211. *The Kinetics of Aromatic Sulphonation Reactions. Sulphonation by Sulphuric Acid in Nitrobenzene Solution.*

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The sulphonation by sulphuric acid of nitrobenzene itself and of various aromatic compounds in nitrobenzene solution has been studied at a series of temperatures.

The following equation is derived empirically for the rate of reaction :

$$\text{Rate} = \frac{k_1[\text{Ar}][\text{A}]}{(x + x_0)^{1/3}} - \frac{k_2 x[\text{A}]}{1 + \beta x}$$

where [A] = concentration of sulphuric acid, [Ar] = concentration of aromatic compound, x = water formed in the reaction, and k_1, k_2, x_0, and β are constants.

This equation is given a tentative explanation in terms of a mechanism in which $SO_2 \cdot OH^+$ is the sulphonating agent, and the reverse reaction of hydrolysis is brought about by $Ph \cdot NO_2 \cdot H^+$.

The relation between activation energy, E, and log k_1 is of the form to be expected if the changes in rate from compound to compound are determined almost entirely by changes in E. The halogen compounds (which are of interest in connexion with their anomalous behaviour in orientation) constitute no exception in this respect.

The connexion between changes in E and the dipole moments of the substituent groups is considered. Here again the halogen compounds fall into line with the rest.

There is a rough functional relation between log k_1 and log (k_1/k_2).

Previous communications from this laboratory have described experiments on the sulphonation of aromatic compounds by sulphur trioxide in nitrobenzene solution (Vicary and Hinshelwood, *J.*, 1939, 1372; Wadsworth and Hinshelwood, *J.*, 1944, 469; Dresel and Hinshelwood, *ibid.*, p. 649). The present work extends the study to sulphonation by sulphuric acid in the same medium.

The chief experimental difficulty lies in the fact that the rate of sulphonation slows down very markedly as water is formed in the reaction which, therefore, can be followed conveniently only in its initial stages. To do this by the obvious method of titration with alkali is inaccurate since there are, in the circumstances, only small changes in a large acid titre. The difficulty was overcome as follows. 100% Sulphuric acid is completely miscible with nitrobenzene, but the addition of a few per cent. of water causes turbidity. If the phase relations of the ternary system nitrobenzene–water–sulphuric acid have been established, then, for any given

Ph·NO$_2$: H$_2$SO$_4$ ratio, the amount of water at the turbidity point is known. If a mixture of nitrobenzene and 100% sulphuric acid is titrated with another mixture containing nitrobenzene and, say, 95% sulphuric acid, a definite titre of the latter will bring the system to the turbidity point. If now the mixture of nitrobenzene and 100% sulphuric acid is allowed to react for some time so that a small quantity of water is formed, and if the final mixture is titrated again with the 95% acid, the titre will be less than before, and from the change the amount of water present before titration can be calculated. By suitable choice of the concentration of acid in the titrating solution, the titre can be magnified to any required degree so that we have available a micro-method for the direct estimation of the water formed.

The method has proved very satisfactory provided that suitable calibrations are made, separate ones being naturally required for each concentration of each aromatic compound employed.

In the first experiments nitrobenzene itself was both solvent and reactant. Its rate of sulphonation is so much slower than that of many other aromatic compounds that it can be used as a solvent for them in other experiments. If necessary, a small correction for the sulphonation of the solvent can be applied, but it is usually negligible.

The rate of sulphonation is dependent upon the precise water content of the sulphuric acid, and this has to be controlled very carefully. The method of thermal analysis proved extremely convenient for this purpose.

The rate of reaction proves to be proportional to the total sulphuric acid concentration, [A], and the concentration of the aromatic compound [Ar]. Thus the *initial* rate of reaction, in the absence of added water, is given by k[Ar][A]. Over the range studied [Ar] and [A] scarcely change during the sulphonation. Nevertheless, the rate, and therefore k, drops very steeply as reaction proceeds. An example is shown in Figs. 3 and 4. The drop is due to two separate causes. On the one hand, the rate of the forward reaction itself falls as water is formed, and, on the other hand, a back reaction soon sets in. The two effects were disentangled by making measurements on the initial rate of reaction with varying quantities of added water, and comparing their effect with that of corresponding amounts of water formed by reaction. Figs. 5 and 6 show examples of the comparison. The upper curves give the effect of added water, the lower that of water formed in the sulphonation. The difference provides a measure of the reverse reaction, the existence of which was also proved by direct experiment. Every compound examined gave results of the general form shown in Figs. 5, 6, and 8.

These results can be expressed in the following way :

$$\text{Rate of sulphonation} = k[\text{Ar}][\text{A}] = \frac{k_1[\text{Ar}][\text{A}]}{\{x + (k_1/k_0)^3\}^{1/3}} - \frac{k_2x[\text{A}]}{(1 + \beta x)}$$
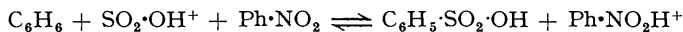
or so long as [Ar] and [A] remain constant

$$k = \frac{k_1}{\{x + (k_1/k_0)^3\}^{1/3}} - \frac{k_2'x}{(1 + \beta x)}$$

where x is the amount of water formed in the reaction; k_1/k_0 is the same for all the compounds.

These expressions represent the rates empirically, so that the ratio of k_1/k_2 will be proportional to, though not equal to, the equilibrium constant.

With certain approximations about the equilibria prevailing in the nitrobenzene solutions, these equations may be given a tentative theoretical interpretation. They appear in fact to be consistent with the hypothesis that the sulphonating agent is the ion SO$_2$·OH$^+$, that this expels a proton from the aromatic compound, the proton being taken up by the nitrobenzene to form Ph·NO$_2$·H$^+$, and that, in accordance with the principle of detailed balancing, the reverse reaction is caused by the attack on the sulphonic acid, not of the ion H$_3$O$^+$ but of Ph·NO$_2$H$^+$; *e.g.*,

$$\text{C}_6\text{H}_6 + \text{SO}_2\text{·OH}^+ + \text{Ph·NO}_2 \rightleftharpoons \text{C}_6\text{H}_5\text{·SO}_2\text{·OH} + \text{Ph·NO}_2\text{H}^+$$

This view is consistent with the preparative experience that increasing water content hinders both sulphonation *and* hydrolysis of the sulphonic acid. The principal object of the experiments was to obtain information about the influence of substituents on the activation energy so that this incidental conclusion is given with due reserve, since other mechanisms might conceivably be made also to fit.

