365. *The Hydrolysis of Arylsulphuric Acids. Part III.*

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In Parts I and II (Burkhardt, Ford, and Singleton, this vol., p. 17; Burkhardt, Warhurst, and Evans, *ibid.*, p. 25) it was shown that the rate of the acid hydrolysis of a substituted potassium phenylsulphate is approximately proportional to the concentration of phenylsulphate and of hydrogen ion, and that the influence of a series of simple substituents on the rate of reaction is directly comparable with the effects of these substituents on other reactions. The present communication presents further evidence that the correct kinetic expressions have been used, and considers the results obtained by measurements of increased accuracy and by the study of a wider range of substituents in the aromatic nucleus.

Salt Effect and Possible Secondary Catalytic Effects.—With solutions of highly purified potassium *p*-tolylsulphate ($M/12$) and hydrochloric acid ($N/24$) the addition of potassium chloride up to a concentration equal to that of the tolylsulphate produced only a slight decrease in velocity. This is the normal salt effect if the reaction occurs, as is assumed, between the oppositely charged phenylsulphate and oxonium ions:

$$\begin{tikzcd} \mathrm{Ph{\cdot}O{\cdot}SO_2{\cdot}O' + H_3O^{\cdot} + H_2O + (K^{\cdot} + Cl')} \arrow[r] & \mathrm{Ph{\cdot}OH +} & \mathrm{HSO_4'} \arrow[d, shift left] & \mathrm{+ H_3O^{\cdot} + (K^{\cdot} + Cl')} \\ & & \mathrm{H^{\cdot} + SO_4''} \arrow[u, shift left] & \end{tikzcd}$$

On the preliminary evidence available, it was assumed that the oxonium ion was the sole catalyst, and although satisfactory constants were obtained on this basis, there was a possibility that other ions (particularly the bisulphate ion) could exert minor catalytic effects. In order to study the effect of the bisulphate and sulphate ions, measurements of the rates of hydrolysis were made with potassium hydrogen sulphate as the source of hydrogen ions. Constant concentrations of bisulphate ($0{\cdot}1M$) and phenylsulphate ($0{\cdot}0833M$) were used, and increasing amounts of potassium sulphate added. A marked retardation occurs with successive additions, and finally, as shown in Fig. 1, reaction velocity becomes negligible. This contrasts with the considerable final speed obtained by a similar method in the hydrolysis of ethyl acetate in the presence of potassium hydrogen sulphate (Dawson, Pycock, and Spivey, J., 1933, 291). The rapid fall in velocity is considered to be due to suppression of the bisulphate ion dissociation, and the negligible velocity finally attained is in accord with the absence of a catalytic effect from the bisulphate and sulphate ions.

No evidence was obtained to suggest that the phenol formed during the reaction had any marked catalytic effect. Only in the hydrolysis of the nitro- and carboxy-phenylsulphates was there an upward drift of the calculated velocity " constants " which might be ascribed to the hydroxy-derivative liberated in the course of the reaction, and in these cases the more strongly acidic nature of the phenols made the titration more difficult.

In Part I the dissociation constant (K) of the bisulphate ion has been taken as 0·01, the value found by Dawson, Pycock, and Spivey (*loc. cit.*) for salt-free solution in the hydrolysis of ethyl acetate at 25°. An estimate of the heat of dissociation of the bisulphate ion (Pedersen, *J. Physical Chem.*, 1934, **38**, 613) indicates a fairly large decrease of the ionisation constant with temperature. This is confirmed by Hamer's results (*J. Amer. Chem. Soc.*, 1934, **56**, 860), but extrapolation of his values (which agree with those obtained by Dawson, Pycock, and Spivey at 25°) gives a value near 0·002 for salt-free solution at 80°. The inconsistency between this conclusion and the application of the value $K = 0{\cdot}01$ at both temperatures in Part I would be explained if the temperature coefficients of the salt effect and of the ionisation of HSO_4' counterbalanced one another in the phenylsulphate hydrolysis. The use of potassium hydrogen sulphate as the source of hydrogen ions gives velocity constants much more sensitive to the values of K adopted than those obtained by using mineral acid, but with the correct value of K the same constants should be obtained with both sources of catalyst in the absence of other catalytic influences. The results given in Table I have been obtained by taking two arbitrary values for K and they show agreement of the calculated constants when $K = 0{\cdot}01$. Experiments are compared where the salt concentrations are approximately the same (the amount of hydrochloric acid not being included; cf. Dawson, Pycock, and Spivey).

Fig. 1.

