126. *The Kinetics of Aromatic Sulphonation Reactions: The Sulphonation of* p-*Nitrotoluene and of Chlorobenzene by Sulphur Trioxide*

By K. D. WADSWORTH and C. N. HINSHELWOOD.

In continuation of a kinetic investigation of certain aromatic substitution reactions (see J., 1939, 1372), the sulphonations of *p*-nitrotoluene and of chlorobenzene by sulphur trioxide have been examined. Both reactions show characteristics similar to those found in the sulphonation of nitrobenzene, being of the second order with respect to sulphur trioxide and exhibiting a strong retardation due to the formation of a complex between sulphur trioxide and the sulphonic acid produced. The activation energies and log *PZ* factors found were for *p*-nitrotoluene 11,025 cals. and 4·78 respectively, and for chlorobenzene 7720 cals. and 5·14, compared with 11,400 cals. and 3·91 for nitrobenzene.

FOR many organic reactions there is a direct correlation between the effect of substituents and the activation energies of a series of reactions in which the substituent groups are varied (cf. Hinshelwood, Laidler, and Timm, J., 1938, 848). Little quantitative kinetic information is, however, available to test these correlations when applied to some of the most interesting examples of organic reactions, namely, the aromatic substitution reactions. Little kinetic investigation of the reactions has been carried out, mainly on account of the complexity of the processes involved (cf., *inter alia*, Ingold *et al.*, J., 1927, 2918; 1931, 1959,; 1938, 905, 918, 929).

Vicary and Hinshelwood (J., 1939, 1372), however, found that the sulphonation of nitrobenzene by sulphur trioxide was reasonably amenable to kinetic study. Nitrobenzene was both reactant and solvent, the reaction being followed at several temperatures in the range 25—100° by the change in acidity as dibasic sulphur trioxide is converted into monobasic sulphonic acid: $C_6H_5{\cdot}NO_2 + SO_3 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}SO_3H$.

The reaction: (1) was of second order with respect to sulphur trioxide, (2) exhibited a marked retardation ascribable to the formation of a 1 : 1 complex between the product and sulphur trioxide, and (3) was little influenced by sulphuric acid at higher temperatures, though retarded by it at lower temperatures.

The second order of the reaction with respect to sulphur trioxide shows that it must proceed by a mechanism involving either (*a*) S_2O_6 molecules in equilibrium in small amount with SO_3 molecules, or (*b*) two SO_3 molecules. It is not known whether the dimer is in fact present to any appreciable extent in dilute solutions in nitrobenzene, though Michael and Weiner (*J. Amer. Chem. Soc.*, 1936, **58**, 294) present evidence of certain preparative reactions, indicating that S_2O_6 is the active agent in sulphonations. If the mechanism involved two trioxide molecules, the second molecule might (i) enter into some relation with the nitro-group which enhances the activity of the benzene nucleus, or (ii) act, in a manner analogous to a basic catalyst, by providing a temporary home for proton replaced from the C–H bond by the first sulphur trioxide molecule.

The various possibilities can only be resolved by the study of further aromatic compounds, with and without substituent nitro-groups. In the present work we have examined the sulphonation by sulphur trioxide of *p*-nitrotoluene and of chlorobenzene. Since both the compounds studied are sulphonated more rapidly than nitrobenzene, this was used as solvent, in order to ensure that the medium conditions were as near as possible to those of the nitrobenzene–sulphur trioxide reaction. In the latter the aromatic reactant was present in large excess and this condition is now only approximately fulfilled.

The reactions were started by mixing measured volumes of the aromatic reactant solution and a freshly prepared sulphur trioxide solution, both preheated to the requisite temperature. After the desired time interval, the reaction was stopped by pouring the reaction mixture into water and shaking vigorously. The extent of the change was determined by titration with alkali.

The error introduced by reaction between nitrobenzene and sulphur trioxide during the preheating was small at the lower temperatures but was appreciable at 60° and a correction was applied. The initial rates measured from the " percentage change "–time curves were also corrected for the simultaneous nitrobenzene–sulphur trioxide reaction.