<div align="center">EXPERIMENTAL.</div>

Materials.—Nitrobenzene was purified by distillation and then by four successive recrystallisations in which it was frozen and re-melted with rejection of the first portions of the melt. The other aromatic compounds were distilled and crystallised to constant b. p. or m. p. " Pure " sulphuric acid and oleum

were used in the preparation of the acids, which were standardised as described below. Precautions were taken at all stages to minimise the exposure of materials to moist air.

Standardisation of Sulphuric Acid.—The method was based upon that of Somiya (*Proc. Imp. Acad. Japan*, 1927, **3**, 76). A known quantity of the acid to be tested was run into a standard excess of approximately 10% oleum in a small, covered Dewar vessel provided with a stirrer, and the rise in temperature determined by a thermometer graduated in $\frac{1}{25}$ths. The apparatus was calibrated as follows. From " pure " sulphuric acid, containing a small unknown percentage of water, x, a series of acids were prepared (by weighing) which contained $(x + y)\%$ of water, y being the percentage of added water. The rise in temperature, $\Delta\theta$, caused in the standard test by each of these was measured. $\Delta\theta$ plotted against the known values of y gave an accurately linear relation, and by extrapolation to $\Delta\theta = 0$, x could be found. $\Delta\theta$ was independent of the strength of the oleum used in the test and no temperature change occurred when two samples of oleum of different strengths were mixed. The knowledge of x for the " pure " sulphuric acid allowed the preparation from it of any required acid, the final strength always being tested by the direct thermometric method.

Phase Relations of the Reactants.—The ternary system nitrobenzene–sulphuric acid–water was studied by Bailey and Hilton (*J.*, 1936, 1571), but for our present purpose more detailed investigation over special ranges was needed. Curves of the type shown in Fig. 1 were plotted for each set of conditions

FIG. 1.

Ternary system : $C_6H_5 \cdot NO_2$–H_2SO_4–H_2O *with small additions of* C_6H_6.
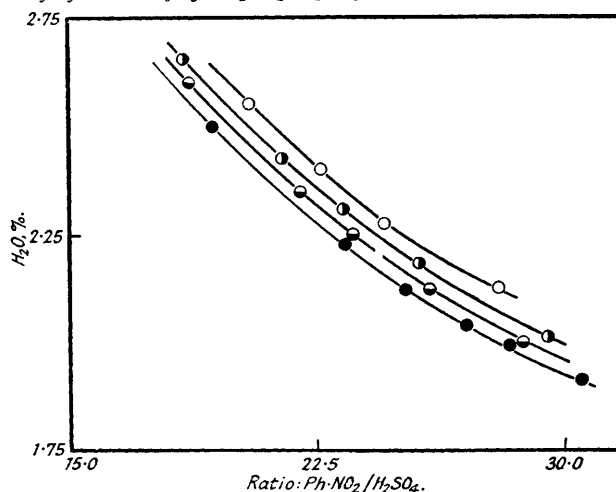
Successive curves correspond to $[C_6H_6] = 0 \cdot 1404, 0 \cdot 273, 0 \cdot 411$ *and* $0 \cdot 542$ *molar, respectively.*

to be employed. A volume of nitrobenzene (32·0 c.c.) was placed in a stoppered tube, a certain quantity of the aromatic compound under investigation added if necessary, and the appropriate quantity of approximately 100% sulphuric acid added (exact water content known). The mixture was titrated with 96% sulphuric acid (also in nitrobenzene but in a different proportion) until it was just turbid. From the weights and compositions of the solutions the total water content at this point could be calculated, and expressed as a percentage of the total acid. The addition of the small amounts of benzene and other reactants in fact made relatively little difference to the results though they were always allowed for.

To obviate any error that may have been due to an initial rapid reaction between sulphuric acid and the aromatic compound before titration, the system was sometimes titrated half way to turbidity before the addition of the 100% acid. At this stage there was enough water present to make reaction quite negligibly slow. It was found, however, that this procedure gave the same titre as when the acid was added before any partial titration. Thus the usual method was to add the aromatic reagent, then the acid, and to titrate immediately.

In connexion with the choice of the titrating solution there arises a point which is explained by Fig. 2; a, b, and c are the compositions of the initial mixture, T that of the titrating acid. End-points are reached at a', b', and c', but with an acid T' no end-point would be reached with c. Hence T must be chosen so as to lie close to the equilibrium line. In other words, the titrating solution must be only just clear. Compositions much to the left of c cannot be employed. This restricts somewhat the range over which the initial acid concentration can be varied in the reaction velocity experiments.

The form of the ternary diagrams obtained with any given specimen of nitrobenzene provides a criterion of its quality. If the solvent contains water the curve becomes steeper. Measurements made with nitrobenzene after successive crystallisations showed that there was no appreciable change in the slope after the fourth, and for this reason all samples were recrystallised four times before use. A separate ternary diagram was determined for each sample of solvent and for each concentration of each aromatic compound, whenever possible on the same day as the reaction measurements.

Reaction Velocity Measurements.—Measurements were made in stoppered tubes in thermostats

($\pm 0.02°$). Typical quantities employed were : nitrobenzene 32·0 c.c.; sulphuric acid 0·2268M; aromatic compound 0·08—1·0M. The composition in respect of all components except reaction products could be taken as nearly constant during the reaction. The samples were titrated from a micro-burette

FIG. 2.
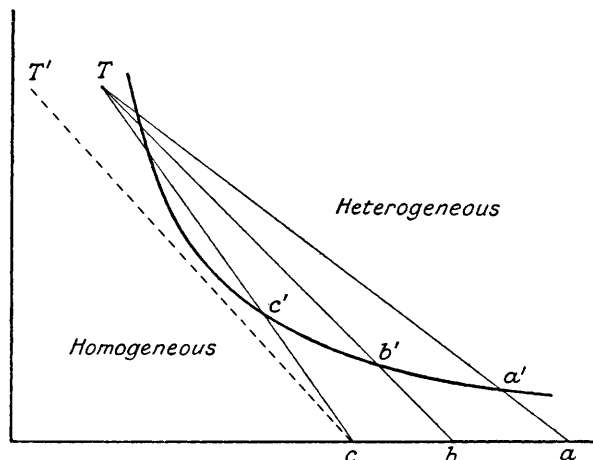
at suitable intervals of time, and the amount of water formed was calculated. The calculation is carried out as follows :

	Ph·NO$_2$.	H$_2$SO$_4$.	H$_2$O.
From reaction mixture	ϕ_1	S_1	w_1
From titration	$\phi_2 = aT$	$S_2 = \beta T$	$w_2 = \gamma T$

where T = titre in g. and $a + \beta + \gamma = 1$, and are known.

$$\text{Ratio at end point} = \frac{\phi_1 + \phi_2}{S_1 + S_2} = R$$

A curve of R against P is available where P = % of water in the acid. P is read off.

