177. *The Kinetics of the Sulphonation of Some Aromatic Compounds by Sulphur Trioxide.*

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The kinetic investigation of the sulphonation of aromatic compounds by sulphur trioxide in solutions of nitrobenzene (Vicary and Hinshelwood, J., 1939, 1372; Wadsworth and Hinshelwood, this vol., p. 469) has been extended to the reactions of benzene, bromobenzene, *m*-dichlorobenzene, α-nitronaphthalene, and *p*-nitroanisole. All reactions are found to be of the second order with respect to sulphur trioxide, and to exhibit the characteristic retardation by the product. The first order with respect to the aromatic reactant, which had been anticipated, has now been confirmed experimentally. Except with *p*-nitroanisole, the effects of substituents on the rate of sulphonation have been accounted for by changes in activation energy, and a correlation is found between such changes and the electronic effects of substituents as measured by dipole moments.

In the study of aromatic substitution reactions we are confronted with two main problems which, it appears, could best be solved by a kinetic investigation of such processes. The first is the specific mechanism of substitution in aromatic compounds, and about this little information is available. The second problem is concerned with physical interpretation of the postulates of the electronic theory of organic reactions with regard to the effects of substituents on the rate of further substitution (Robinson, *J. Soc. Dyers Col.*, Jubilee Issue, 1934, 65; Ingold, J., 1927, 2918; *Chem. Rev.*, 1934, **15**, 225). Some light has been thrown on the latter aspect by work in the field of dipole moments (Sutton, *Proc. Roy. Soc.*, 1931, **133**, *A*, 668; Ri and Eyring, *J. Chem. Physics*, 1940, **8**, 433). Furthermore, with various reactions of substituted aliphatic compounds, Hinshelwood, Laidler, and Timm (J., 1938, 848) have shown a correlation between changes in activation energy and the effects of substituents as postulated by the electronic theory of organic reactions.

For aromatic substitution reactions, kinetic data are difficult to obtain, since the usual experimental conditions are unsuitable for quantitative work and the reactions are generally complex (cf. Benford and Ingold, J., 1938, 929).

Some interesting results, however, emerged from the work begun by Vicary and Hinshelwood (*loc. cit.*) and continued by Wadsworth and Hinshelwood (*loc. cit.*) and by H. Paneth (unpublished). In the course of this series of investigations the kinetics of the sulphonation by sulphur trioxide were studied first with nitrobenzene and then with *p*-nitrotoluene and chlorobenzene in a medium of nitrobenzene. All three reactions showed similar characteristic features, *viz.*, the second order with respect to sulphur trioxide and a marked retardation by the sulphonic acid produced. The second order suggested a mechanism of substitution involving either one molecule of S_2O_6, which must be supposed to exist in equilibrium, in small amounts, with the monomeric form, or the simultaneous action of two single SO_3 molecules. With regard to the effects of substituents, the evaluation of the parameters of the Arrhenius equation showed that the changes in the rate of sulphonation were due to differences in activation energy rather than to a change in the probability of reaction, the value of the *P* factor being similar in the three cases. It is, however, desirable to obtain kinetic data for the reactions of other aromatic derivatives before drawing any far-reaching conclusions. The reaction of the unsubstituted compound, benzene itself, is of great interest. The halogenobenzenes which, owing to their *op*-directing power coupled with a decrease in nuclear reactivity, have sometimes been said to behave abnormally, also merit special attention.

In the present work we have, therefore, carried out kinetic studies under similar conditions with benzene, bromobenzene, and *m*-dichlorobenzene. [Some preliminary work had already been done on the benzene reaction by H. Paneth (unpublished), indicating a second order with respect to SO_3 and a rough value of 5500 cals. for the activation energy.] After a preliminary investigation of various other simple aromatic derivatives, α-nitronaphthalene and *p*-nitroanosole were selected as the only suitable compounds for this type of work. The experimental difficulties, which had always been appreciable, were accentuated by the high speeds of most reactions studied in the present work, but in view of the inherent interest attached to kinetic data for substitution reactions of a series of benzene derivatives, the application of the original method of investigation to these fast reactions appeared justified in spite of the inevitably large experimental errors. Nitrobenzene was retained as the medium so that it would be possible to compare the kinetics of all reactions under similar solvent conditions. No correction for the sulphonation of the solvent was required, since all rates measured here were 10^2 to 10^4 times as fast as that of nitrobenzene.

Experimental.

