) and (3). (The calcium and barium ion molalities are, of course, half those shown on the hydrogen sulphate co-ordinate.)

Rate of Nitration of 0·25 *Molal Benzenesulphonic Acid in the Presence of Various Molalities of Added Electrolytes.*—The first-order rate constants are summarised in Figure 2, where all added electrolyte concentrations are expressed in terms of the hydrogen sulphate ion molality. A point at $k_1 \sim 0{\cdot}25$ sec.$^{-1}$ and $m_{HSO_4^-} = 0{\cdot}25$ molal can be added to this diagram from the results for calcium and barium summarised in Figure 1.

All the additives studied clearly accelerate the reaction, but they seem to fall into three groups according to the magnitude of their effects. The first includes the alkali-metal and ammonium hydrogen sulphates, all of which produce approximately the same linear increase in the first-order constant. The second group consists of the hydrogen sulphates of *m*-nitrobenzoic acidium and the 4-protonated [13] hexamethylenetetramine. At the same hydrogen sulphate concentration these two cations have about twice the effect of the alkali metals, although the hexamethylenetetramine points (but not those for *m*-nitrobenzoic acid) can be brought on to the common line with the alkali metals by plotting the ionic strength instead of the hydrogen sulphate ion molality. Calcium and barium form the third group, having an extremely large accelerating effect on the reaction, whether compared at the same HSO_4^- molality or the same ionic strength.

The general form of Figure 2 was confirmed with similar experiments at a benzenesulphonic acid molality of 0·1.

Cryoscopic Measurements.—The standard procedure for cryoscopy in sulphuric acid was used.[2]

Purified benzenesulphonic acid gave *i*-factors of 1·01, 1·15, 1·08, and 1·02 at molalities of 0·0905, 0·0956, 0·0981, and 0·1408 in pure sulphuric acid. An experiment was also carried out

[13] R. J. Gillespie and S. Wasif, *J.*, 1953, 221.

in which a slightly moist sample of the solute was added to an oleum of known disulphuric acid concentration, which was afterwards titrated with water to the maximum freezing point, thus permitting an estimate of both the quantity of water present as an impurity in the solute (from the " horizontal " shift in the maximum) and the freezing-point depression produced at the maximum of the curve by a corrected molality of the solute. At a corrected molality of 0·0275, the *i*-factor came out in this way as 1·01. In view of the difficulty of distinguishing slight protonation from non-electrolyte activity coefficient effects, it can only be concluded that benzenesulphonic acid is most likely to be unprotonated; at most the extent of protonation cannot exceed about 5%.

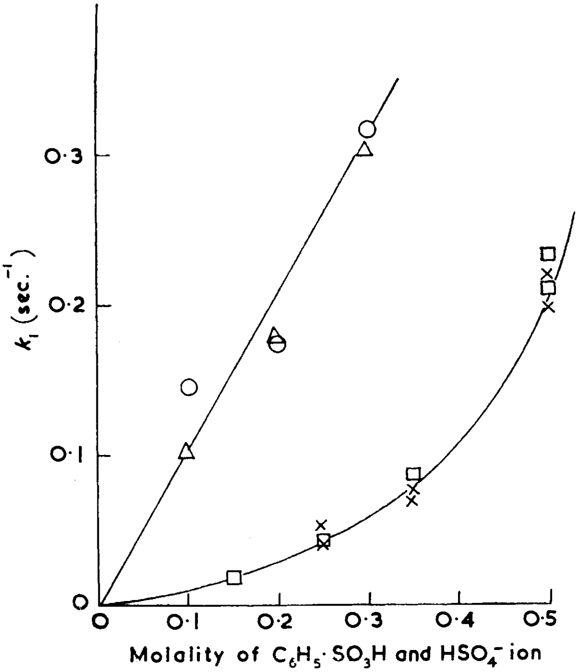

FIGURE 1. First-order rate constants for the nitration in 100% sulphuric acid of benzenesulphonic acid added in the form of a benzenesulphonate

× Sodium salt
□ potassium salt
○ calcium salt
△ barium salt

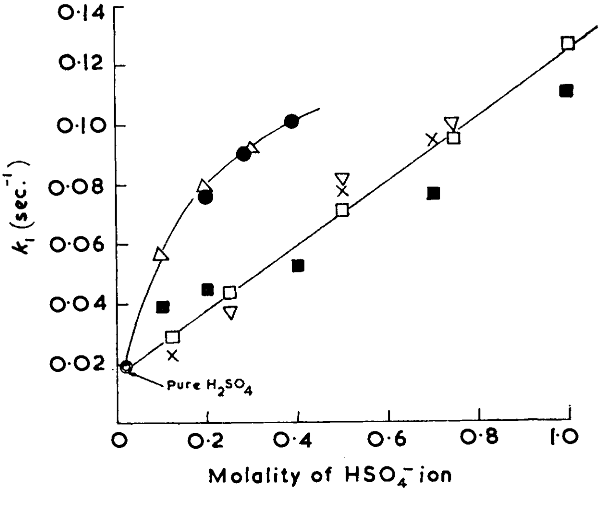

FIGURE 2. First-order rate constants for the nitration of 0·25 molal benzenesulphonic acid in the presence of hydrogen sulphates in solvent sulphuric acid