Sulphone formation, which would also lead to a 50% titre drop, $2C_6H_6 + 2SO_3 \longrightarrow (C_6H_5)_2SO_2 + H_2SO_4$, gives sulphuric acid, which was determined gravimetrically in the end-products.

The reactions consistently show retardation by their products, which can be explained by the removal of sulphur trioxide in the formation of a 1 : 1 complex with the sulphonic acid.

EXPERIMENTAL.

Nitrobenzene was dried over calcium chloride for several weeks and then distilled. The middle fraction was redistilled at 207—209°.

p-Nitrotoluene was recrystallised from light petroleum until a product melting sharply at 54° was obtained. This was dissolved in nitrobenzene in proportions necessary for a 3M-solution.

Chlorobenzene was dried over calcium chloride and distilled several times. It was then mixed with nitrobenzene to give a 0·5M-solution. (The rate of sulphonation is considerably greater than that of *p*-nitrotoluene, and for a measurable rate it is necessary to use a less concentrated solution.)

Sulphur trioxide in nitrobenzene was freshly prepared for each experiment, from 65% fuming sulphuric acid. This was usually done by heating the oleum to 60—70° and passing a stream of dry air over the surface. The sulphur trioxide carried over was collected in nitrobenzene, an all-glass apparatus being used. This method gave solutions containing less sulphuric acid than those obtained by the method of Vicary and Hinshelwood.

For 15°, 25°, 40°, and 60°, electrically heated water- or oil-baths were used. The measurements at 0° were carried out in a Dewar vessel filled with melting ice. The end-point measurements were made at 120° in an oil-bath heated by boiling perchloroethylene (b. p. 121·2°). Thermometers were calibrated against N.P.L. standards.

Three different arrangements for preheating and mixing the reactants and for stopping the reaction were used according to the rate to be measured. They were :

1. 2-C.c. portions of the aromatic reactant were pipetted into tubes of about 5—10 c.c. capacity. These were then placed in the thermostat together with the bottle containing freshly-prepared sulphur trioxide solution. After time had been allowed for thermal equilibrium to be established, 2-c.c. portions of the sulphur trioxide solution were pipetted into the reaction tubes, which were closed with rubber caps, and a further 2-c.c. portion was run into water in order to determine the initial titre. The reaction was stopped by rapidly pouring the contents of the tube into water, shaking vigorously, and washing out the reaction tube. This method was used for all reaction times greater than about 2½ minutes.

2. 2-C.c. portions of the reactant solutions were pipetted into the separate limbs of an inverted Y-tube placed in he thermostat. After a suitable interval, the reactant solutions were mixed by tipping the tube, so that the solutions ran from limb to limb. The reaction was stopped as in (1) above. . The initial titre in these runs was found by placing a tube containing 2 c.c. of sulphur trioxide solution in the thermostat for the same length of time as was required for preheating. This method was used for reaction times between ½ and 2½ minutes.

3. A pair of tubes, the ends of which were blown into bulbs, and which fitted one inside the other, was used. These tubes were carried in a cork fitting tightly into a boiling-tube which contained water. The chlorobenzene solution was pipetted into the outer tube and the sulphur trioxide solution into the inner tube, which was closed by a rubber cap. The reactants could be mixed by breaking the bulb of the inner tube with a glass rod. The reaction could be stopped by breaking the second bulb in a similar manner and shaking the reaction mixture vigorously with the water. The initial titre was determined in the same way as in (2) above. This method was used for all reaction times less than ½ minute.

Titrations were made with N/20-alkali and methyl-red, the end-point being determined by adding excess alkali, shaking vigorously, back-titrating with N/20-hydrochloric acid, and repeating until successive additions of acid and alkali were equivalent.

For reaction end-points, 2 c.c. were heated at 120° for 24 hours. The dark colour made it impossible to use methyl-red, but bromothymol-blue proved satisfactory.