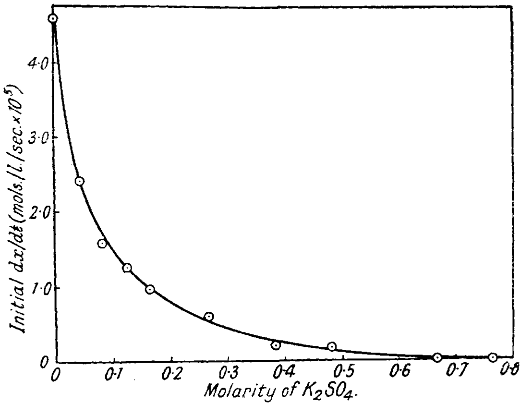


TABLE I.

Hydrolysis of p-*tolylsulphate by potassium hydrogen sulphate at* 78·7°.

(Values of k in g.-mols./l./sec.)

p-Tolylsulphate.	HCl.	KHSO₄.	KCl.	Value of 100 k for	
				$K = 0{\cdot}007$.	$K = 0{\cdot}01$.
(a) $N/12$	$N/12$	—	—	0·234	0·238
$N/24$	—	$N/24$	—	0·280	0·241
$N/24$	—	$N/48$	$N/48$	0·275	0·240
(b) $N/18$	$N/24$	—	—	0·240	0·237
$N/36$	—	$N/72$	$N/72$	0·269	0·237
(c) $N/24$	$N/24$	—	—	0·242	0·238
$N/48$	—	$N/48$	—	0·271	0·237
$N/48$	—	$N/96$	$N/96$	0·263	0·235

On the basis of the previous work cited above, the deviation from a value of 0·01 for K would be expected to be greater at 78·7° than at 48·7°. At the latter temperature the hydrolysis with similar concentrations of potassium hydrogen sulphate is very slow, but experiments with $N/24$-*p*-tolylsulphate and $N/72$- or $N/24$-potassium hydrogen sulphate indicate satisfactory values of K to be 0·0095 and 0·007 respectively. The use of $K = 0{\cdot}01$ in Parts I and II is, therefore, not liable to any serious error, and this value has been employed in the evaluation of velocity constants at all the temperatures used in the present work.

Results.—Velocity constants have been obtained as in Parts I and II, but in a number of cases, particularly when the concentrations given there were inconvenient and the approximate expression was therefore inapplicable in the form stated, an integrated expression without approximations was used, *viz.*,

$$\frac{k(t_2 - t_1)}{2{\cdot}303} = \frac{2}{D-F}\log\frac{D+z_2}{D+z_1} + \frac{2}{D+F}\log\frac{D-z_1}{D-z_2} - \frac{F}{0{\cdot}01(a+b)}\log\frac{F+z_2}{F+z_1} \quad . \quad . \quad (1)$$

where a and b are respectively the initial concentrations of bisulphate and arylsulphate, x is the increase in bisulphate concentration in time t, $D^2 = (a + 0{\cdot}01)^2 + 0{\cdot}04b$, $F = a - 0{\cdot}01$, $z^2 = (a + 0{\cdot}01)^2 + 0{\cdot}04x$, and D and F are, therefore, constants for any one experiment. The subscripts refer to the value of z at times t_1 and t_2. With this expression, satisfactory constants have been obtained as shown in Table II.

TABLE II.

Hydrolysis of potassium p-*ethylphenylsulphate with hydrochloric acid.*

$a = 0{\cdot}0398$; $b = 0{\cdot}0935$; temp. = 78·7°.

x_1	0	0·005	0·010	0·015	0·020	0·025	0·030
x_2	0·02	0·025	0·030	0·035	0·040	0·045	0·050
100 k (mols./l./sec.) ...	0·247	0·248	0·252	0·253	0·248	0·253	0·253

In the experiments with p-tolylsulphate, potassium hydrogen sulphate being used to provide the initial hydrogen-ion concentration, velocity constants were derived from the expression $dx/dt = k(b - x)[H_3O^{\bullet}]$, where b and x have the same significance as previously, and $[H_3O^{\bullet}]$ is obtained from $[H^{\bullet}]([H^{\bullet}] + r)/\{(a + x) - [H^{\bullet}]\} = K$, where r is the initial concentration of sulphate ion due to the small amount of stabilising alkali in the phenylsulphate solution. Values of dx/dt obtained by a tangent method were in good agreement with those obtained by the integrated expression analogous to (1).

Data for p-nitro- and p-methyl-phenylsulphates have been obtained at additional temperatures (p-NO_2, $k_{67{\cdot}6^{\circ}} = 4{\cdot}58 \times 10^{-3}$; $k_{24{\cdot}9^{\circ}} = 2{\cdot}43 \times 10^{-5}$; p-CH_3, $k_{67{\cdot}7^{\circ}} = 6{\cdot}72 \times 10^{-4}$), and a satisfactory linear relationship between log k and $1/T$ is found. Velocity constants for the other substances have been determined at 48·7° and 78·7°, and the data analysed by application of the Arrhenius equation $k = \alpha e^{-E/RT}$, which is assumed to apply to all the substituted phenylsulphates. The results are in Table III, which includes those obtained in Part I for comparison.