▽ $LiHSO_4$
× $NaHSO_4$
□ $KHSO_4$
■ NH_4HSO_4
▲ *m*-nitrobenzoic acidium hydrogen sulphate
● hexamethylenetetramine tetra(hydrogen sulphate)

The cryoscopic confirmation of the stoicheiometry of reaction (1) was made using potassium benzenesulphonate, which was added as a solute to sulphuric acid already containing a little nitric acid. In two experiments of this kind the molecular depressions of the potassium salt were found to be 1·20 and 1·13, in sufficiently good agreement with a value of slightly greater than 1 expected from the equation

$$C_6H_5{\cdot}SO_3K + NO_2^+ \longrightarrow O_2N{\cdot}C_6H_4{\cdot}SO_3H + K^+ \qquad (4)$$

(The non-electrolyte would be expected to contribute 10—20% more than 1 to i in these solutions.)

Our i-factor of 4·86 for the solute hexamethylenetetramine confirms the conclusion of Gillespie and Wasif,[13] whose conductance results showed that this base takes up four protons. This behaviour was further confirmed by the method of Leisten *et al.*,[14] using a sulphuric acid solution containing $H_2S_2O_7$ and $(NH_4)HS_2O_7$, the freezing point of which is insensitive to hydrogen sulphate ions. In this solution hexamethylenetetramine gave an i-factor of 1·19, in satisfactory agreement with the 1 expected for the single cation.

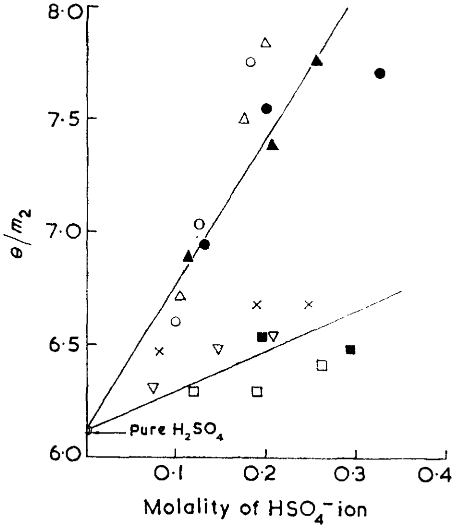

FIGURE 3. Molal freezing-point depressions of sulphuric acid by benzenesulphonic acid in the presence of added electrolytes (Labelling as in Figures 1 and 2)

The i-factor of m-nitrobenzoic acid (1·86) shows that it is, as expected, a weaker base than benzoic acid, but it is nevertheless nearly 90% protonated. It was used as an organic electrolyte in the kinetic experiments because it is not nitrated rapidly, unlike benzoic acid itself which is nitrated faster than benzenesulphonic acid.[9]

Several determinations were made of the freezing-point depression per mole of the solute benzenesulphonic acid in the presence of varying quantities of added hydrogen sulphates. As with the polynitro-compounds,[5] the molecular depressions were found to vary not only with the concentration of added electrolyte but also with the concentration of the non-electrolyte itself. For the sake of comparison with the kinetic results, interpolated values of the molecular depression at a non-electrolyte molality of 0·25 are shown in Figure 3. Compared at the same hydrogen sulphate molality, the effects of the various additives fall roughly into two groups, as indicated by the two lines on the diagram, with the alkali metals (including ammonium) in one group and all the rest in the other. Since the freezing point only gives direct information about the solvent activity, the fluctuations of the non-electrolyte molecular depression from the cryoscopic constant (6·12 deg. mole^{-1} kg. in the pure solvent) incorporate not only the effects of the electrolyte on the non-electrolyte activity coefficient but also the corresponding effect of the non-electrolyte on the electrolyte. The results in Figure 3 therefore only give a qualitative indication of the way the non-electrolyte activity coefficient varies in these solutions. Attempts to separate out the true f_B from the data do, however, persuade us that this alone cannot vary enough to account for the whole of the kinetic effects observed.

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[14] J. A. Leisten, *J.*, 1961, 2191; J. A. Leisten and K. L. Wright, *J.*, 1964, 3173; J. A. Leisten and P. R. Walton, *J.*, 1964, 3180.

Unlike the polynitro-compounds,[5] benzenesulphonic acid produces a molecular depression which exceeds the cryoscopic constant in all the solutions studied. This is a pity since some decreased values, if associated with decreases in the reaction rate, would have strengthened the single salt-effect interpretation.