Investigation of Sulphone Formation.—Formation of sulphone is accompanied by the production of an equivalent amount of sulphuric acid. Initially the solutions contain sulphuric acid in an amount which is given by (Initial Titre − 2 × Titre Drop), and when gravimetric analysis of the end-point products reveals sulphuric acid appreciably in excess of this, the discrepancy is due to sulphone formation. 5-C.c. portions of each reactant solution were sealed off and heated at 120° for two days. The product was extracted with water and with benzene, the nitrobenzene dissolving in the benzene and the sulphuric and sulphonic acids in the water. The benzene layer was washed several times with water and with alkali. The combined aqueous layer was concentrated to about 100 ml., and the sulphuric acid determined by precipitation as barium sulphate.

Correction to the Initial Sulphur Trioxide Concentrations in Runs at 60°.—Suppose the initial titre before preheating is *a* ml., and that after preheating is *b* ml. Now :

$$\mathrm{Ar{\cdot}H} + \mathrm{SO_3} \longrightarrow \mathrm{Ar{\cdot}SO_3H} \text{ and } \mathrm{Ar{\cdot}SO_3H} + \mathrm{SO_3} \rightleftharpoons [\mathrm{Ar{\cdot}SO_3H,SO_3}] \xrightarrow{\text{water}} \mathrm{Ar{\cdot}SO_3H} + \mathrm{H_2SO_4}$$

Hence the amount of sulphur trioxide used up by reaction with nitrobenzene during preheating is equivalent to $2(a - b)$ ml. titre. Since we may assume that complex formation is complete at the large initial sulphur trioxide concentrations, the amount of trioxide used in complex formation is equivalent to $2(a - b)$ ml. titre also. Hence the " effective " initial titre is $\{a - 4(a - b)\}$ ml. As the complex breaks up in water, its formation will not affect titres during the course of the runs and the titre fall is given by $\{a - (a - b)\} - x$, *i.e.*, $(b - x)$ ml., where x is the particular titre concerned.

Results.—(a) *The order of the reaction, the velocity constants, and the activation energy.* The extent of reaction was expressed in terms of percentage change, and plotted against time. Initial rates were determined from the reaction curves, by drawing the tangent at the origin, and were corrected where necessary for the simultaneous nitrobenzene reaction.

The values of the initial rates found with *p*-nitrotoluene at 25° and with chlorobenzene at 15° are shown in Table I.

TABLE I.

Initial Rates and Sulphur Trioxide Concentrations.

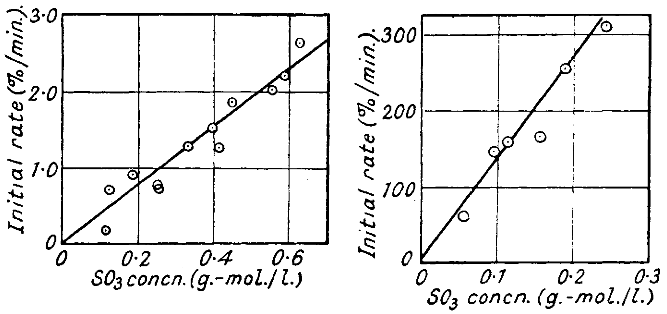
p-*Nitrotoluene at* 24·91°.

SO_3 concn., g.-mol./l.	Initial rate (%/m.).	Nitrobenzene initial rate (%/m.).	Corrected initial rate (%/m.).	SO_3 concn., g.-mol./l.	Initial rate (%/m.).	Nitrobenzene initial rate (%/m.).	Corrected initial rate (%/m.).
0·394	1·620	0·078	1·542	0·446	1·940	0·088	1·852
0·187	0·945	0·035	0·910	0·125	0·737	0·025	0·712
0·251	0·815	0·049	0·766	0·254	0·780	0·050	0·730
0·551	2·150	0·109	2·041	0·585	2·340	0·116	2·224
0·332	1·360	0·066	1·294	0·112	0·202	0·022	0·180
0·412	1·350	0·082	1·268	0·622	2·770	0·123	2·647

Chlorobenzene at 14·91°.

SO_3 concn., g.-mol./l.	0·096	0·156	0·189	0·114	0·056	0·241
Initial rate (%/m.)	148·0	166·4	256·0	160·4	62·5	310·4

FIG. 1.