(a) *Reagents and Apparatus.*—Nitrobenzene, bromobenzene, *m*-dichlorobenzene, benzene, α-nitronaphthalene, and *p*-nitroanisole were all redistilled or recrystallised to constant b. p. or m. p. A fresh solution of sulphur trioxide in nitrobenzene was prepared for each run from 65% fuming sulphuric acid, by carrying sulphur trioxide fumes from the surface of the oleum into the nitrobenzene by means of a current of air. Work at 25° and 40° was done in electrically heated and stirred water-baths. At the low temperature, about 3°, a semi-solid slush of freezing benzene in a Dewar vessel was used as the thermostat. End-point measurements were carried out, as before, at 121° in an oil-bath heated by boiling perchloroethylene.

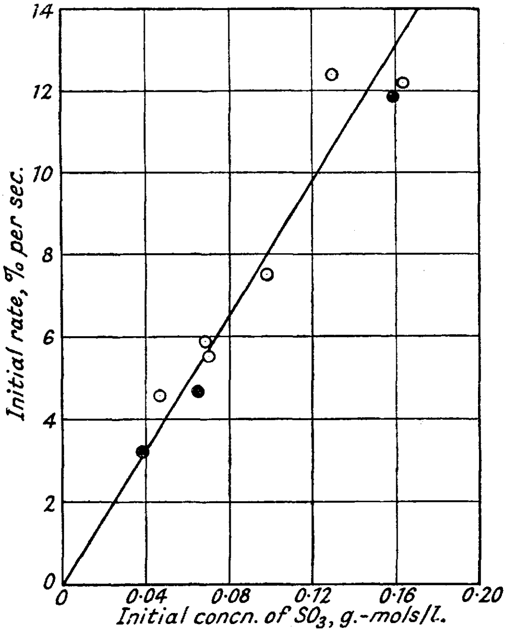
(b) *Observation of the Course of Reaction.*—The method used for following the progress of the reaction with time did not differ in principle from that previously described. All reaction rates measured in the course of the present investigation were faster than those found for *p*-nitrotoluene, and with benzene, faster even than the chlorobenzene reaction.

A form of inverted Y-tube was used as the reaction vessel, 2-c.c. portions of the aromatic and the sulphur trioxide solution being pipetted into the respective limbs. 5-C.c. portions were used for the faster reactions, especially for benzene, in order to increase the accuracy with which titres could be determined at the very low sulphur trioxide concentrations which had to be used. When the reagents contained in the Y-tube had attained the required temperature in the thermostat, the reaction was started by tilting and shaking the tube. After a suitable reaction time, which was recorded by means of an accurate stop-watch, the reaction was arrested suddenly by pouring the contents of the tube into about ten times the volume of electrically stirred water which contained excess alkali. The titration of the resulting emulsion was carried out with N/50-sodium hydroxide and hydrochloric acid, the end-point being approached from both sides and the solution shaken vigorously after each addition of acid or alkali. Bromothymol-blue was used as indicator.

The acidity at the beginning of reaction was obtained by titrating the contents of a tube containing 2 c.c. of the sulphur trioxide solution only, the same procedure being adopted for filling, preheating, and emptying the tube as was used for the rate measurements. Reaction end-points were determined by heating equal volumes of pure nitrobenzene and sulphur trioxide solution at 121° for 24 hours.

Results.—(a) *Order with respect to sulphur trioxide.* The extent of reaction was expressed as a percentage of the total change and plotted against the reaction time. The reaction curves all become almost parallel to the time axis after about 50% change, as was found by previous workers. From the slopes of the tangents drawn to the reaction–time curves at the origin, the initial rates of change were deduced. For a given concentration of the aromatic reagent initial rates (in % per sec.) were plotted against the sulphur trioxide concentrations. The straight lines passing through the origin (see Fig. 1) pointed to the second-order nature of the reaction with respect to sulphur trioxide. From the slopes of these lines, the measured velocity constants, k', were calculated at each temperature (Table I).

FIG. 1.



○ *Runs with initial concentration of α-nitronaphthalene* = 0·25 *g.-mol./l.*
● ,, ,, ,, ,, ,, ,, ,, = 0·10 ,, (*Plotted rates* = 2·5 × *measured rates.*)

TABLE I.

Velocity constants at different temperatures.

