207. *Aromatic Sulphonation. Part II. Kinetics of Sulphonation in Fuming Sulphuric Acid.*

By J. C. D. Brand.

The kinetics of sulphonation of *p*-tolyltrimethylammonium methyl sulphate, phenyltrimethylammonium methyl sulphate, *p*-nitrotoluene, and nitrobenzene have been measured between 0° and 45° in oleum containing up to 33% of sulphur trioxide. The effect of varying initial concentrations and the retarding influence of potassium sulphate, barium sulphate, and barium di(methyl sulphate) have been studied. The experiments were conducted with an excess of sulphur trioxide and were of the first order with respect to the concentration of organic reactant, $-d[ArH]/dt = k_1[ArH]$. *p*-Nitrotoluene and nitrobenzene were present in the medium chiefly in a totally unreactive ionised form, and sulphonation occurred through the small equilibrium proportion of un-ionised base. For the quaternary ammonium methyl sulphates and for un-ionised *p*-nitrotoluene and nitrobenzene the variation of k_1 with the composition of the medium is expressed by the equation $\log k_1 = \log A + 2{\cdot}3 \log R$, where A is a parameter characteristic of the substance undergoing suphation and R is the stoicheiometric molar ratio $H_2S_2O_7 : H_2SO_4$. The constants of the Arrhenius equation have been evaluated.

The kinetics are shown to be consistent with the assumption that the governing step in sulphonation is : $SO_3H^+ + ArH = Ar{\cdot}SO_3H + H^+$. Relative values of the velocity coefficient of this reaction have been determined.

With emphasis on the theory of reaction kinetics, Hinshelwood and his collaborators (*J.*, 1939, 1372; 1944, 469, 649; 1948, 1065) have studied the kinetics of sulphonation of several aromatic compounds by solutions in nitrobenzene of both sulphuric acid and sulphur trioxide. In this solvent the velocity of sulphonation by sulphur trioxide was of the second order with respect to sulphur trioxide and the reaction was retarded by the product; this was shown to be accounted for if the governing step involved S_2O_6 molecules :

$$2SO_3 \rightleftharpoons S_2O_6;\ S_2O_6 + ArH = ArS_2O_6H;\ ArS_2O_6H \rightleftharpoons ArSO_3H + SO_3.$$

The kinetics of sulphonation by sulphuric acid in nitrobenzene were consistent with a reversible mechanism involving attack by SO_3H^+ ions and represented by the equilibria

$$2H_2SO_4 \rightleftharpoons SO_3H^+ + SO_4H^- + H_2O$$
$$PhNO_2 + ArH + SO_3H^+ \rightleftharpoons PhNO_2H^+ + ArSO_3H$$

Sulphonation in Fuming Sulphuric Acid.—Little attention has been paid to the quantitative side of this reaction. The kinetics are quite different from those encountered with nitrobenzene as a solvent : the reaction is more vigorous and is usually not reversible, in the sense that the forward and reverse reactions do not occur under the same conditions. Lauer and others (*J. pr. Chem.*, 1935, **144**, 32; *Ber.*, 1936, **69**, 2618; 1937, **70**, 333) investigated the sulphonation of anthraquinone in oleum but, by varying the concentrations of both reactants simultaneously, obtained a very complicated result which will be discussed later (§ 3). Lauer concluded that molecular (undissociated) sulphuric acid acted as the sulphonating agent both in concentrated and in fuming media, and that sulphur trioxide facilitated the reaction only through its ability to combine with the eliminated water molecule. The kinetics of sulphonation of *p*-nitrotoluene were examined by Martinsen (*Z. physikal. Chem.*, 1908, **62**, 713) in oleum containing 2·4% of sulphur trioxide and by Cowdrey and Davies (*J.*, 1949, 1871) in media containing 1—5·5% of sulphur trioxide. Martinsen also experimented in anhydrous sulphuric acid, and both authors made measurements in acids containing a small proportion of water. In weak oleum, Cowdrey and Davies found that the rate of reaction was given by the differential equation :

$$-d[C_7H_7{\cdot}NO_2]/dt = k_2[C_7H_7{\cdot}NO_2][SO_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[SO_3]$ represents the stoicheiometric concentration of free sulphur trioxide. Martinsen's results also conform to equation (1) (Joffe, *J. Gen. Chem. Russia*, 1933, **3** 437, 505; *Abstr.*, 1934, 178) and a comparison of some of the published results with those reported in this paper is given in Table IV. However, because of a complicating ionisation of the *p*-nitrotoluene (Part I), these kinetics are not altogether typical of sulphonation. In the following discussion, the kinetics of the most general case will be presented in § 1, and the nature of the changes introduced when the organic reactant is involved in a simultaneous ionisation will be reviewed in §§ 2 and 3.

1. *Kinetics of Sulphonation of Phenyltrimethylammonium and* p-*Tolylmethylammonium Salts.*—In the kinetic experiments the quaternary ammonium salts were introduced as their methyl sulphates, and the progress of the reaction was followed by a modification of Martinsen's

method. The *p*-tolyltrimethylammonium ion reacted exclusively in the *m*-position with respect to the trimethylammonium group, but the phenyltrimethylammonium ion yielded approximately 78% of phenyltrimethylammonium 3-sulphonate, *m*-$Me_3N^+{\cdot}C_6H_4{\cdot}SO_3^-$, together with 22% of the *o*- and *p*-isomers (Brand and Rutherford, *Research*, 1949, **2**, 195). The details of the analysis of the products will be published shortly. Because the initial concentration of the quaternary ion was low, the concentration of sulphur trioxide did not change significantly during reaction and individual experiments obeyed equation (2) :

$$-d[ArNMe_3^+]/dt = k_1[ArNMe_3^+] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The results of a typical experiment are given below.

Expt. 120.

Temp., 25°. Medium, 15·74% of SO_3.

$[SO_3]\begin{cases}\text{initial : } 1{\cdot}968 \text{ mols./kg.}\\ \text{final : } 1{\cdot}923 \text{ mols./kg. (calc. : } 1{\cdot}937 \text{ mols./kg.).}\end{cases}$

Time, mins.	Concn. of $PhNMe_3^+ SO_4Me^-$, mol./kg.	Total reaction, %.	10^3k_1, min.$^{-1}$.
0·0	0·0312	0	—
2·8	0·0280	10·4	39·5
5·7	0·0247	20·9	41·2
9·6	0·0211	32·5	40·8
13·6	0·0177	43·5	41·6
18·7	0·0144	53·9	41·5
24·6	0·0112	64·1	41·6
			41·0 ± 0·6

The results of all velocity measurements are collected in Tables I—VII. Concentrations are expressed in moles per kg. of solution and the time is in minutes. For a given temperature the results may be summarised as follows.

(a) *Influence of composition of medium.* The rate of reaction is a function of the free sulphur trioxide concentration raised to a high and variable power. The reaction order with respect to the molar concentration rises from 2·7 in 4—8% oleum to 4·6 in 16—20% oleum, and a relation of the form $k_1 \propto [SO_3]^n$ applies only if n is expressed as a function of the composition of the medium. A satisfactory empirical correlation exists between k_1 and the molar ratio $H_2S_2O_7 : H_2SO_4$ of the form

$$\log k_1 = \log A + 2{\cdot}3 \log([H_2S_2O_7]/[H_2SO_4]) \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

where A is a constant characteristic of the substance undergoing sulphonation (Fig. 1).* The ratio $H_2S_2O_7 : H_2SO_4$ will be written hereafter as R. R is calculated assuming (1) that bisulphate ions react quantitatively according to the equation $SO_3 + SO_4H^- = S_2O_7H^-$, and (2) that the remainder of the free sulphur trioxide is present as molecular pyrosulphuric acid, $H_2S_2O_7$. Methosulphate ($MeSO_4^-$) ions † are counted as bisulphate (SO_4H^-). Assumption (2) is a reasonable first approximation in the moderately dilute oleum under discussion, where the proportion of *molecular* sulphur trioxide is small (Miles, Niblock, and Wilson, *Trans. Faraday Soc.*, 1940, **36**, 345; Miles, Niblock, and Smith, *ibid.*, 1944, **40**, 281); moreover, equation (3) is, for the time being, used quite empirically. The experimental results are given in Table I; values of k_1 are in column 8.