A. p-*Nitrotoluene at* 25°. B. *Chlorobenzene at* 15°

Plots of the initial rates (in %/min.) against the sulphur trioxide concentration (see Figs. 1, A and B) give fair straight lines passing through the origin, thus demonstrating the second-order nature of the reaction with respect to sulphur trioxide. From the slopes of such lines we obtain the reaction velocity constants given in Table II.

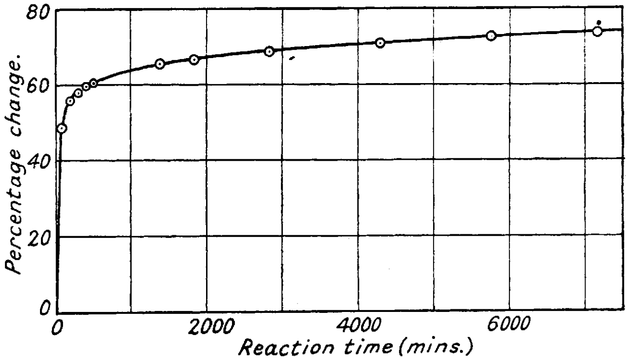
TABLE II.

Reaction Velocity Constants at Different Temperatures.

p-*Nitrotoluene.*		*Chlorobenzene.*	
Temp.	Mean $k \times 10^5$ (l./g.-mol. sec.).	Temp.	Mean k (l./g.-mol. sec.).
0·0°	9·2	0·0°	0·102
14·9	31·8	14·9	0·216
24·9	62·3	24·9	0·369
39·9	143	39·9	0·600
60·0	354		

FIG. 2.

p-*Nitrotoluene at* 40°. $SO_3 = 0·351$ M.



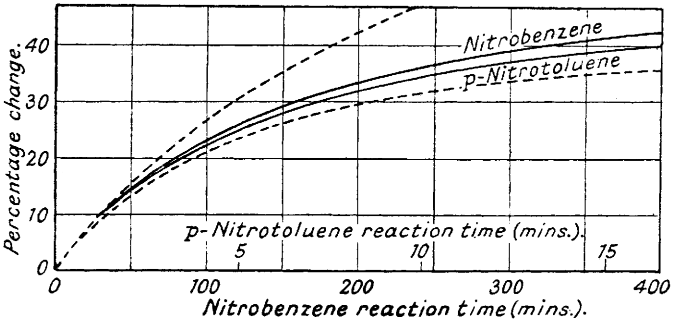
By application of the Arrhenius equation, the following values of the activation energies and non-exponential factors were calculated :

	p-Nitrotoluene.	Chlorobenzene.	Nitrobenzene (Vicary and Hinshelwood).
E (cals.)	11,025	7720	11,400
$\log_{10} PZ$	4·79	5·14	3·91

(b) *The retardation of the reaction.* The reaction curves in Fig. 2 show that the reaction rate falls off as the reaction proceeds. Thus in the *p*-nitrotoluene reaction, only a little more than 50% reaction has occurred after 3 days and in the fourth day the reaction proceeded only another 4% towards completion. Vicary and Hinshelwood found the same characteristic in the nitrobenzene sulphonation and showed that it was explainable by the formation of a 1 : 1 complex between the sulphonic acid and sulphur trioxide. In the later stages, the reaction will be controlled by the concentration of trioxide in equilibrium with the complex. From the rates of the reaction at different stages, Vicary and Hinshelwood determined the ratios " Free SO_3/Total SO_3 " throughout the reaction and so were able to calculate velocity constants from the later course as well as from the initial rates of the reaction.

With *p*-nitrotoluene, the complex appears to be formed somewhat more completely than with nitrobenzene, as is shown by Fig. 3, in which a nitrobenzene and a *p*-nitrotoluene run at 40° have been compared on an adjusted time scale.

FIG. 3.



Broken curves :—upper 0%, *lower* 100% *of* 1 : 1*-complex formation.*

(c) *Sulphone formation.* Table III gives some typical results of the gravimetric analyses for sulphuric acid. In the *p*-nitrotoluene reaction, these determinations were made on end-point products at 120°, and it is seen that sulphone formation is unimportant.