Now

$$P = 100 \left[\frac{(w_1 + \gamma T)}{(S_1 + \beta T) + (w_1 + \gamma T)} \right]$$

whence w_1 is known. A typical set of observations is recorded in Table I.

TABLE I.

Example of determination of points on a reaction–time curve.

Titrating solution : Nitrobenzene = 141·277 g. Strength of acid = 96·30%. Sulphuric acid = 19·496 g. Density of solution = 1·258. $a = 0·8788$; $\beta = 0·1167$; $\gamma = 0·0045$.

m-Xylene, 15° : [*m*-Xylene] = 0·099M = 0·40 c.c. [Acid] = 0·2268M = 0·40 c.c. Ph·NO$_2$ = 32·0 c.c.

| Time, hrs.	Titre, c.c.	Nitrobenzene, ($\phi_1 + aT$) g.	Sulphuric acid, ($S_1 + \beta T$) g.	Ratio R $= \dfrac{\phi_1 + aT}{S_1 + \beta T}$.	P%, from ternary diagram.	Water formed (g. $\times 10^4$) per reaction tube.
0	6·46	45·69	1·6802	27·20	2·145	0·0
½	6·27	45·43	1·6525	27·52	2·132	6·1
1	5·86	45·03	1·5923	28·28	2·103	11·1
3	5·44	44·57	1·5308	29·12	2·076	20·5
5	4·88	43·95	1·4486	30·34	2·042	26·8
8	4·44	43·46	1·3841	31·40	2·018	33·3
10	4·12	43·11	1·3371	32·24	2·000	39·0

The calculation of velocity constants was carried out by drawing tangents to reaction–time curves, such as those shown in Fig. 3. The rate was first expressed in the form : g. of water formed per hour.

But rate = kc_1c_2, where c_1 and c_2 are the (practically steady) concentrations of acid and aromatic compound respectively, and from this relation k was expressed in g.-mol./l.-sec. units.

Influence of Concentration of Acid and of Aromatic Compound.—The influence of the concentration of the sulphuric acid is shown in Table II(a). The reaction is of the fir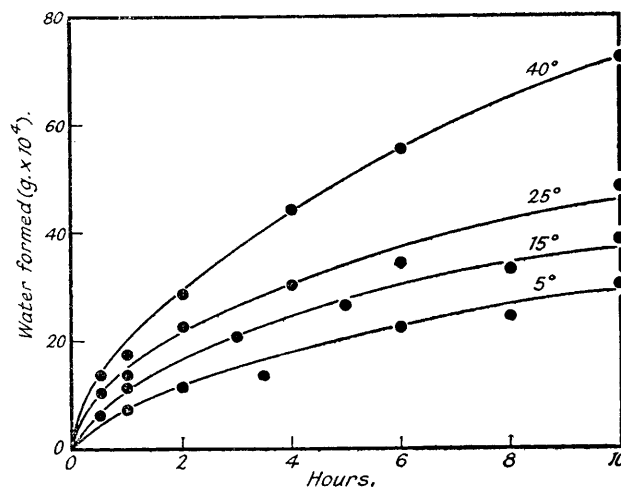st order with respect to [H$_2$SO$_4$]. The influence of the concentration of aromatic compound is shown in Table II(b). The reaction is of the first order with respect to the aromatic compound.

FIG. 3a.
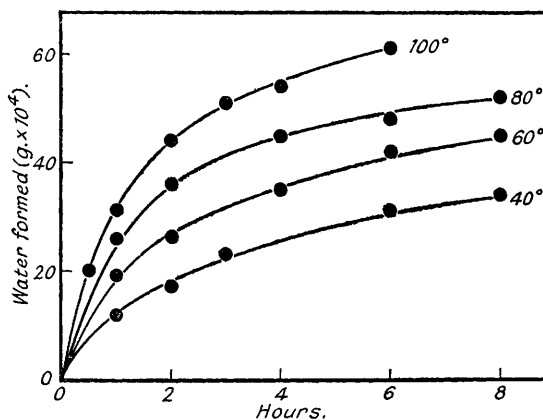
Sulphonation of nitrobenzene at various temperatures.

FIG. 3b.

Sulphonation of m-xylene at various temperatures.

TABLE II.

(a) *Order of reaction with respect to the sulphuric acid concentration.*

Compound.	Sulphuric acid concn., g.-mols. per l.	Initial reaction rate × 10⁷, g.-mols./l./sec.	Ratio.	Compound.	Sulphuric acid concn., g.-mols. per l.	Initial reaction rate × 10⁷, g.-mols./l./sec.	Ratio.
Benzene	0·170	7·00	41·1	Chlorobenzene	0·168	1·83	10·9
	0·227	9·31	41·0		0·258	2·76	10·7
	0·281	12·00	42·6		0·336	3·88	11·5

(b) *Order of reaction with respect to the aromatic reagent concentration.*

Compound.	Concn., g.-mols. per l.	Initial reaction rate × 10⁷, g.-mols./l./sec.	Ratio.	Compound.	Concn., g.-mols. per l.	Initial reaction rate × 10⁷, g.-mols./l./sec.	Ratio.
Benzene	0·140	4·70	33·6	Chlorobenzene	0·120	1·47	(12·3)
	0·273	9·75	35·7		0·236	2·22	9·4
	0·411	12·00	29·2		0·350	3·17	9·1
	0·542	15·90	29·4		0·462	4·00	8·7

Variation of k *during the Course of the Reaction.*—The rate is given by $k[Ar][A]$ and drops rapidly as the reaction proceeds. The corresponding drop in $[Ar][A]$ is negligible, so that k itself must change. Typical results are given in Table III and in Fig. 4.

TABLE III.

Variation of k *with progress of reaction.*

(k is measured in g.-mol./l. sec.)

Chlorobenzene.

Water concn. × 10⁴ (g.-mol./l.).	$k \times 10^6$.				Water concn. × 10⁴ (g.-mol./l.).	$k \times 10^6$.			
	15·0°.	25·0°.	40·0°.	60·0°.		15·0°.	25·0°.	40·0°.	60·0°.
0	2·65	4·88	10·62	22·96	70	—	—	2·83	5·96
10	2·11	4·07	8·49	18·91	80	—	—	2·33	5·30
20	1·69	3·42	6·39	15·10	90	—	—	2·04	4·87
30	1·34	2·75	4·93	12·30	100	—	—	—	4·45
40	0·98	2·19	4·08	10·07	110	—	—	—	3·76
50	—	1·65	3·82	8·52	120	—	—	—	3·33
60	—	1·19	3·25	7·24					

m-Xylene.