(b) *Influence of basic substances and reactant concentration.* Most inorganic salts are basic towards oleum, and experiments were made to determine the kinetic influence of potassium sulphate, potassium hydrogen sulphate, and barium di(methyl sulphate). These salts retard sulphonation powerfully, and the measured velocities of reaction are given in Table II, column 10. The reaction was also retarded by increasing the concentration of quaternary ammonium ion, but, by simultaneously varying the concentrations of the latter and those of barium di(methyl sulphate) in such a way that the total concentration of methosulphate ions remained constant, it could be shown that the velocity coefficient was approximately independent of the concentration of quaternary ion although very sensitive to alterations in the concentration of methosulphate ions. Equation (2) was, however, essentially valid to cover variations of the initial concentration of quaternary ammonium ion. (This follows, for example, if experiments 97 and 98, Table II, are compared with experiments

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* Equations (3), (5), (7), (8), and (9) were empirically satisfactory in oleum containing 1—33% of sulphur trioxide, but are meaningless if extrapolated to 100% sulphuric acid ($R = 0$) or to very strong oleum.

† Salts containing the grouping $\geqslant\overset{+}{N}Me\{MeSO_4^-$ are commonly termed "methosulphates," *e.g.*, pyridine methosulphate. The convenient wording "methosulphate ion" is, however, used to denote $MeSO_4^-$, as this is unlikely to cause confusion. Ed.

TABLE I.

Influence of medium on the rate of sulphonation (*temp*. 25°).

	Medium.							
	Sulphur trioxide.					Initial		
Acid no.	%.	mol./kg.	log R.	H_0.	Expt. no.	concn. of $C_7H_7\cdot NMe_3,SO_4Me$.	10^3k_1, min.$^{-1}$.	H_0 + log 10^3k_1 − log R.
13	2·44	0·305	−1·54	−11·52	87	0·0330	85	−8·05
13	2·44	0·305	−1·54	—	84	0·0300	86	−8·05
13	2·44	0·305	−1·54	—	83	0·0283	86	−8·05
18	4·10	0·513	−1·28	−11·81	155	0·0308	302	−8·05
18	4·11	0·514	−1·28	—	158	0·0302	303	−8·05
12	7·92	0·990	−0·94	−12·14	82	0·0316	1500	−8·02
12	7·92	0·990	−0·94	—	81	0·0273	1800	−7·94
12	7·94	0·992	−0·94	—	80	0·0252	1800	−7·94
11	11·50	1·439	−0·74	−12·27	78	0·0888	5400	−7·80
						$PhNMe_3,SO_4Me$.		
18	4·08	0·510	−1·28	−11·81	167	0·0301	0·741	−10·66
18	4·10	0·513	−1·28	—	156	0·0304	0·748	−10·66
17	8·23	1·03	−0·92	−12·17	152	0·0301	4·80	−10·57
17	8·23	1·03	−0·92	—	154	0·0300	4·81	−10·57
11	11·60	1·451	−0·72	−12·42	105	0·0296	13·7	−10·56
11	11·60	1·451	−0·72	—	107	0·0302	13·6	−10·57
6	13·04	1·63	−0·66	−12·32	50	0·1036	12·4	−10·57
15	13·39	1·674	−0·64	−12·55	140	0·0304	22·1	−10·57
15	13·40	1·675	−0·64	—	141	0·0299	22·7	−10·55
14	15·74	1·968	−0·53	−12·73	120	0·0312	41·8	−10·58
14	15·74	1·968	−0·53	—	122	0·0297	42·2	−10·57
16	20·12	2·515	−0·35	−13·04	146	0·0300	129	−10·58
16	20·12	2·515	−0·35	—	143	0·0303	127	−10·59
10	24·2	3·02	−0·20	—	73	0·112	240	—
10	24·2	3·02	−0·20	—	74	0·0974	240	—
10	24·2	3·02	−0·20	—	75	0·106	230	—
5	33·1	4·13	+0·20	—	72	0·0964	2000	—

$C_7H_7\cdot NMe_3^+$: $\log k_1 = 2{\cdot}3_3 + 2{\cdot}2_2 \log R$. $PhNMe_3^+$: $\log k_1 = -\ 0{\cdot}12 + 2{\cdot}3_6 \log R$.

84, Table I, or 99 and 104 with 101.) Potassium sulphate and barium di(methyl sulphate) exerted roughly the same kinetic effect at the same molar concentration, and the small difference which was observed was probably due to the methyl hydrogen sulphate released in solution from the latter, because the retardation produced by potassium and barium sulphates was indistinguishable (Table VI).

Qualitatively, the retardation by bases is readily interpreted. The effect is caused by the bisulphate ions into which both sulphate and methosulphate ions are converted by the reactions $SO_4^{--} + H_2SO_4 = 2SO_4H^-$ and $SO_4Me^- + H_2SO_4 = MeSO_4H + SO_4H^-$ respectively. The bisulphate ions and molecular pyrosulphuric acid establish the equilibrium

$$SO_4H^- + H_2S_2O_7 = S_2O_7H^- + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the position of which lies on the right hand side (Brand, *J.*, 1946, 880). The consumption of pyrosulphuric acid according to equation (4) will diminish the rate of sulphonation, but this effect alone is insufficient to account for the observed retardation, even on the assumption that reaction (4) proceeds quantitatively from left to right. This is illustrated, for example, by the fact that the retardation produced by bisulphate ions is more than twice as great as that brought about by the same number of moles of water. [More exactly, the comparison is between the number of moles of potassium hydrogen sulphate (n_1) and of water (n_2) which produce the same change in R, but n_1 and n_2 are approximately equal.] The difference is not a primary salt effect, because no change occurs if the potassium ions are replaced by barium ions, and it is assumed to arise from a mass-action effect of the hydrogen pyrosulphate anions on the equilibria which determine the concentration of the sulphonating agent. The empirical equation (3) does not hold in the presence of added bisulphate ions, unless an additional term is included.

2. *Kinetics of Sulphonation of* p-*Nitrotoluene*.—The velocity of sulphonation of *p*-nitrotoluene was measured by the method referred to in § 1. The experiments yielded first-order rate coefficients (equation 2*a*), except in a limited number of cases in which the concentrations of sulphur trioxide and *p*-nitrotoluene were commensurate and equation (1) was obeyed (Table IV).

$$-[dArNO_2]/dt = k_e[ArNO_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a$$

TABLE II.

Influence of basic substances and reactant concentration (*temp.*, 25°).