Compound.	Temp.	Concn. of aromatic compd. (g.-mol./l.).	Mean k' (l./g.-mol. sec.).
Benzene	3·1°	0·05	0·86
	40·1	0·05	2·44
Bromobenzene	3·1	0·25	0·97 × 10^{-1}
	40·1	0·25	5·26 × 10^{-1}
m-Dichlorobenzene	1·9	0·50	0·275 × 10^{-2}
	40·1	0·50	2·18 × 10^{-2}
α-Nitronaphthalene	3·3	0·25	1·47 × 10^{-1}
	25·1	0·25	3·25 × 10^{-1}
	40·1	0·25	8·17 × 10^{-1}
p-Nitroanisole	2·0	0·10	2·41 × 10^{-1}
	40·1	0·10	6·29 × 10^{-1}

(b) *Order with respect to aromatic reagent.* With bromobenzene, α-nitronaphthalene, and *p*-nitroanisole, experiments were made at two different concentrations of the aromatic reagent. The reaction being assumed to be of the first order with respect to the aromatic compound, the experimental initial rates found with the more dilute solution were multiplied by the required factor, and the rates thus calculated were included in the plots (cf. Fig. 1). The calculated rates were found to fall well on the lines, confirming the first order which had been anticipated from the results of early work on sulphonations (Martinsen, *Z. physikal. Chem.*, 1908, **62**, 713).

(c) *Activation energies.* From the velocity constants at different temperatures the activation energies were calculated by the Arrhenius equation. Since, in the present work, most reactions were studied at two temperatures only, the corresponding activation energies (see Table II) represent only approximate values.

DISCUSSION.

The second order of the sulphonation reaction with respect to sulphur trioxide is found to be a common feature of the eight reactions so far investigated by this method. If from this result we conclude that two single sulphur trioxide molecules are required for reaction, then the function of the second molecule can no longer be attributed to some physical interaction with the substituent. Such interaction, if of a dipolar nature, might have explained the behaviour of nitro- and halogeno-compounds, but the hypothesis must be discarded in view of the second order found for the sulphonation of unsubstituted benzene. Alternatively, the second trioxide molecule might act as a basic catalyst temporarily accepting a proton, the removal of which facilitates the approach of the attacking trioxide molecule. Although there is no definite evidence against such a mechanism, it now seems equally likely that the dimeric form, S_2O_6, is the active species of sulphur trioxide. If the dimer is supposed to exist in equilibrium, in small amounts, with two monomeric molecules, then the rate of sulphonation would be proportional to the square of the sulphur trioxide concentration. In this connection, it is noteworthy that Michael and Weiner (*J. Amer. Chem. Soc.*, 1936, **58**, 294) have already suggested that S_2O_6 is the active sulphonating agent in the action of sulphur trioxide on the olefins. Although the information at present available is still insufficient to settle conclusively the detailed mechanism of substitution by sulphur trioxide, the scheme

FIG. 2.

Initial rates for α-nitronaphthalene at 40°.

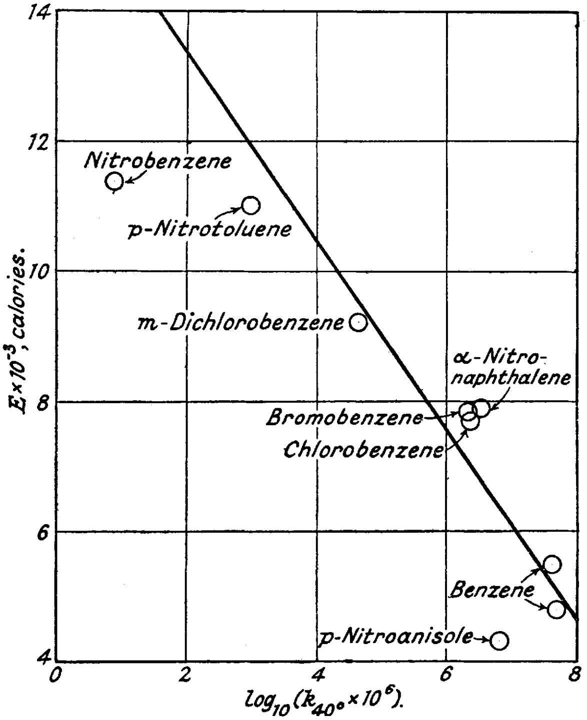
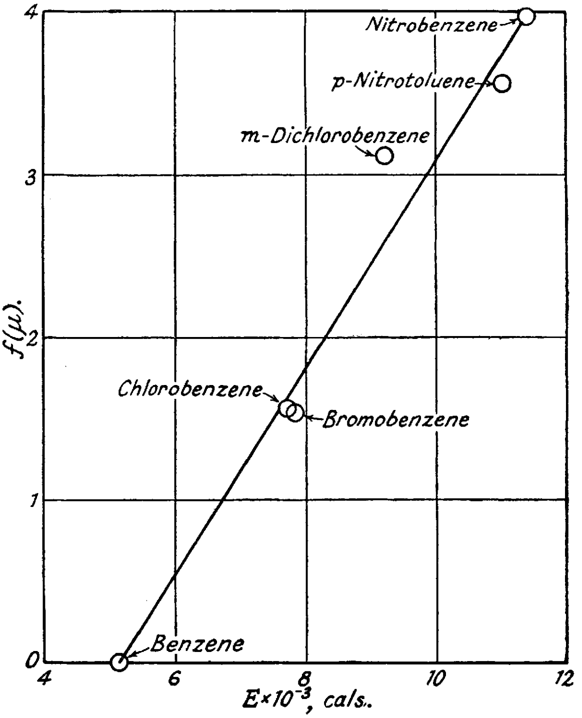