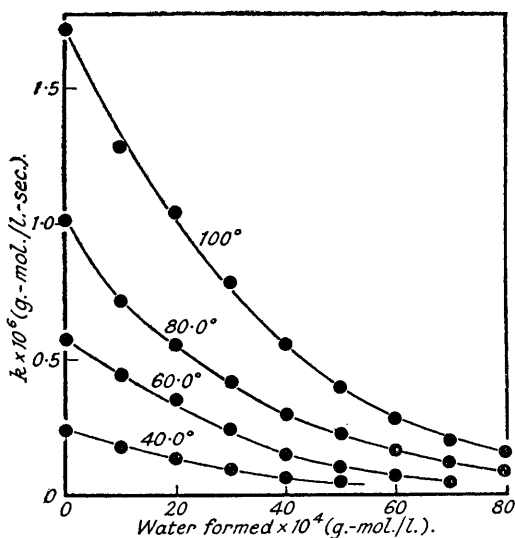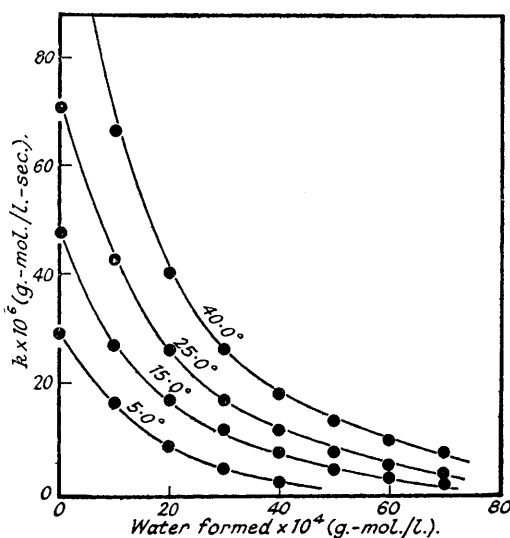| Water concn. × 10⁴ (g.-mol./l.).	$k \times 10^6$.				Water concn. × 10⁴ (g.-mol./l.).	$k \times 10^6$.			
	5·0°.	15·0°.	25·0°.	40·0°.		5·0°.	15·0°.	25·0°.	40·0°.
0	29·18	47·95	70·9	116·8	40	2·08	7·51	11·47	18·35
10	16·68	27·10	42·75	66·71	50	—	4·80	7·51	13·55
20	8·55	17·10	26·27	40·65	60	—	3·13	5·21	10·00
30	4·59	11·47	17·10	26·48	70	—	2·08	4·17	7·92

FIG. 4a.

FIG. 4b.

Sulphonation of nitrobenzene at various temperatures.

Sulphonation of m-xylene *at various temperatures.*

Influence of Initially Added Water on the Initial Rate.—For several compounds the initial rate was determined in experiments with a range of acids made up to contain small known percentages of water. The initial rate falls with the water content (Figs. 5 and 6). These figures also show lines calculated from the formula $k = k_1/(x + x_0)^{1/3}$ where x is the amount of water initially added and x_0 is a constant, which proves to be nearly independent of the aromatic compound used (and according to a possible theory should be completely independent). The form of this relation is discussed later. In the meantime the figures show that it is a satisfactory empirical representation of the results. Experimental values found for k_1/k_0 were : benzene 0·109, *m*-dichlorobenzene 0·135, toluene 0·1007, α-nitronaphthalene 0·1114, naphthalene 0·0844. It is assumed therefore that where the experimental value has not been directly determined a mean value may be used for all the aromatic compounds studied. In contrast with the nearly constant effect of added water on the initial rate, the variation in rate with water formed in the reaction is very specific and different for each aromatic compound, as is shown by the selection of curves

in Fig. **7**. **Thus part at least** of the effect of the water formed in reaction is due to the setting up of a reverse change.

FIG. 6.

α-Nitronaphthalene at 40·0°.

FIG. 5.

Benzene at 40·0°.
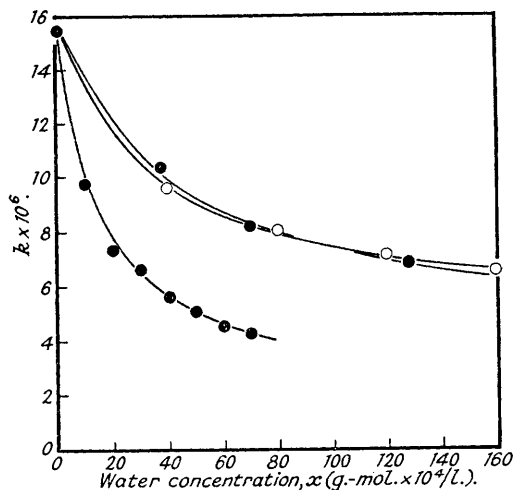
Upper curves : *full circles, experimentally found influence of* added *water on initial value of* k; *open circles, calculated from* $k = k_1/[x + (0·109)^3]^{1/3}$, *where* $k_1 = 15·4 \times 10^{-6}$. *Lower curve* : *influence of water formed in reaction on* k.
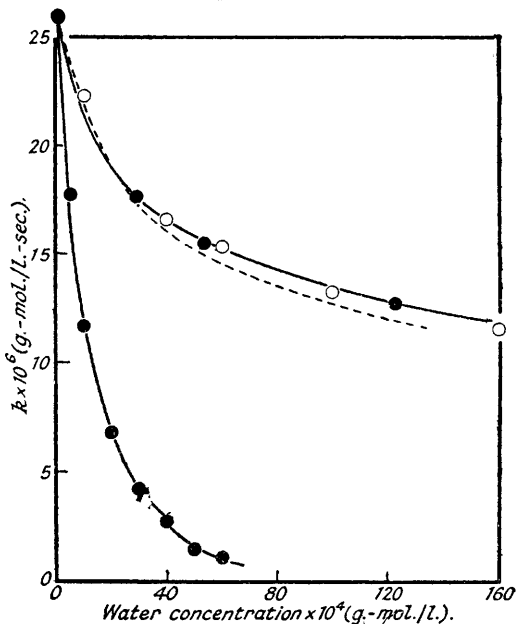
Lower curve : *influence of water formed in reaction on* k. *Upper curves* : *full circles, experimental*; *open circles, calculated from* $k = k_1 [x + (0·1114)^3]^{1/3}$ *with* $k_1 = 2·98 \times 10^{-6}$; *broken line, calculated with* $k_1/k_0 = 0·108$ *(average value).*