DISCUSSION

Whatever may be the proper explanation, it is clear that electrolytes do have a large accelerating effect upon the nitration of benzenesulphonic acid. Furthermore, there is a certain correspondence between the kinetic and the cryoscopic effects depicted in Figures 2 and 3. The accelerating effect of calcium and barium is so great, compared even with the more highly charged hexamine ion, and so reminiscent of ion-pairing effects in water [15] as to suggest that some kind of complexing effect with a reactant may be involved, although it is difficult to see how the presence of a doubly charged positive ion could help the attack of a nitronium ion on a non-electrolyte. Of the remaining ions, 4-protonated hexamine could be brought into line with the alkali metals by comparison at the same ionic strength, and this would leave *m*-nitrobenzoic acidium as the only anomaly, apart from the alkaline earths, and lend support to a theory of activity-coefficient effects determined principally by the ionic strength. The anomalous *m*-nitrobenzoic acidium, being rather like the aromatic substrate, might possibly then be accommodated by supposing that it has a special additional effect like that produced by an increase in the concentration of the non-electrolyte itself.

Considered on their own, the common effects of the uni-univalent electrolytes (Figure 2) would ordinarily be regarded as demonstrating base catalysis by the hydrogen sulphate ion;[16] but the absence of kinetic isotope effects [17] rules this out. Explanations of the apparent hydrogen sulphate dependence in terms of protonation or solvation of the substrate [18] cannot help much in this particular case, however, since the extent of protonation of the aromatic compound is so small and the solvent activity is almost constant throughout. This leaves a salt effect on the kinetic activity factor as the most plausible explanation. Our measurements do, of course, extend to rather high concentrations (especially in molarity terms) and Dr. J. G. Jones informs us that similar effects have been observed in the nitration of nitrobenzene in hydrogen fluoride.[19]

[A Referee has made the interesting suggestion that, judged by the large effect of water on its nitration rate compared with that of other non-electrolytes,[18] benzenesulphonic acid is perhaps untypical as a non-electrolyte in nitration and may even lose a proton from the SO_3H group at a critical stage. We had, in fact, considered, and provisionally rejected as unlikely, unorthodox mechanisms of this kind, which would, of course, raise once again the question of base catalysis. In this respect some recent measurements in this laboratory are helpful. Mr. M. A. Akand finds that the salt $NaB(HSO_4)_4$ is about as effective as $NaHSO_4$ in accelerating the reaction, and this would not be expected if HSO_4^- appeared in the rate equation. Perhaps it should be emphasised that we are not claiming that variable solvation [18] cannot explain the water-dependence of the rate of nitration of benzenesulphonic acid, only that the salt effects observed seem too large to be explained by shifts in the solvation equilibrium.]

EXPERIMENTAL

The inorganic salts were added in the form of sulphates, which were of AnalaR quality dried at 110° for several hours and stored over sulphuric acid. Samples of sodium, potassium,

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[15] C. W. Davies, "Progress in Reaction Kinetics," vol. I, ed. G. Porter, Pergamon, Oxford, 1961, p. 161.

[16] G. M. Bennett, J. C. D. Brand, D. M. James, T. G. Saunders, and G. Williams, *J.*, 1947, 474.

[17] L. Melander, *Nature*, 1949, **163**, 599; *Arkiv Kemi*, 1950, **2**, 211; T. G. Bonner, F. Bowyer, and G. Williams, *J.*, 1953, 2650.

[18] R. J. Gillespie and D. J. Millen, *Quart. Rev.*, 1948, **2**, 277; R. J. Gillespie and D. G. Norton, *J.*, 1953, 971.

[19] M. Kilpatrick, M. L. Kilpatrick, and J. G. Jones, *J. Phys. Chem.*, 1965, **69**, 2248.

calcium, and barium benzenesulphonates were dried and stored in the same way. Hexamine (hexamethylenetetramine), benzoic acid, and *m*-nitrobenzoic acid were all recrystallised from alcohol and dried at 110°, and hexamine was stored over phosphorus pentoxide.

Pure nitric acid was distilled at room temperature from a mixture of 98% sulphuric acid and ordinary concentrated nitric acid, and pure sulphuric acid was prepared by adding the AnalaR acid to a pure oleum until the maximum freezing point was reached, the pure oleum being obtained by distilling sulphur trioxide into AnalaR sulphuric acid.

Benzenesulphonic acid was purified in two ways. The commercial " 98% " acid was twice recrystallised from chloroform, filtered quickly through a sintered glass crucible, and pumped dry for several hours in a vacuum-desiccator over phosphorus pentoxide. The last traces of moisture were removed under a vacuum at 50°, leaving a product of 99·8% purity, as determined by acidimetry and microanalysis. With starting material containing less than 90% of benzenesulphonic acid, such as the commercial 70% acid, it was found better to dissolve in about 5 parts of water, filter off the sulphone impurity, add barium carbonate, and heat on a steam-bath for 1 hr. before filtering off the sulphate, precipitate the excess barium with a little sulphate, and then distil until slight fuming starts. Crystals which separate on cooling are collected, and the remaining liquid is then frozen to the walls of a round-bottomed flask in an ethanol–solid carbon dioxide bath. After evacuation of the flask for 4 hr., the temperature is raised, and the final removal of water is shown by a tendency of the molten acid to darken and to fume slightly.

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[*Received, June 9th*, 1965.]