Acid no.	Medium. Sulphur trioxide. %.	Medium. Sulphur trioxide. mol./kg.	Medium. log R.	Medium. H_0.*	Expt. no.	Initial concn. of p-C_7H_7·NMe_3,SO_4Me.	Added substance.	Added substance. equiv./kg.	10^3k_1.	$H_0 + \log 10^3k_1 - \log R$.
13	2·46	0·307	−1·52	−11·59	86	0·0151	—	—	109	−8·03
		0·307	−1·52	−11·59	85	0·0156	—	—	109	−8·03
		0·305	−1·54	−11·52	Table I	0·030	—	—	86	−8·05
		0·290	−1·64	−11·34	101	0·0744	—	—	49	−8·01
		0·292	−1·66	−11·32	104	0·0304	K_2SO_4	0·0509	47	−7·99
		0·291	−1·75	−11·15	102	0·0300	K_2SO_4	0·0903	30	−7·92
	2·31	0·289	—	—	103	0·0297	K_2SO_4	0·179	15	—
		0·302	−1·55	−11·52	97	0·0150	$Ba(SO_4Me)_2$	0·0147	91	−8·01
		0·300	−1·55	−11·51	98	0·0152	$Ba(SO_4Me)_2$	0·0161	89	−8·01
		0·295	−1·65	−11·33	99	0·0294	$Ba(SO_4Me)_2$	0·0500	55	−7·94
		0·291	−1·77	−11·11	100	0·0286	$Ba(SO_4Me)_2$	0·1007	32	−7·84
						$PhNMe_3$,SO_4Me				
11	11·60	1·45	−0·72	−12·41	Table I	0·0300	—	—	13·6	−10·55
		1·43	−0·72	−12·31	109	0·0733	—	—	10·0	−10·57
		1·43	−0·74	−12·31	110	0·0747	—	—	10·0	−10·57
		1·44	−0·74	−12·30	111	0·0296	$Ba(SO_4Me)_2$	0·0503	10·8	−10·53
		1·44	−0·74	−12·30	108	0·0292	$Ba(SO_4Me)_2$	0·0496	11·3	−10·51
		1·38	—	—	119	0·0297	$Ba(SO_4Me)_2$	0·248	4·58	—
		1·44	−0·74	−12·30	112	0·0295	K_2SO_4	0·0501	10·2	−10·55
		1·43	−0·75	−12·20	117	0·0303	K_2SO_4	0·0870	8·19	−10·54
		1·43	−0·78	−12·04	116	0·0303	K_2SO_4	0·150	5·85	−10·49
	11·28	1·41	−0·82	−11·80	118	0·0300	K_2SO_4	0·250	3·66	−10·42
14	15·64	1·968	−0·53	−12·73	Table I	0·030	—	—	42·0	−10·57
		1·934	−0·56	−12·43	128	0·0292	$Ba(SO_4Me)_2$	0·100	27·6	−10·43
		1·951	−0·56	−12·43	131	0·0303	K_2SO_4	0·098	25·4	−10·47
		1·925	−0·60	−12·14	135	0·0299	K_2SO_4	0·250	12·1	−10·46
	14·97	1·871	−0·69	−11·69	137	0·0303	K_2SO_4	0·501	4·40	(−10·36)
		1·844	−0·75	—	139	0·0302	K_2SO_4	0·649	2·47	—
		1·942	−0·56	−12·43	134	0·0305	$KHSO_4$	0·100	25·1	−10·47
		1·942	−0·56	−12·43	132	0·0301	$KHSO_4$	0·100	24·5	−10·48
16	20·12	2·515	−0·35	−13·04	Table I	0·0301	—	—	128	−10·58
		2·49	−0·37	−12·75	148	0·0305	K_2SO_4	0·0101	77·0	−10·49
		2·46	−0·41	−12·40	149	0·0302	K_2SO_4	0·246	39·0	−10·40
	19·20	2·40	−0·48	−11·95	151	0·0305	K_2SO_4	0·498	14·2	(−10·32)

* Part I.

(a) *Influence of medium composition.* The variation of the coefficient k_e with the strength of the medium is shown in Table III, column 8. In weak oleum the order of the reaction with respect to the concentration of sulphur trioxide was close to unity (cf. Cowdrey and Davies, *loc. cit.*), but it failed to remain constant, becoming greater in stronger media (Table IV). The results were satisfactorily expressed by the equation :

TABLE III.

Influence of medium on the rate of sulphonation of p-*nitrotoluene* (pK_a = −10·28).

Medium.								
	Sulphur trioxide.							
Acid no.	%.	mol./kg.	log R.	Expt. no.	Temp.	Initial concn. of p-$C_7H_7{\cdot}NO_2$, mol./kg.	10^3k_e, min.$^{-1}$.	pK_a + log 10^3k_e − log R.
3	0·75	0·094	−2·17	21	35°	0·0257	2·20	−7·77
3	0·78	0·097	−2·16	20	—	0·0282	2·15	−7·79
1	2·13	0·267	−1·60	10	—	0·0241	7·27	−7·82
1	—	0·270	−1·60	7	—	0·0247	7·18	−7·82
2	7·37	0·921	−0·97	28	—	0·0246	36·5	−7·75
2	—	0·923	−0·97	15	—	0·0242	37·8	−7·73
2	—	0·923	−0·97	14	—	0·0264	37·0	−7·74
4	13·76	1·720	−0·62	32	—	0·0244	107	−7·63
4	—	1·720	−0·62	33	—	0·0248	103	−7·67
2	7·26	0·908	−1·02	22	—	0·1198	34·8	−7·72
2	—	0·911	−1·02	13	—	0·1205	34·3	−7·72
9	7·45	0·931	−1·01	61	—	0·1208	36·2	−7·71
9	—	0·931	−1·01	62	—	0·1216	36·0	−7·71
8	11·35	1·419	−0·76	63	—	0·1191	75·8	−7·64
4	—	1·696	−0·64	35	—	0·1248	102·6	−7·63
4	—	1·696	−0·64	36	—	0·1266	102·8	−7·63
4	—	1·698	−0·64	31	—	0·1203	103·1	−7·63
4	13·61	1·701	−0·64	30	—	0·1211	104·3	−7·62
18	4·11	0·514	−1·28	160	25°	0·0302	5·58	−8·25
18	—	0·516	−1·28	157	—	0·0302	5·50	−8·26
17	8·28	1·035	−0·92	153	—	0·0299	15·6	−8·17
15	13·38	1·672	−0·64	142	—	0·0307	33·4	−8·11
14	—	1·974	−0·53	127	—	0·0322	45·3	−8·09
14	15·8	1·975	−0·53	129	—	0·0296	45·2	−8·09
16	20·2	2·52	−0·35	144	—	0·0308	73	−8·07
16	—	2·52	−0·35	150	—	0·0301	73	−8·07
9	7·45	0·931	−1·01	60	—	0·1196	13·7	−8·13
8	11·35	1·419	−0·76	59	—	0·1163	26·2	−8·10
8	—	1·420	−0·76	58	—	0·1201	26·3	−8·10
11	—	1·437	−0·75	106	—	0·1189	26·0	−8·11
4	—	1·696	−0·64	39	—	0·1181	35·5	−8·09
4	13·6	1·699	−0·64	37	—	0·1180	35·7	−8·09

$$\log k_e = -0{\cdot}74 + 1{\cdot}1_7 \log R \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

which resembles equation (3) except that the order of reaction with respect to R is now $1{\cdot}1_7$ (Fig. 1). The reaction was much slower than might have been expected from the results in § 1. For example, in oleum containing 16% of sulphur trioxide, *p*-nitrotoluene reacted more slowly than the phenyltrimethylammonium ion although in the same medium the *p*-tolyltrimethylammonium ion reacted too rapidly for measurement. This lack of reactivity was associated with the ability of *p*-nitrotoluene to ionise as a base in sulphuric acid (equation 6) since the

$$C_7H_7{\cdot}NO_2 + H_2SO_4 \rightleftharpoons C_7H_7{\cdot}NO_2H^+ + SO_4H^- \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

ionised form would react less readily than the uncharged molecule with an electrophilic reagent. In oleum, the proportion of reactive, un-ionised base is quite small as shown by the figures below (10^{-4}—10^{-5}M-solution) :

SO_3, %	0	2	4	6	8	10	12	14	16
Un-ionised *p*-nitrotoluene, %	19·7	4·1	2·4	1·7	1·1	0·81	0·56	0·40	0·27

In solutions which are more concentrated with respect to *p*-nitrotoluene the proportion of the un-ionised form is somewhat greater. Assuming that the ion, $C_7H_7{\cdot}NO_2H^+$, is so unreactive that sulphonation occurs entirely through the small equilibrium proportion of

TABLE IV.