FIG. 7.
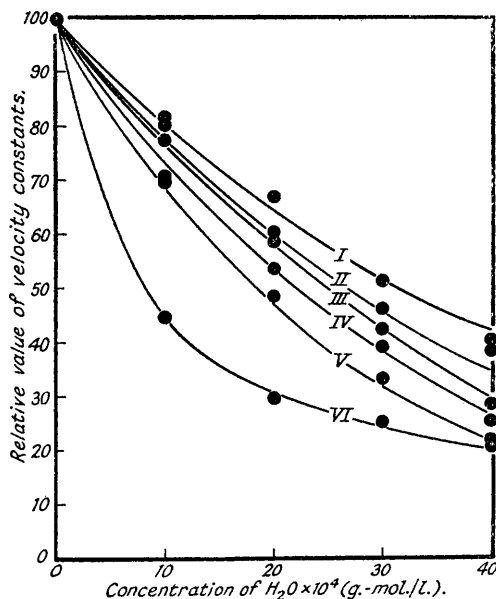
k *as a function of water formed.* (*I*) PhBr. (*II*) PhCl. (*III*) PhMe. (*IV*) Ph·NO$_2$. (*V*) C$_6$H$_4$(NO$_2$)Me. (*VI*) m-C$_6$H$_4$Cl$_2$.

Influence of Reaction Products.   Reverse Reaction.—A comparison of the pairs of curves in Figs. 5 and 6 shows that initially added water has less effect than a corresponding amount formed by reaction.   This provides further evidence that the setting in of a reverse reaction contributes to the diminution of the gross reaction rate, as measured by k.   The existence of the reverse reaction was confirmed in the following way.

A reaction mixture of the following composition was weighed into a flask : nitrobenzene, 200 c.c. ; sulphuric acid of 95·26% strength, 1·8965 g. ; sodium benzenesulphonate, 0·6056 g.   The salt was 88·0% pure (remainder sodium chloride).   Thus the mixture was 0·0248M in water and 0·0147M in benzene-sulphonic acid.   The turbid reaction mixture was shaken, and a 10 c.c. portion titrated until clear with 100% sulphuric acid in nitrobenzene (1 : 80), the titre being 8·48 c.c.   The remainder was kept at 25·0°, and 10 c.c. portions were titrated at intervals.   From the gradual drop in titre occurring as water was used up in the hydrolysis the progress of this reaction could be followed.   The results are shown in Fig. 9.   For the calculations the titre had to be calibrated against water content of the reaction mixture. Suppose that y g. of water are removed to form $98y/18$ g. of H_2SO_4; the amounts of H_2SO_4 and of H_2O now present are $0·9526 \times 1·897 + 98y/18$ and $0·047 \times 1·897 - y$, respectively, that is, the total weight of "sulphuric acid" present is $1·897 + 4·44y$ and its percentage strength is expressible in terms of y.   For the calibration experiment a titration is made with an acid somewhat stronger than the original, namely, 96·07%.   This would have been formed by an amount of reaction such that $y = 0·01362$.   To imitate a reaction mixture for which this value of y has been reached it is necessary to take $1·897 + (0·01362 \times 4·44)$

FIG. 8.
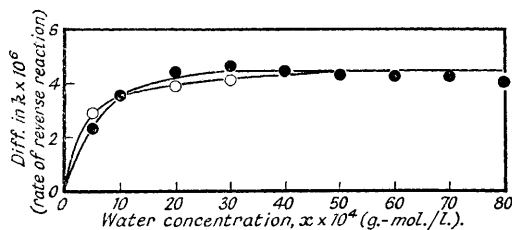
Reverse reaction with benzene at 40·0°.

FIG. 9.
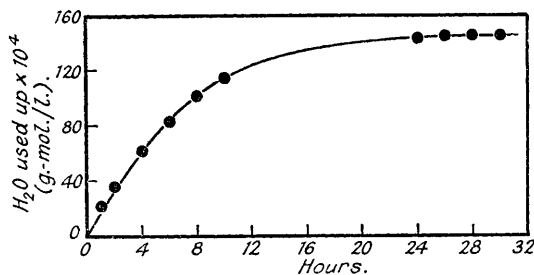
Hydrolysis of benzenesulphonic acid.

= 1·958 g. of the 96·07% acid and the appropriate amount of the sodium benzenesulphonate, that is, 0·6056 g. less the amount reacting with the 0·01362 g. of water.   Allowing for the purity of the salt, we find the amount required to be 0·4501 g.   The mixture is therefore made up to contain : nitrobenzene, 200 c.c.; sulphuric acid (96·07%), 1·9660 g.; sodium benzenesulphonate, 0·45 g.   This is 0·0214M in water and 0·0111M in the sulphonic acid.   A 10 c.c. portion of this required 6·68 c.c. of the 100% titrating solution.   Thus we have : water, 0·0248M, titre, 8·48 : water, 0·214M, titre, 6·68. From calibrations of this kind a curve can be drawn from which the concentration of water at any stage of the reaction can be read off.   The results in Fig. 9 show that the water concentration dropped by 0·0145 g.-mol./l.   If the hydrolysis had proceeded to completion the drop would have been 0·0147, so that in the conditions of the experiment the reaction was nearly complete.   The conditions are not quite comparable with those prevailing during the sulphonation.   Nevertheless the results show that the reverse reaction must be taken very seriously into account.

The principal information about the reverse reaction was obtained indirectly.   Its magnitude is in fact given by the difference between two curves such as those shown in Figs. 5 and 6.   The result, which is of similar form in all the examples studied, is illustrated in Fig. 8, where the rate of the reverse reaction is plotted against x, the amount of water or sulphonic acid formed.   The result is rather surprising, the contribution to the net rate being, not a term ($- k'x^2$) as might perhaps have been expected, but one of the form $k_2'x/(1 + \beta x)$.   This for the present will be taken as an empirical result, and discussed later.

Since $k_1[Ar][A]/(x + x_0)^{1/3}$ does in fact represent the forward rate and $k_2'x/(1 + \beta x)$ the reverse rate, the ratio k_1/k_2' will be proportional to an equilibrium constant, which thus becomes determinable. Results are collected in Table VII.

Temperature Coefficients and Activation Energies.—The values of k (in the expression rate = $k[Ar][A]$)

for different values of x were plotted and k_0 determined at four or more different temperatures for each of the compounds studied. The results are recorded in Table IV.

From the plots of ln k_0 against $1/T$ the activation energies were determined by the method of least squares. They are given in Table V, and log k_0 for 40° is plotted against E in Fig. 10. The line is drawn with the slope $-2 \cdot 303RT$.

With nitrobenzene, where the reactant is itself the solvent, the reaction is determined by solvent–solute encounter, and not as in the other examples by solute–solute encounters. The viscosity correction has

TABLE IV.