FIG. 3.

Dipole moment functions and activation energies.



$$2SO_3 \rightleftharpoons S_2O_6 ; \; ArH + S_2O_6 \longrightarrow Ar{\cdot}S_2O_6H ; \; Ar{\cdot}S_2O_6H \rightleftharpoons Ar{\cdot}SO_3H + SO_3$$

would explain the second order with respect to SO_3, the first order with respect to ArH, and the retardation by the product.

With regard to the specific influence of substituents on the reactivity of the nucleus, some tentative conclusions may now be drawn. In Fig. 2 the logarithms of the velocity constants, k, at 40°, which were made comparable by dividing the observed constants, k', by the molar concentration of the aromatic reagent, have been plotted against the activation energies. If the effects of substituents on the rate of sulphonation were entirely accounted for by the differences of the activation energies of the substituted compounds from that of benzene, then the points should fall on a straight line, drawn through the value for benzene, with a slope of $- 2{\cdot}303\boldsymbol{R}T$. A line of the theoretical slope has been drawn through the mean of the two values available for benzene, and it is seen that, except for nitrobenzene and *p*-nitroanisole, this relation is roughly obeyed. From this line an average value of 5·24 can be deduced for the $\log_{10} PZ$ factor of the sulphonations.

The fact that nitrobenzene does not fall on the line is not surprising, since the measured velocity constant was divided by the total molar concentration of the medium, but *p*-nitroanisole probably represents a truly anomalous case, though the activation energy for this compound should be confirmed by further measurements. It is, however, of interest to find that the three halogen derivatives conform with the relation between rate and activation energy, and that α-nitronaphthalene behaves as a substituted benzene in this case. The change of activation energy in the series: benzene 5,200 cals., chlorobenzene 7,700 cals., *m*-dichlorobenzene 9,200 cals., is also noteworthy.

TABLE II.

Velocity constants, activation energies, and dipole-moment functions.

Compound.	$k_{40°}$ (l./g.-mol. sec.).	E (cals./g.-mol.).	f(μ).
Benzene	48·8	4,800	0·00
*Benzene (Paneth)	40·8	5,500	0·00
*Chlorobenzene	2·40	7,720	1·56
Bromobenzene	2·10	7,840	1·53
m-Dichlorobenzene	$4·36 \times 10^{-2}$	9,220	3·12
*Nitrobenzene	$7·85 \times 10^{-6}$	11,400	3·97
**p*-Nitrotoluene	$9·53 \times 10^{-4}$	11,025	3·56
p-Nitroanisole	6·29	4,320	5·13
α-Nitronaphthalene	3·27	7,900	—

* Indicates results obtained by previous workers.

In order to correlate further the kinetic and electronic aspects of aromatic substitution, a function of dipole moments of monosubstituted benzenes has been used as a rough measure of changes in the electronic density of the benzene nucleus. This function f(μ) is plotted against the activation energy in Fig. 3, and in spite of the difficulty of the experimental measurements a definite connection between f(μ) and changes in E appears. *p*-Nitroanisole, which again represents the only exception to the general relation, is not included in the plot in view of the known peculiar effect of methoxyl groups on the dipole moments of benzene derivatives. For the monosubstituted compounds f(μ) is simply the dipole moment, but for the disubstituted compounds it is the algebraic sum of the two group moments. Moments are given positive signs for electronic displacements in the direction away from the nucleus. It thus appears that in general for this series of compounds, the effect of substituents on the activation energy is correlated with changes of electron density at the point of attack of the reagent, and that these changes are of a permanent nature, as is evident from the corresponding changes in dipole moments. With certain substituent groups, perhaps for instance with $\cdot OCH_3$, the time-variable effects may well come into operation on the approach of the reagent, and this would probably give an abnormal value for P. Although it is too early to generalise about the effects of substituents, we may conclude from the present results that halogen does not fall into the class which brings about changes in the probability factor.

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