Second-order velocity coefficients of the sulphonation of p-*nitrotoluene* (*temp.* 25°).

Medium. Sulphur trioxide.					
%.	mol./l.	Expt. no.	Initial concn. of $C_7H_7{\cdot}NO_2$, mol./l.	10^3k_2, (min. mole/l.)$^{-1}$.	Ref
2·4	0·56	—	0·20	5·6	1
2·4	0·56	—	0·40	4·8	1
2·18	0·50	4	0·17	4·4	3
2·16	0·50	3	0·26	4·1	3
2·17	0·50	1	0·29	4·0	3
2·14	0·49	5	0·36	3·7	3
4·12	0·96	—	0·05	5·2	3
7·45	1·75	60	0·22	7·3	3
13·3	3·14	46	0·44	11·3	3
0·91	0·21	—	0·20	5·0	2
2·47	0·69	—	0·20	5·2	2
5·47	1·27	—	0·20	5·7	2

References: 1, Martinsen, *loc. cit.* 2, Cowdrey and Davies, *loc. cit.* 3, This paper.
N.B.—In this Table, concentrations are expressed in *moles per litre*.

un-ionised base, the true velocity of reaction, calculated on the concentration of *un-ionised* *p*-nitrotoluene, would be obtained by dividing the observed values of k_e by the proportion of un-ionised molecules. When this is done (Table V and Fig. 1), the corrected coefficients, k_1, show (i) that the order of reaction with respect to R is 2·3, and (ii) that the absolute rate of reaction is similar to that observed for the *p*-tolyltrimethylammonium ion. The empirical equation which fits the results is

$$\log k_1 = 2{\cdot}32 + 2{\cdot}3_2 \log R \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The kinetics of sulphonation of the quaternary ammonium ions and of *p*-nitrotoluene are compatible, therefore, if allowance is made for the basic ionisation of the latter.

TABLE V.

Velocity of sulphonation of un-ionised p-*nitrotoluene* (*temp.* 25°) (pK_a = −10·28).

Medium. Sulphur trioxide.		Medium.				
%.	mol./kg.	log R.	H_0.	Fraction of un-ionised $C_7H_7{\cdot}NO_2$.	log 10^3k_e.	log 10^3k_1
2·14	0·267	−1·56	−11·65	0·0464	0·41	1·74
4·12	0·515	−1·24	−11·89	0·0239	0·74	2·36
7·38	0·922	−0·966	−12·17	0·0127	1·11	3·01
8·24	1·03	−0·906	−12·25	0·0106	1·19	3·16
11·36	1·42	−0·730	−12·48	0·0063	1·42	3·62
13·36	1·67	−0·632	−12·63	0·0045	1·52	3·87
15·76	1·97	−0·527	−12·81	0·0029	1·66	4·19
20·16	2·52	−0·349	−13·12	0·0014	1·86	4·70

(b) *Influence of added bases.* The sulphonation of *p*-nitrotoluene is retarded by increasing the concentration of reactant and by adding potassium sulphate or other bases to the solution (Table VI). Potassium and barium sulphates produce the same retardation at the same molar concentration. The diminution in velocity brought about by increasing the concentration of *p*-nitrotoluene is accounted for by the basicity of the compound, since the same effect is produced by an equivalent of other bases (*e.g.*, experiments 165 and 166, Table VI). The retarding influence of potassium and barium sulphates on the rate of sulphonation is much smaller than was observed with the quaternary ammonium ions, and is accounted for quantitatively by the removal of free sulphur trioxide according to equation (4). This is illustrated by the entries in the final column of Table VI, where it is shown that (log k_1 − log R) is approximately constant. (The agreement would be improved by introducing the empirical order of 1·17 from equation 5.) The velocity of reaction is, therefore, a function of the medium composition only, and equation (5) is valid in the presence of bases.

The failure of the hydrogen pyrosulphate ions to retard the reaction is only apparent. It has been shown (Part I) that these ions would displace the equilibrium of *p*-nitrotoluene in favour of the un-ionised form and this effect, which of itself would increase the velocity of reaction, opposes the inherently retarding influence of the $S_2O_7H^-$ ions. The fact that these effects so nearly balance one another is an important clue to the nature of the sulphonating agent, because it demonstrates that the concentrations of un-ionised *p*-nitrotoluene and substituting agent are affected proportionately, but in opposite senses, by a change in the acidity of the medium. With a small qualification, this is precisely the property possessed by two independent acid–base systems ($B_1H^+ \overset{K_1}{\rightleftharpoons} B_1 + H^+$; $B_2H^+ \overset{K_2}{\rightleftharpoons} B_2 + H^+$), it being readily shown that

$$[B_1][B_2H^+]/[B_1H^+][B_2] = K_1/K_2$$

(Square brackets refer to concentrations; the terms involving activity coefficients are symmetrical and have been disregarded.) The analogy with the sulphonation kinetics is demonstrated as follows: let $[B_1]$ represent the fraction of the total concentration of *p*-nitrotoluene present in the un-ionised form, let $[B_2H^+]$ represent the fractional concentration of the sulphonating agent similarly, and assume that the degree of conversion of B_2 into B_2H^+ is small. Then, because both $[B_1]$ and $[B_2H^+]$ are small compared with $[B_1H^+]$ and $[B_2]$ respectively, the rate of sulphonation, which is proportional to the product $[B_1][B_2H^+]$, is seen by rearrangement of the equation above to be constant if the *acidity* of the medium changes, *i.e.* if the total concentrations of $[B_1] + [B_1H^+]$ and $[B_2] + [B_2H^+]$ remain constant. This is the experimental result.

FIG. 1.

Variation of rate coefficients and acidity function with composition of the medium.

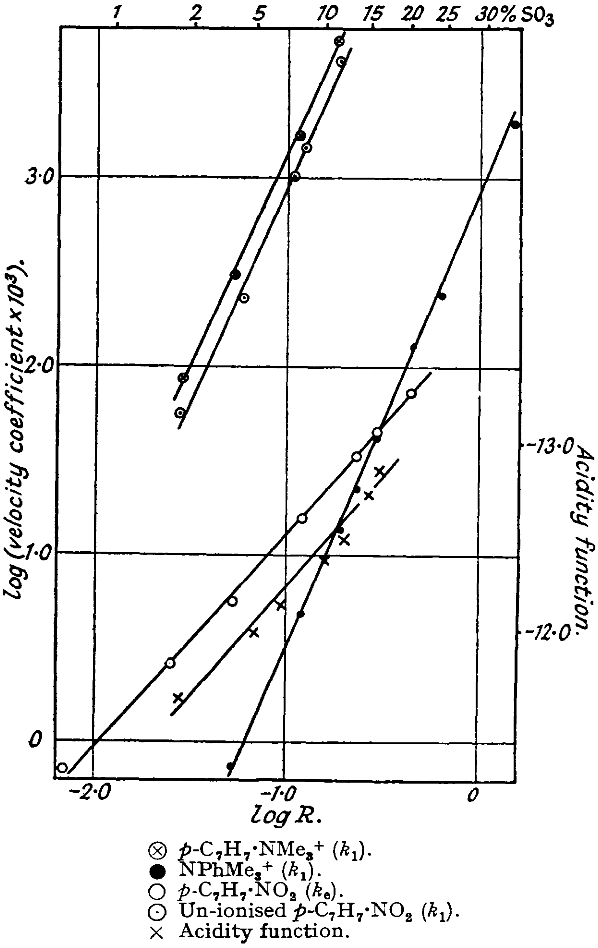

FIG. 2.