Compound.	Temp.	$k_0 \times 10^6$.	Compound.	Temp.	$k_0 \times 10^6$.
Benzene	15°	5·1	p-Dibromobenzene	25°	0·46
	25	8·0		40	1·01
	40	15·5		60	2·46
	60	30·0		80	5·01
Toluene	15	31·1	p-Chlorotoluene	15	5·41
	25	42·7		25	9·32
	40	78·7		40	17·1
	60	151·2		60	33·3
m-Xylene	5	29·2	1 : 2 : 4-Trichlorobenzene	25	0·34
	15	48·0		40	0·73
	25	70·9		60	1·95
	40	116·8		80	4·23
Chlorobenzene	15	2·65	Nitrobenzene	40	0·24
	25	4·88		60	0·57
	40	10·6		80	1·01
	60	23·0		100	1·72
Bromobenzene	15	3·01	p-Nitrotoluene	25	1·50
	25	4·42		40	3·26
	40	9·55		60	7·95
	60	24·4		80	19·6
m-Dichlorobenzene	25	2·51	Naphthalene	5	40·0
	40	6·70		15	61·2
	60	15·6		25	82·4
	80	35·2		40	141·3
p-Dichlorobenzene	25	0·49	a-Nitronaphthalene	15	7·76
	40	0·98		25	13·1
	60	2·26		40	26·1
	80	5·34		60	57·2

FIG. 10.

Activation energy and log (rate).
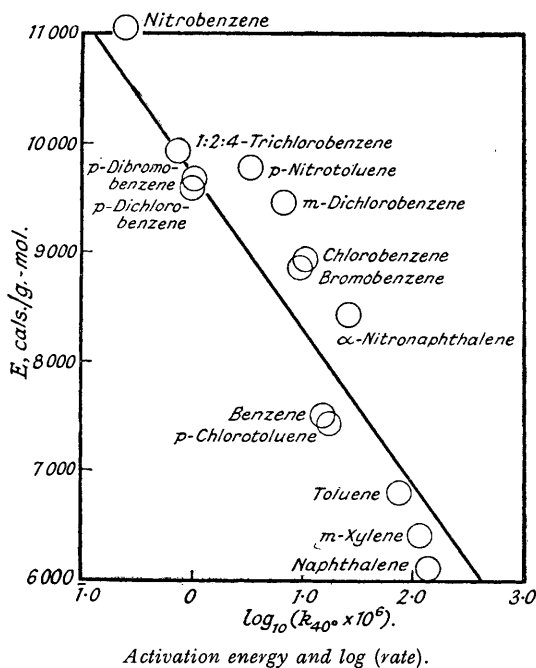
TABLE V.

Compound.	$k_0 \times 10^6$ at 40°.	E.	Compound.	$k_0 \times 10^6$ at 40°.	E.
Naphthalene	141·3	6,100	Bromobenzene	9·5	8,850
m-Xylene	116·7	6,400	*m*-Dichlorobenzene	6·7	9,460
Toluene	78·7	6,790	*p*-Nitrotoluene	3·3	9,770
α-Nitronaphthalene	26·1	8,430	*p*-Dichlorobenzene	0·98	9,570
p-Chlorotoluene	17·1	7,440	*p*-Dibromobenzene	1·01	9,670
Benzene	15·5	7,500	1 : 2 : 4-Trichlorobenzene	0·73	9,940
Chlorobenzene	10·6	8,940	Nitrobenzene	0·24	11,060

therefore been applied (Moelwyn-Hughes, " Kinetics of Reactions in Solution ", 1st Ed., p. 158). The value of Q in the equation $\dfrac{d \ln (1/\eta)}{dT} = \dfrac{Q}{RT^2}$ is 3000 cals., and this has been added to the observed activation energy to correct for the effect of diminution in encounter numbers as the temperature rises.

DISCUSSION.

(a) *Kinetics of Forward and Reverse Reactions.*—The possible equilibria in the system sulphuric acid–nitrobenzene–water are rather complex, and the complete treatment of the system is difficult. The kinetic relationships are, however, of a distinctive form, and an approximate interpretation seems possible in the following way, though, in view of the assumptions and approximations which have to be made, the treatment must be regarded as tentative.

The hydrolysis of the sulphonic acid is not promoted by water in a way which admits H_3O^+ as the attacking agent (Fig. 8). It proves more satisfactory to assume $Ph \cdot NO_2 \cdot H^+$. If this hypothesis is adopted, it follows from the principle of detailed balancing that $SO_2 \cdot OH^+$ would probably be the active agent in the sulphonation, thus :

$$\text{(ring)} H + SO_2 \cdot OH^+ + Ph \cdot NO_2 \rightleftharpoons \text{(ring)} SO_2 \cdot OH + Ph \cdot NO_2 H^+$$
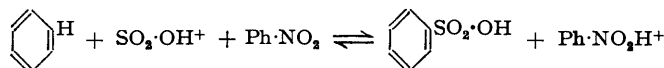
The consequences of this assumption may be developed approximately as follows :

$$2H_2SO_4 \rightleftharpoons SO_2 \cdot OH^+ + HSO_4^- + H_2O$$
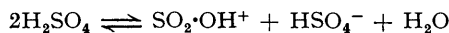
$$\frac{[SO_2 \cdot OH^+][HSO_4^-][H_2O]}{[H_2SO_4]^2} = K_1$$

The ionisation may be taken to be small, the conductivity of sulphuric acid in nitrobenzene being low, and if the water content is sufficiently small

$$[H_2SO_4] \gg [SO_2 \cdot OH^+] \gg [H_3O^+]$$

Also

$$[SO_2 \cdot OH^+] \sim [HSO_4^-] = f$$

Therefore

$$f^2[H_2O]/[A]^2 = K_1$$

where [A] = total concentration of acid.

$$f = [A]\sqrt{K_1}/\sqrt{[H_2O]} \qquad \qquad \qquad (1)$$

If

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

$$\frac{[H_3O^+][HSO_4^-]}{[H_2O][H_2SO_4]} = K_2 \quad \text{or} \quad [H_2O] = \frac{[H_3O^+][HSO_4^-]}{K_2[H_2SO_4]}$$