With chlorobenzene, however, it seemed that appreciable sulphone formation took place at temperatures considerably lower than 120°, and therefore analyses were made on end-point products at 15°, 25°, and 40°. In general, the proportion of sulphone formed tended to fall off as the temperature of reaction increased, but the results were irregular and very possibly vitiated by some uncontrollable hydrolysis of the sulphonic acid in the analysis.

TABLE III.

Sulphone Formation : Results of Gravimetric Analyses. (*All data are in terms of ml. of* N/20.)

			p-*Nitrotoluene.*				
Initial titre	79·5	81·0	26·5	51·8	22·0	124·2	100·5
Initial titre −2 × titre drop	14·5	9·6	6·6	11·2	4·1	14·7	12·3
Equiv. of $BaSO_4$ found	13·8	9·3	7·5	11·1	5·9	10·0	10·2
			Chlorobenzene.				
			At 15°.				
Initial titre	30·6	19·0	28·1	33·8	22·2	12·2	41·6
Initial titre −2 × titre drop	2·5	3·6	3·2	3·5	3·9	3·2	3·1
Equiv. of $BaSO_4$ found	7·0	5·1	8·7	7·9	5·5	4·4	5·3
			At 25°.				
Initial titre	24·1	36·5	20·9	37·0	11·9		
Initial titre −2 × titre drop	2·9	4·1	3·7	4·8	5·1		
Equiv. of $BaSO_4$ found	9·1	7·3	4·4	11·2	3·7		
			At 40°.				
Initial titre	11·3	23·1	22·4	38·3	18·3	39·5	
Initial titre −2 × titre drop	5·5	4·3	4·3	5·6	5·1	5·0	
Equiv. of $BaSO_4$ found	3·1	5·5	5·0	11·5	4·3	4·5	

DISCUSSION.

Since the sulphonation of chlorobenzene, like that of the nitro-compounds, depends on the second power of the sulphur trioxide concentration, it follows that the second-order reaction does not arise from a specific property of the nitro-group. It might, however, depend upon a property of all strongly polar substituent groups. If the bimolecularity were connected with some interaction, possibly of a dipolar nature, between sulphur trioxide and the substituent group, then the chlorine atom might behave similarly to the nitro-group. The problem of the detailed mechanism must, therefore, remain unsolved until data for benzene or derivatives containing no strongly polar substituent groups have been obtained.

Apart from possible doubts about the inherent unlikelihood, under the conditions prevailing, of S_2O_6 as the active species, the scheme $2SO_3 \rightleftharpoons S_2O_6$; $ArH + S_2O_6 \longrightarrow Ar{\cdot}S_2O_6H$; $Ar{\cdot}S_2O_6H \rightleftharpoons Ar{\cdot}SO_3H + SO_3$ is attractive, since it would explain both the second order with respect to SO_3 and also the retardation of the reaction as it proceeds.

Turning to the kinetic and electronic aspects, it appears that the values calculated for the probability factor, *P*, do not differ very greatly for the three reactions. The value of the collision frequency, *Z*, required for these calculations, was estimated on the assumption that whenever two sulphur trioxide molecules meet there will be a molecule of the aromatic reactant suitably disposed for reaction. This assumption is probably quite justified for the nitrobenzene and the *p*-nitrotoluene reaction, where there are respectively a large excess and a moderate excess of aromatic reactant, but it is not strictly true under the conditions used for chlorobenzene. This will make the estimate of Z for the latter somewhat too large and hence the value of P rather too small. The values of P, and of E, are :

	E, cals.	P.
Nitrobenzene	11,400	$1{\cdot}9 \times 10^{-7}$
p-Nitrotoluene	11,025	$1{\cdot}65 \times 10^{-6}$
Chlorobenzene	7,720	$3{\cdot}2 \times 10^{-6}$

It appears then that the conditions under which the molecules react in the three reactions are not very different.

The very much greater rate of the chlorobenzene sulphonation is clearly associated with a considerably smaller activation energy rather than with an increased reaction probability. With *p*-nitrotoluene, which contains an activating and a deactivating group, it appears that it is the latter which determines the reactivity, since the activation energy is little different from that for nitrobenzene.

Oxford University.

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