Variation of the velocity of sulphonation of nitrobenzene with the composition of the medium.

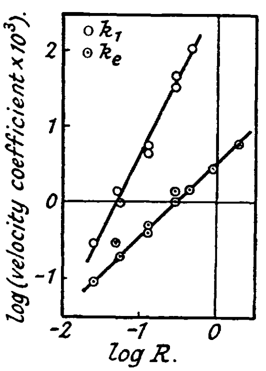

FIG. 3.

Variation of the partial pressure of sulphur trioxide with medium composition.

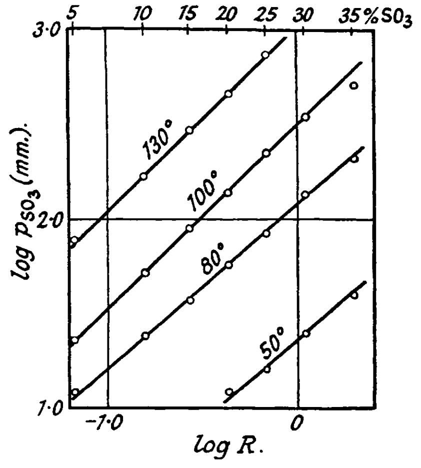

TABLE VI.

Influence of basic substances and reactant concentration upon the velocity of sulphonation of p-*nitrotoluene* (pK_a −10·28).

Medium.										
	Sulphur trioxide.						Added substance.			
Acid no.	%.	mol./kg.	log *R*.	Temp.	Expt. no.	Initial concn. of p-$C_7H_7{\cdot}NO_2$.		equiv./kg.	10^3k_e, min.$^{-1}$.	pK_a + log 10^3k_e − log *R*.
1	2·14	0·268	−1·60	35°	Table III	0·0244	—	—	7·23	−7·82
		0·269	−1·67	—	8	0·0614	—	—	7·0	−7·77
2	7·37	0·922	−0·98	—	Table III	0·025	—	—	37·1	−7·73
		0·915	−1·01	—	12	0·0873	—	—	34·0	−7·74
		0·910	−1·05	—	27	0·0251	K_2SO_4	0·130	32·0	−7·72
		0·898	−1·15	—	26	0·0256	K_2SO_4	0·281	26·0	−7·71
	7·28	0·910	−1·02	—	Table III	0·120	—	—	34·5	−7·72
		0·901	−1·09	—	25	0·119	K_2SO_4	0·098	31·2	−7·70
		0·900	−1·10	—	24	0·114	K_2SO_4	0·126	29·6	−7·71
		0·892	−1·17	—	23	0·119	K_2SO_4	0·217	26·3	−7·69
18	4·12	0·515	−1·28	25°	Table III	0·0304	—	—	5·54	−8·26
		0·508	−1·33	—	166	0·0790	—	—	5·20	−8·23
		0·508	−1·33	—	165	0·0306	$Ba(SO_4Me)_2$	0·0504	5·22	−8·23
4	13·6	1·697	−0·64	—	Table III	0·118	—	—	35·6	−8·08
		1·673	−0·68	—	47	0·120	K_2SO_4	0·1188	32·8	−8·08
		1·668	−0·71	—	40	0·117	K_2SO_4	0·1938	30·2	−8·09
		1·648	−0·76	—	41	0·117	K_2SO_4	0·3168	27·4	−8·09
		1·633	−0·79	—	44	0·117	K_2SO_4	0·3990	25·0	−8·09
		1·661	−0·70	—	42	0·128	$BaSO_4$	0·1644	31·9	−8·08
		1·644	−0·73	—	45	0·118	$BaSO_4$	0·2370	30·0	−8·08
		1·627	−0·77	—	43	0·117	$BaSO_4$	0·3516	25·5	−8·10
14	15·8	1·974	−0·53	—	Table III	0·031	—	—	45·2	−8·09
		1·947	−0·57	—	133	0·0304	K_2SO_4	0·158	41·7	−8·09
		1·921	−0·60	—	136	0·0302	K_2SO_4	0·253	38·0	−8·10
		1·878	−0·68	—	138	0·0308	K_2SO_4	0·498	31·1	−8·11

3. *Kinetics of Sulphonation of Nitrobenzene.*—The velocity of sulphonation of nitrobenzene was measured spectrometrically at 20°. The variation of the experimental coefficient, k_e, with the composition of the medium was similar to that described for *p*-nitrotoluene in § 2 (Fig. 2). The results are expressed by the empirical relation

$$\log k_e = -2{\cdot}4 + 1{\cdot}0 \log R \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

The ionisation of nitrobenzene in oleum is extensive, although not so complete as that of *p*-nitrotoluene as the following figures illustrate:

SO_3, %	0	4	8	12	16
Percentage of un-ionised nitrobenzene	70	19	9·9	5·1	2·5

The velocity of sulphonation of un-ionised nitrobenzene can be obtained by the method of § 2*a*, and is given (Fig. 2) by

$$\log k_1 = -0{\cdot}2 + 2{\cdot}3_4 \log R \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Comparing the reactivity of nitrobenzene ($k_{1(a)}$) and the phenyltrimethylammonium ion ($k_{1(b)}$), we obtain from Tables I and VII and equation (9), $k_{1(a)}/k_{1(b)} = 1{\cdot}3$ at 20°. In 87—97% sulphuric acid, where nitrobenzene is un-ionised, the relative rate of nitration is 1·9 at 25° (Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955).

Table VII.

Variation of temperature.

	Medium.					
		Sulphur trioxide.				
Temp.	Acid no.	%.	mol./kg.	Expt. no.	Initial concn. of *p*-C_7H_7·NMe_3,SO_4Me.	10^3k_1 min.$^{-1}$.
14·9°	13	2·44	0·305	91	0·0280	39
14·9	13	2·44	0·305	92	0·0293	41
14·9	13	2·43	0·304	93	0·0307	40
20·0	13	2·44	0·305	94	0·0259	64·3
20·0	13	2·43	0·304	95	0·0314	53·8
20·0	13	2·42	0·303	96	0·0303	62·8
35·0	13	2·44	0·305	88	0·0320	180
35·0	13	2·45	0·306	89	0·0301	210
35·0	13	2·44	0·305	90	0·0277	188
0·0	18	4·09	0·512	161	0·0301	38·9
0·0	18	4·11	0·514	159	0·0303	38·7
					$NPhMe_3$, SO_4Me.	
45·0°	18	4·09	0·512	164	0·0301	4·21
45·0	18	4·07	0·512	163	0·0302	4·26
0·0	11	11·60	1·450	113	0·0292	1·38
40·0	11	11·58	1·448	114	0·0301	45·2
40·0	11	11·61	1·451	115	0·0291	46·8
0·0	14	15·73	1·969	121	0·0290	4·24
0·0	14	15·72	1·968	124	0·0307	4·12
15·4	14	15·73	1·969	126	0·0302	18·4
40·0	14	15·73	1·969	123	0·0301	139·4
40·0	14	15·72	1·968	125	0·0302	140·4
0·0	16	20·1	2·515	147	0·0302	13·1
					p-C_7H_7·NO_2.	10^3k_e.
45·0°	18	4·08	0·514	162	0·0306	44·7
15·0	9	7·45	0·931	66	0·120	4·38
45·0	9	7·45	0·931	65	0·119	115
15·0	8	11·35	1·42	67	0·120	5·81
45·0	8	11·35	1·42	64	0·119	147
0·0	14	15·75	1·97	130	0·0308	2·30
0·0	16	20·2	2·52	145	0·0300	3·82