Now the water content, by hypothesis, is small; so that $[HSO_4^-] \gg [H_3O^+]$ (remembering that much of the HSO_4^- is balanced by $Ph \cdot NO_2 \cdot H^+$), but such water as there is will be predominantly in the form H_3O^+ and

$$[H_2O] \sim \frac{(W + W_0)f}{K_2[A]} \qquad \qquad \qquad (2)$$

W being any small amount of *added* water and W_0 that naturally present in equilibrium when 100% sulphuric acid is dissolved in pure nitrobenzene. The simple summation of $(W + W_0)$ is of course an approximation, but one which will be nearly correct. Substituting for $[H_2O]$ from (1), we have

$$\frac{K_1[A]^2}{f^2} \sim \frac{(W + W_0)f}{K_2[A]} \quad \text{whence} \quad f = \frac{(K_1 K_2)^{1/3}[A]}{(W + W_0)^{1/3}}$$

Now in excess of Ph·NO$_2$ the rate of the forward reaction will be proportional to [Ar]f, and thus, for *small* water contents, we shall have

$$\text{Forward rate} = \frac{k_1[\text{Ar}][\text{A}]}{(W + W_0)^{1/3}}$$

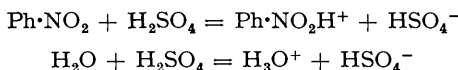or, if the water is all formed in the reaction, $W = x$, so that

$$\text{Forward rate} = \frac{k_1[\text{Ar}][\text{A}]}{(x + x_0)^{1/3}} \qquad \cdots \cdots \cdots \quad (3)$$

where x_0 has the same meaning as W_0.

This, as has been shown, expresses the results adequately. At higher water contents it must cease to apply.

For the reverse reaction the important quantity is [Ph·NO$_2$H$^+$]. The magnitude of this, over certain ranges, will be principally determined by the competition

$$\text{Ph·NO}_2 + \text{H}_2\text{SO}_4 = \text{Ph·NO}_2\text{H}^+ + \text{HSO}_4^-$$

$$\text{H}_2\text{O} + \text{H}_2\text{SO}_4 = \text{H}_3\text{O}^+ + \text{HSO}_4^-$$

If $\qquad\qquad [\text{H}_2\text{SO}_4] \sim [\text{A}],\ [\text{H}_3\text{O}^+] \sim (W + W_0) \sim W'$

$$[\text{Ph·NO}_2] = [\text{S}]$$

then $\qquad\qquad\qquad [\text{Ph·NO}_2\text{H}^+] = \dfrac{K_3[\text{S}][\text{A}]}{[\text{HSO}_4^-]}$

but $\qquad\qquad\qquad [\text{H}_3\text{O}^+] + [\text{Ph·NO}_2\text{H}^+] = [\text{HSO}_4^-]$

$$[\text{Ph·NO}_2\text{H}^+] = \frac{K_3[\text{S}][\text{A}]}{W' + [\text{Ph·NO}_2\text{H}^+]}$$

$$[\text{Ph·NO}_2\text{H}^+] = \tfrac{1}{2}\left[-W' + W'\left(1 + \frac{4K_3[\text{S}][\text{A}]}{W'^2}\right)^{1/2} \right]$$

and if the second term in the bracket is small this becomes approximately

$$[\text{Ph·NO}_2\text{H}^+] \sim K_3[\text{S}][\text{A}]/W'$$

Now the rate of the back reaction will be proportional to [sulphonic acid][Ph·NO$_2$H$^+$] and thus

$$\text{Back rate} = \text{const.}\ \frac{x[\text{S}][\text{A}]}{W'} \qquad \cdots \cdots \cdots \quad (4)$$

Combining (3) and (4) and putting $W' = W + W_0 = x + x_0$ when no water is added initially $(x_0 \equiv W_0)$

$$\text{Net rate} = k[\text{Ar}][\text{A}] = \frac{k_1[\text{Ar}][\text{A}]}{(x + x_0)^{1/3}} - \frac{k''x[\text{A}]}{(x + x_0)}$$

When $x = 0$, $k = k_0$, so that $k_0 = k_1/(W_0)^{1/3}$

$$k = \frac{k_1}{\{x + (k_1/k_0)^3\}^{1/3}} - \frac{k_2 x}{[\text{Ar}](1 + \beta x)} \qquad \cdots \cdots \quad (5a)$$

where k_2 and β are new constants.

Since [Ar] does not change appreciably, this becomes

$$k = \frac{k_1}{\{x + (k_1/k_0)^3\}^{1/3}} - \frac{k_2' x}{(1 + \beta x)} \qquad \cdots \cdots \quad (5b)$$

This equation, as has been shown, gives a fair account of the experimental results.

It is recognised that the above contains many approximations but may be regarded as a preliminary interpretation of the general form of the experimental results. The approximations are such that the expression for the forward reaction will be best at lower water contents, and that for the reverse reaction at the higher water contents. In any event as an empirical equation (5b) is satisfactory. k_1/k_2 is therefore used as a measure of an equilibrium constant.

(b) *Relation between Activation Energy and Rate.*—The summarised results of Table V are plotted in Fig. 10, which shows that the changes in E due to the substituents play the principal part in determining the changes in reaction rate. If they played the sole part the points would

lie on a line of slope $- 2\cdot303RT$. Such a line is shown in the figure, and, it is evident that, having regard to the large scale of the plot, the points do not lie far from it. However, all the points in the upper half of the diagram lie on or to the right of the line, while all those in the lower half lie to the left. Thus the best line would be a little steeper than that drawn; that is, the rate does not decrease as rapidly as would be expected simply from the changes of activation energy. In other words the well-known compensation of the energy and entropy factors is in evidence, but only to a small extent.

The next matter of interest is that the point for nitrobenzene lies just as expected in relation to the others. E for nitrobenzene involved the " viscosity " correction of 3000 calories. If this had not been applied the point would lie in a completely inconsistent relation to the others. Thus the coherence of the results vindicates the application of the correction. It may be noted that the addition of the corresponding correction to the results of Dresel and Hinshelwood (*loc. cit.*), which was not done, would correspondingly improve their coherence.

FIG. 12.

FIG. 11.

Activation energy and dipole moment.
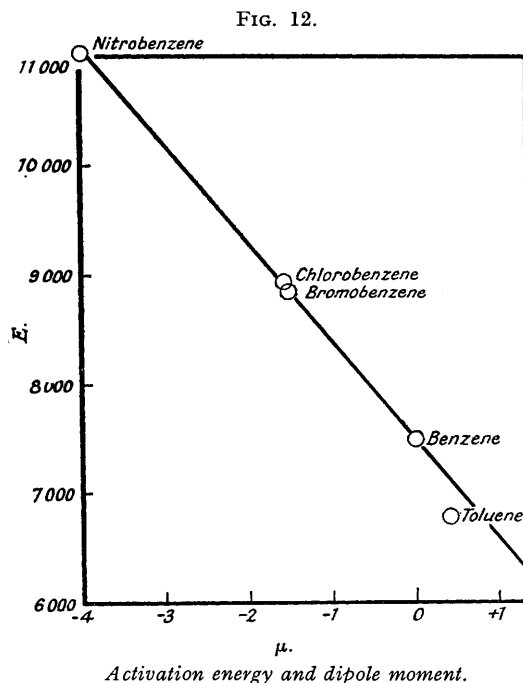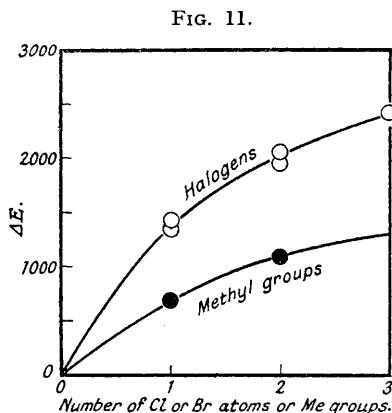
The points for the seven halogen derivatives lie in a coherent relation to the others. As is well known, the behaviour of halogens as directing groups is anomalous in certain respects, but the present results confirm those of Dresel and Hinshelwood in indicating that the anomaly does not lie in the nature of the activation energy–entropy of activation relationship.

Fig. 11 shows the effect on E of introducing one, two, and three halogen atoms, or one and two methyl groups respectively into the ring. The tendency to saturation in the effect of the increasing substitution is evident.

(c) *Activation Energy and Dipole Moment.*—In Fig. 12 the values of E for benzene and the monosubstitution products are plotted against the corresponding dipole moments, and a fairly definite fuctional relation is evident. The halogen derivatives appear to fall in line, despite the anomaly referred to above, while toluene deviates somewhat, the effect of methyl groups corresponding to a value of μ rather greater than the actual one.

That the relation of E and μ for chloro- and bromo-benzene should be normal is interesting in view of the current interpretation of the orientating influence of halogens. They are deactivating, as is to be inferred from the moments, but *o*- and *p*-directing in a way which shows reaction to depend upon a tautomeric change provoked by the attacking agent. This change involves a temporary reversal of the natural moment, and requires the expenditure of work. The present result shows that the amount of this work is adjusted to the moment which has to be reversed.

In Table VI are given the actual moments of the various compounds together with the effective moments of the poly-substitution products, that is, the value of μ corresponding,

TABLE VI.

Activation energy and dipole moment.

Compound.	E.	Experimental μ.	Effective μ.
Toluene	6,790	+0·41	—
Benzene	7,500	0	—
Chlorobenzene	8,940	−1·56	—
Bromobenzene	8,850	−1·53	—
Nitrobenzene	11,060	−3·97	—
Naphthalene	6,100	—	+1·60
m-Xylene	6,400	—	+1·26
α-Nitronaphthalene	8,430	—	−1·04
p-Chlorotoluene	7,440	—	+0·10
m-Dichlorobenzene	9,460	—	−2·17
p-Nitrotoluene	9,770	—	−2·53
p-Dichlorobenzene	9,570	—	−2·33
p-Dibromobenzene	9,670	—	−2·40
1 : 2 : 4-Trichlorobenzene	9,940	—	−2·70

according to the line in Fig. 12, to the observed values of E. In the *p*-dihalogen derivatives the effective moment would not be expected to bear any relation to the observed moment since in the former there must be some degree of reinforcement and in the latter there is complete cancellation of the separate effects of the two atoms. Actually the effective moment of the di-derivatives is considerably less than $2\mu_{mono}$, and of the tri-derivative much less than $3\mu_{mono}$.

The effective moment of xylene is greater than twice the observed value for toluene (though it is less than twice the effective value for toluene). Naphthalene has a high effective moment, nearly 4 times the observed value for toluene. The activating effect of hydrocarbon substituents is uniformly greater than would be inferred from $\mu_{toluene}$. This same influence is in evidence with nitronaphthalene, nitrotoluene, and chlorotoluene, where the contribution of the hydrocarbon substituent in opposing the deactivating effect of Cl or NO_2 is far greater than would be expected from the measured dipole moments of monoalkyl compounds.

(d) *Relation of* k_1 *and* K.—In Table VII are collected the values of the principal constants. Most of them have already been discussed. One further matter remains. The ratio k_1/k_2, according to the theory given above, should be proportional to an equilibrium constant, K, and it is of interest
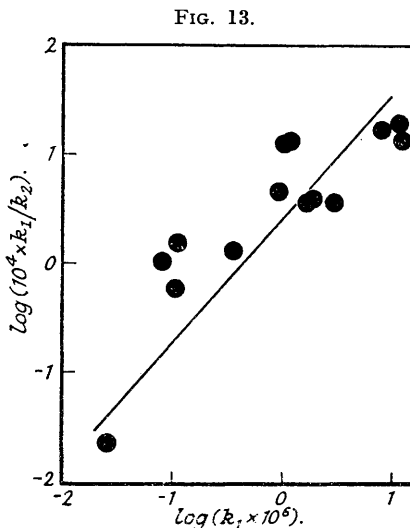
FIG. 13.

Velocity constant and equilibrium constant.

TABLE VII.

Compound.	k_1/k_0.	$k_1 \times 10^6$.	$k_2 \times 10^3$.	$\beta \times 10^{-3}$.	$10^4 k_1/k_2$.
Naphthalene	0·084	11·41	5·636	1·444	20·24
m-Xylene	—	12·38	8·794	1·615	14·08
Toluene	0·101	7·952	4·666	0·947	17·04
α-Nitronaphthalene	0·111	2·978	8·168	3·572	3·647
p-Chlorotoluene	—	1·847	4·586	3·357	4·026
Benzene	0·109	1·682	4·634	3·890	3·629
Chlorobenzene	—	1·145	0·850	1·049	13·41
Bromobenzene	—	1·037	0·816	1·050	12·71
m-Dichlorobenzene	0·135	0·919	1·992	2·357	4·613
p-Nitrotoluene	—	0·350	2·749	1·110	1·274
p-Dichlorobenzene	—	0·106	1·715	3·000	0·618
p-Dibromobenzene	—	0·109	0·699	2·214	1·561
1 : 2 : 4-Trichlorobenzene	—	0·079	0·769	3·625	1·028
Nitrobenzene	—	0·0255	11·31	1·530	0·0225

(Where k_1/k_0 was not determined experimentally the mean value was taken, namely, 0·108.)

to see whether there is any sign of the well-known logarithmic correlation between rate constant and equilibrium constant.   Accordingly, log k_1 has been plotted against log (k_1/k_2) in Fig. **13,** and it appears that there is a general correlation in the sense to be expected, though no accurate relationship seems to exist.