Note on the Sulphonation of Anthraquinone.—The measurements of Lauer and others (*loc. cit.*) on the velocity of sulphonation of anthraquinone in oleum media were conducted with equal concentrations of anthraquinone and sulphur trioxide. First-order velocity coefficients were obtained which varied in a complicated fashion with reactant concentration. Dilute solutions of anthraquinone in oleum are almost quantitatively converted into the conjugate ion ($pK_a = -8{\cdot}15$), but the exceedingly concentrated solutions employed by Lauer contained a kinetically significant proportion of un-ionised anthraquinone, and the interpretation of the results is not straightforward. The view of Lauer and his associates that undissociated sulphuric acid is the effective substituting agent in oleum depended on a mistaken process of correcting the experimental heat of activation by addition of the heat of solution of the product in different oleum media.

4. *Influence of Temperature.*—The variation of the velocity coefficients with temperature for several media may be seen from Table VII, together with results at 25° and 35° from previous tables. For a given medium, log k_1 or log k_e is a linear function of $1/T$. The constants of the Arrhenius equation are assembled in Table VIII. The observation that the apparent heat of activation of *p*-nitrotoluene exceeds that of either of the quaternary ions is an independent argument for the existence of an unreactive form in solution, because in this case the temperature-dependent factor contains a term corresponding to the heat of the reaction represented by equation (10), reading from right to left :

$$p\text{-}C_7H_7{\cdot}NO_2 + H_2S_2O_7 \rightleftharpoons p\text{-}C_7H_7{\cdot}NO_2H^+ + S_2O_7H^- \quad . \; . \; . \; . \; . \quad (10)$$

The fact that the pre-exponential factor, A, is close to 10^{11} has been quoted elsewhere as evidence of a bimolecular reaction, but is misleading.

Within the error of measurement, the relative rate of sulphonation of the *p*-tolyl- and phenyl-trimethylammonium ions is accounted for by the difference in activation energies. The activation energies themselves are probably composite quantities.

TABLE VIII.

Constants of the equation, $k_1 = A.e^{-E/RT}$*.

Sulphur trioxide.		$NPhMe_3,SO_4Me$.		$p\text{-}C_7H_7{\cdot}NMe_3,SO_4Me$.		$p\text{-}C_7H_7{\cdot}NO_2$.	
%.	concn. mol./kg.	*E*.	log *A*.	*E*.	log *A*.	*E*.†	log *A*.
2·13	0·267	—	—	—	—	19·9	10·23
2·44	0·305	—	—	13·5	7·07	—	—
4·10	0·513	16·3	7·05	13·2	7·42	19·6	10·32
7·45	0·931	—	—	—	—	19·7	10·75
11·35	1·42	—	—	—	—	19·5	10·91
11·60	1·45	14·9	7·30	—	—	—	—
13·7	1·71	—	—	—	—	19·4	10·99
15·7	1·97	15·0	7·83	—	—	19·3	11·06
20·1	2·52	14·9	8·27	—	—	19·2	11·18
24·2	3·02	15·2	8·72	—	—	—	—

* k_e was used in the case of *p*-nitrotoluene : k_1 and k_e were expressed in *seconds*$^{-1}$ at 25° for the calculation of the pre-exponential factor.

† Cowdrey and Davies (*loc. cit.*) found $E = 18$ kcals.

DISCUSSION.

Interpretation of the kinetics is handicapped by incomplete knowledge of the equilibria prevailing in oleum, and by lack of information concerning the influence of the medium and other dielectric effects. It is possible, however, to account for the foregoing in a self-consistent way by assuming that the sulphonating agent in oleum is the ion SO_3H^+, and that substitution occurs according to the equation :

$$SO_3H^+ + ArH = ArSO_3H + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

Stubbs, Williams, and Hinshelwood (*loc. cit.*) have previously assumed that the reactive ion SO_3H^+ is formed in solutions of sulphuric acid in nitrobenzene.

Variation of the Rate of Sulphonation with Composition of the Medium.—If the velocity coefficient of equation (11) is denoted by k, the equation for the rate of sulphonation takes the form

$$-d[ArH]/dt = k[ArH][SO_3H^+] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

Experimentally, equation (2) applies to a particular set of initial concentrations in a given medium. By combining it with equation (12) we obtain

$$\log k_1 = \log k + \log [SO_3H^+] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

Equation (13) should describe the variation of k_1 with change of medium (apart from purely physical changes), change of reactant concentration, or any other condition except change of temperature. Assuming that *molecular* sulphur trioxide (SO_3) and the SO_3H^+ ion can be treated as a normal acid–base pair, their concentrations will be related to the acidity function of the medium by equation (14), where K_A is the acidic ionisation constant of the ion SO_3H^+, a quantity of unknown magnitude :

$$H_0 = pK_A + \log [\mathit{SO}_3] - \log [SO_3H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The concentration of molecular sulphur trioxide will be italicised to distinguish it from the stoicheiometric concentration of free sulphur trioxide. These quantities are not independent of one another (equilibrium 15), but are altogether different in magnitude.

The concentration of molecular sulphur trioxide is determined by the equilibrium (15), the equilibrium constant, K, of which, expressed in terms of concentrations, is given by $K = [H_2S_2O_7]/[H_2SO_4][\mathit{SO}_3]$.

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If the dissociation of pyrosulphuric acid, by equilibrium (15) or otherwise, is assumed to be small, the expression for the concentration of molecular sulphur trioxide becomes

$$\log [\mathit{SO}_3] = -\log K + \log R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where R is the stoicheiometric molar ratio, $H_2S_2O_7/H_2SO_4$, defined in § 1*a*. Equation (16) may be tested by plotting $\log p_{(SO_3)}$ against $\log R$, where $p_{(SO_3)}$ is the partial pressure of sulphur trioxide in oleum (Fig. 3; data of Miles, Niblock, and Wilson, *loc. cit.*) : the relation is linear up to 35% oleum, and the slope is unity at 100° and 0·9 at 50° (at lower temperatures the vapour pressure was insufficient for accurate measurement). This appears to justify the use of equation (16) and, by combination of it with (14), the expression for the concentration of the sulphonating agent becomes

$$\log [SO_3H^+] = (pK + pK_A) + \log R - H_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Equation (17) can be used to evaluate the relative concentration of SO_3H^+ in different media, and the extent to which it is proportional to the velocity of sulphonation is illustrated in Table IX. Equation (17) may also be simplified by expressing the acidity function as an approximately linear function of $\log R$ (Fig. 1), $H_0 = -13{\cdot}5 - 1{\cdot}2 \log R$. Inserting this result into equation (17) gives : $\log [SO_3H^+] =$ a constant $+ 2{\cdot}2 \log R$, which is an expression of the same form as the empirical equations of § 1—3, and furnishes correctly the order of reaction with respect to R.

TABLE IX.

Relation between the velocity of sulphonation of $NPhMe_3^+$ *and the concentration of* SO_3H^+ *ions.*

(Initial concn. of $NPhMe_3,SO_4Me$: 0·03 mol./kg. Temp., 25°.)

Sulphur trioxide %	4·09	8·23	11·60	13·4	15·7	20·1
Sulphur trioxide concn., mol./kg.	0·51	1·03	1·45	1·67	1·97	2·51
Relative concn. of SO_3H^+	0·0069	0·0363	0·102	0·166	0·32	1·0
10^3k_1	0·75	4·8	13·6	22·4	42·0	128
$k_1/[SO_3H^+]$	0·11	0·13	0·13	0·13	0·13	0·13

The complete theoretical expression for the velocity of sulphonation of the quaternary ammonium ions and the un-ionised forms of *p*-nitrotoluene and nitrobenzene is obtained from equations (13) and (17), *viz.* :

$$\log k_1 = \log k + \log R - H_0 + (pK + pK_A) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In the case of the nitro-compounds, the experimental coefficients, k_e, are related to the coefficients k_1 of the un-ionised forms by the equation, $k_e = k_1[B]$, [B] representing the fraction of the total concentration of the reactant present in the un-ionised form. In the regions where sulphonation occurs with measurable speed, both *p*-nitrotoluene and nitrobenzene are almost quantitatively ionised and, therefore, $\log [B] \sim pK_a - H_0$ (where pK_a is the acidic ionisation constant of the ionised form), and the expression for the observed velocity of sulphonation is (cf. Table X)

$$\log k_e = \log k - \log R - pK_a + (pK + pK_A) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Experimentally, the order of reaction with respect to R were observed to be 1·2 and 1·0 for *p*-nitrotoluene (equation 5) and nitrobenzene (equation 8) respectively. If attention is confined to a small range of composition of the medium, the variation of the sulphuric acid mole fraction may be neglected and, therefore, $[\mathit{SO}_3] \propto [SO_3]$ (cf. equation 16). Introducing this approximation in place of equation (16) yields $k_e \propto [SO_3]$, which by combination with equation (2*a*) gives the empirical equation (1), which is a satisfactory expression in weak oleum over a limited range of medium composition.

TABLE X.

Dependence of the velocity of sulphonation of p-*nitrotoluene on the concentration of molecular sulphur trioxide.*

(Initial concn. of $C_7H_7{\cdot}NO_2$: 0·03 mol./kg. Temp., 25°.)

Sulphur trioxide %	0·75	4·11	8·28	13·4	15·8	20·2
Sulphur trioxide concn., mol./kg.	0·094	0·51	1·03	1·67	1·97	2·52
R	0·00676	0·0525	0·120	0·229	0·296	0·45
10^3k_e	0·75	5·58	15·6	33·4	45·3	73
k_e/R	0·11	0·11	0·13	0·15	0·15	0·16

The interpretation of the variation of the velocity of sulphonation with the composition of the medium may be summarised as follows: the substituting agent is assumed to be the ion SO_3H^+, the concentration of which is small compared with that of molecular sulphur trioxide; an increase in the total concentration of sulphur trioxide (all forms) brings about (i) an increase in the concentration of molecular sulphur trioxide, and (ii) an increase of acidity, producing a higher degree of conversion of molecular sulphur trioxide into SO_3H^+ ions. The factors (i) and (ii) co-operate, and contribute almost equally to the overall variation of k_1 with the medium composition. With *p*-nitrotoluene and nitrobenzene, (ii) is compensated by a proportionate diminution in the concentration of un-ionised forms, and the variation is accounted for by changes in the concentration of molecular sulphur trioxide alone.

The Influence of Added Salts.—A preliminary account of this subject was given in § 1*b* and § 2*b*, where it was shown that bisulphate ions retard the reaction (i) by diminishing the concentration of free sulphur trioxide according to equation (4), and (ii) by diminishing the acidity by production of $S_2O_7H^-$ ions; each of these factors lowers the concentration of SO_3H^+ ions (equation 14). For *p*-nitrotoluene and nitrobenzene, the changes in the concentration of the un-ionised forms of the nitro-compounds and in the concentration of SO_3H^+ ions are inversely proportional to one another, and the observed retardation is accounted for entirely by the first of the factors listed above. In the presence of salts giving rise initially to bisulphate ions, the extent to which the velocities of sulphonation of *p*-nitrotoluene and the phenyltrimethylammonium ion are proportional respectively to the concentrations of molecular sulphur trioxide and of SO_3H^+ ions is shown in Table XI.

TABLE XI.

Influence of bisulphate ions on the concentration of molecular sulphur trioxide and on the rate of sulphonation of p-*nitrotoluene.*

(Initial concn. of $C_7H_7{\cdot}NO_2$: 0·12 mol./kg. Temp., 25°.)

Medium. Sulphur trioxide. %.	Medium. Sulphur trioxide. concn., mol./kg.	Medium. R.	Added substance.	Added substance. concn., equiv./kg.	10^3k_e, min.$^{-1}$.	k_e/R
13·6	1·697	0·227	—	—	35·6	0·157
—	1·673	0·207	K_2SO_4	0·1188	32·8	0·158
—	1·661	0·200	$BaSO_4$	0·1644	31·9	0·159
—	1·668	0·196	K_2SO_4	0·1938	30·2	0·154
—	1·644	0·187	$BaSO_4$	0·2370	30·0	0·160
—	1·648	0·175	K_2SO_4	0·3168	27·4	0·156
13·0	1·627	0·169	$BaSO_4$	0·3516	25·5	0·151
—	1·633	0·161	K_2SO_4	0·3990	25·0	0·155

Influence of basic anions on the concentration of SO_3H^+ *and on the rate of sulphonation of* $NPhMe_3^+$ (temp., 25°).

Sulphur trioxide. %.	Sulphur trioxide. concn., mol./kg.	Added substance.	Added substance. concn., equiv./kg.	Initial concn. of $C_7H_7{\cdot}NO_2$, mol./kg.	Relative concn. of SO_3H^+.	10^3k_1.	$k_1/[SO_3H^+]$.
11·6	1·45	—	—	0·030	1·0	13·6	0·0136
—	1·43	—	—	0·074	0·76	10·0	0·0132
—	1·44	K_2SO_4	0·0501	0·029	0·74	10·2	0·0137
—	1·44	$Ba(SO_4Me)_2$	0·0503	0·030	0·74	10·8	0·0145
—	1·43	K_2SO_4	0·0870	0·030	0·58	8·19	0·0141
11·4	1·43	K_2SO_4	0·150	0·030	0·37	5·8	0·0157

The equations (18) and (19) have been tested comprehensively by tabulating values of ($\log k_1 + H_0 - \log R$) and ($\log k_e + pK_a - \log R$) in the final colums of Tables I and II, and

Tables III and VI respectively. Each of these expressions is equal to (log k + a constant), and should, therefore, be constant for a particular aromatic compound at a fixed temperature, in so far as k is itself independent of the composition of the medium. Examination of the Tables shows that the extensive experimental variation of the rate of sulphonation is very largely accounted for by the theoretical equations (18) and (19). The deviations which are observed correspond to a gradual rise of k when the concentration of sulphur trioxide is increased, or in the presence of a large concentration of bisulphate ions. The average results obtained for the relative velocity of substitution according to equation (11) at 25° are :

	Relative velocity coefficient (eqn. 11).
p-$C_7H_7 \cdot NMe_3,SO_4Me$	360
Un-ionised *p*-$C_7H_7 \cdot NO_2$	290
Un-ionised $PhNO_2$ *	1·5
$NPhMe_3,SO_4Me$	1·0 (overall) 0·8 (*m*-positions)

* Calc. from results at 20°, using E = 22 kcals.

The sulphonation of unionised *p*-nitrotoluene occurred more slowly than that of the *p*-tolyltrimethylammonium ion, in spite of the fact that un-ionised nitrobenzene reacted faster than $NPhMe_3^+$. The difference is associated with the large interval between the basic strengths of *p*-nitrotoluene and nitrobenzene (Part I), the withdrawal of electrons from the aromatic nucleus by the nitro-group being quantitatively different in the two cases. The velocity of sulphonation of *p*-nitrotoluene was reduced, apparently, at least one-thousand-fold by the addition of a proton, and no definite kinetic evidence of reactivity on the part of the ionised form was obtained.

The scale of the relative velocities of sulphonation is more condensed than is observed for nitration of the same systems, even after taking account of the fact that the phenyltrimethylammonium ion is not sulphonated exclusively in the *m*-position; these two facts should, indeed, be considered together, for the SO_3H^+ ion, being less powerfully electrophilic, is less susceptible to electrostatic influences than is NO_2^+.

EXPERIMENTAL.

Materials.—Phenyltrimethylammonium methyl sulphate, m. p. 126°, and *p*-tolyltrimethylammonium methyl sulphate, m. p. 144·5°, were obtained from the corresponding tertiary amines and methyl sulphate in acetone. The purification of nitrobenzene and *p*-nitrotoluene was referred to in Part I. AnalaR Potassium sulphate, potassium hydrogen sulphate, and potassium nitrate were used and were dried before use. Pure barium sulphate was prepared by slowly adding 0·1M-barium hydroxide to very dilute ($\frac{1}{3}$%) boiling sulphuric acid. Barium di(methyl sulphate) [Found : Ba, 38·2, 38·4. Calc. for $Ba(SO_4Me)_2$: Ba, 38·2%)] was dried *in vacuo* over phosphoric oxide and used freshly prepared. The preparation and analysis of oleum have been described previously (Brand, *J.*, 1946, 585).

Velocity Measurements.—These were made at 15·0°, 20·0°, 25·0°, 35·0°, 40·0°, and 45·0° in a thermostatically controlled water-bath and at 0° in an ice-bath. The compound to undergo sulphonation was added as a solid to the oleum, and the start of the reaction timed from this addition. Tests made to determine whether thermal effects occurred on mixing showed a rise in temperature amounting in unfavourable cases to several tenths of a degree. Precautions were taken to compensate for this.

Sampling and Analysis.—For convenience, the solutions were prepared and analysed by weight. During the reaction, samples of the solution were removed by pipette and delivered into concentrated sulphuric acid containing sufficient water to react with the sulphur trioxide introduced. The method of analysis depended on the fact that the unsulphonated aromatic molecules were sufficiently reactive to be estimated quantitatively by nitration in the presence of the sulphonic acids (Martinsen, *loc. cit.*). This was accomplished by adding a standard solution of potassium nitrate in concentrated sulphuric acid to the "arrested" sample and, after a suitable interval, determining the nitric acid by pententiometric titration with ferrous sulphate (Treadwell and Vontobel, *Helv. Chim. Acta*, 1937, **20**, 573). The concentration of the reactant was calculated from the consumption of nitric acid.

The time required for quantitative nitration ranged from one minute or less for *p*-nitrotoluene to some 20 hours at 25° for phenyltrimethylammonium methyl sulphate. Tests showed that no nitration of *p*-nitrotoluene-*o*-sulphonic acid, *p*-tolyltrimethylammonium-2-sulphonate, 4 : 1 : 2-$Me_3N^+ \cdot C_6H_3Me \cdot SO_3^-$, or phenyltrimethylammonium-3-sulphonate occurred in a corresponding period. The analysis was tested repeatedly; some typical results for *p*-nitrotoluene were :

Wt. taken, g.	0·1126	0·1304	0·0981	0·0677	0·0956	0·0907
Found, g.	0·1134	0·1302	0·0985	0·0668	0·0961	0·0906

(Total weight of 0·5951 g. estimated as 0·5956 g.)

Similar determinations with *p*-tolyltrimethylammonium methyl sulphate (*M*, 261) and phenyltrimethylammonium methyl sulphate (*M*, 247) gave an average molecular weight of 260 and 245, respectively.

Some decomposition occurred during the sulphonation of *p*-nitrotoluene, generating about 10^{-4} mole of sulphur dioxide during complete reaction in the more concentrated media. Although the loss of *p*-nitrotoluene was, therefore, small, appreciable reduction of nitric acid occurred during the analysis by nitration, and a correction applied to allow for this raised the velocity coefficient by 1—2%.

Disappearance of Sulphur Trioxide during Sulphonation.—In a number of kinetic experiments the concentration of sulphur trioxide was determined at the end of reaction. Some typical results are given below for the sulphonation of phenyltrimethylammonium methyl sulphate, and indicate that the amount of moisture absorbed during manipulation is small. Similar results were obtained on using *p*-tolyltrimethylammonium methyl sulphate and *p*-nitrotoluene.

	Expt. no. :	105	114	115	109	110	120	123
Initial concn. (M.) of $NPhMe_3,SO_4Me$ ...		0·0296	0·0301	0·0291	0·0733	0·0747	0·0312	0·0301
Sulphur trioxide :								
Initial concn. (M.)		1·451	1·448	1·451	1·434	1·435	1·968	1·969
Final concn.	Found (M.)	1·405	1·391	1·432	1·359	1·360	1·923	1·934
	Calc. (M.)	1·421	1·418	1·422	1·361	1·360	1·937	1·939
	%	98·9	98·1	100·7	99·9	100·0	99·3	99·7

Measurement of the Velocity of Reaction by Alternative Methods.—(*a*) *Change in light absorption.* The velocity of sulphonation of nitrobenzene was obtained by measurement of the initial rate of change of the extinction coefficient, at λ 3650 A., of the solution in oleum. The initial concentration of nitrobenzene was approximately 10^{-4}M., and the results are shown in Fig. 2. As a test of the method, the velocity of sulphonation of *p*-nitrotoluene was also measured and compared with the value obtained by chemical analysis (Tables III and VII) :

Temp.	Medium, $[SO_3]$, mol./kg.	k_1 (min.$^{-1}$). By light absorption.	By chem. analysis.
18°	0·513	0·00258	0·00251
—	0·280	0·00107	0·00106

(*b*) *Dilatometry.* Some experiments were made with a dilatometer so constructed that the capillary limb formed the stopper of the reaction vessel, but were discontinued. However the results served as a useful check and agreed with those obtained by chemical analysis :

Expt. no.	Temp.	Medium, $[SO_3]$, mol./kg.	Initial concn. of	mol./kg.	k_e (min.$^{-1}$). By dilatometer.	By chem. analysis.
54	25°	1·437	p-C_7H_7·NO_2	0·025	0·025	0·026
57	25	1·436	p-C_7H_7·NO_2	0·026	0·025	0·026
53	25	1·62	p-C_7H_7·NO_2	0·026	0·033	0·031
68	35	1·426	$NPhMe_3,SO_4Me$	0·046	0·029	0·029 *

* The velocity coefficient is k_1 in this experiment.

(*c*) *Analysis of the sulphonic acid formed.* Experiments on the rate of formation of 4-nitrotoluene-2-sulphonic acid were carried out as follows. Samples of the reaction mixture were diluted with water, and the sulphuric acid was removed with barium carbonate; the resulting solution of barium 4-nitrotoluene-2-sulphonate (containing some barium carbonate) was concentrated to a standard volume and the barium determined gravimetrically by precipitation with sulphuric acid The results of two such experiments were :

Expt. no.	Temp.	Medium, $[SO_3]$, mol./kg.	Initial concn. of p-C_7H_7·NO_2, mol./kg.	k_e (min.$^{-1}$) analysis for 4-nitrotoluene-2-sulphonic acid.	p-nitrotoluene.
70	25°	1·41	0·1212	0·026	0·026
71	25	1·41	0·1214	0·027	

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