TABLE III.

Ref. No.	Substituent or aryl group	$k_{48{\cdot}7^{\circ}} \times 10^4$.	$k_{78{\cdot}7^{\circ}} \times 10^2$.	E.	$\alpha \times 10^{-11}$.
1	p-NO_2	4·50	1·20	24,600	243
2	p-CHO	3·87	1·01	24,400	155
3	o-NO_2	3·58*	0·880	23,800	61
4	p-Ac	3·32	0·770	23,600	35
5	o-CHO	1·75	0·580	26,200	1170
6	m-NO_2	2·05*	0·578	24,850	182
7	m-CHO	1·52	0·453	25,400	293
8	o-OMe	1·33*	0·453	26,350	1060
9	o-Cl	1·30*	0·442	26,200	1020
10	m-Ac	1·40	0·418	25,500	280
11	β-$C_{10}H_7$	1·15	0·382	26,200	790
12	p-Cl	1·08†	0·362	26,200	300
13	m-OMe	1·02*	0·340	26,100	675
14	(H)	0·89*	0·335	27,000	2453
15	m-CH_3	0·88*	0·320	26,700	1483
16	o-CH_3	0·77*	0·272	26,500	883
17	p-C_2H_5	0·74	0·251	26,300	532
18	o-C_6H_5	0·665	0·245	27,000	1533
19	α-$C_{10}H_7$	0·642	0·245	27,300	2250
20	p-CH_3	0·687	0·238	26,600	788
21	p-OMe	0·450*	0·180	27,400	2267
22	Thymyl	0·332	0·146	28,400	6183
23	o-C_2H_5	0·318	0·137	28,200	4400

* At 48·6°.

† At 48·8°.

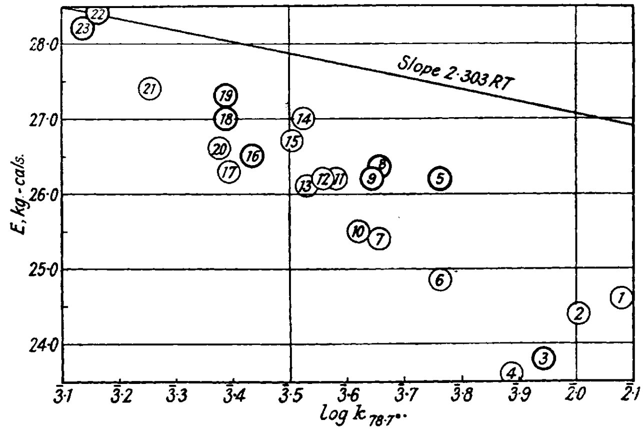
The data for the additional substituents confirm the conclusion reached in Part I, that the reaction velocity is increased by substituents causing electron recession from the sulphate group, and this aspect is discussed in Part IV (following paper).

The Results in Terms of the Arrhenius Equation.—Particularly in reactions involving an ion and a neutral molecule, the empirically determined term α approximates to the calculated total number of collisions Z (Grant and Hinshelwood, J., 1933, 258; Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, 1933), a result which requires special explanation on the collision theory in the case of large molecules, where the number of suitably oriented collisions will be some powers of 10 less than the total number of collisions (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; Hinshelwood and Winkler, this vol., p. 376). Special consideration has been given to the very low values for P ($\alpha = PZ$) found for some reactions, and a few high values have been observed.

The arylsulphuric acid hydrolysis gives values of P greater than unity. The value of Z calculated from simple collision theory is about 3×10^{11}, with negligible variations due to differences of molecular weights and ionic sizes for the various phenylsulphates. If a correction is applied for the uneven distribution of ions in solution (Christiansen, *Z. physikal. Chem.*, 1934, **113**, 35), this will not raise this value of Z by more than a factor of 10, but values for α of 10^{14} or higher are obtained in nearly 50% of the cases examined.

The opposite charges on the reactants may well influence their coming together and interpenetration in a suitable orientation, and so lead to high values of α (cf. Hinshelwood and Winkler, *loc. cit.*). It is also very plausible to regard the inactivity of the bisulphate ion as a catalyst as due similarly to its bearing a negative charge like the phenylsulphate ion. Reactions between similarly charged ions often give low values of α ($\sim 10^8$), and one reaction between oppositely charged ions gives a remarkably high value ($\sim 10^{18}$) (see Moelwyn-Hughes, *op. cit.*, pp. 216, 218), but as the corresponding activation energies are low for similarly charged and high for oppositely charged ions, the effect of the selection of reactions as convenient for investigation may account for this trend in the data available.

FIG. 2.



The numbered circles correspond with substituents as given in Table III. Thickened circles refer to arylsulphates containing o-*groups.*

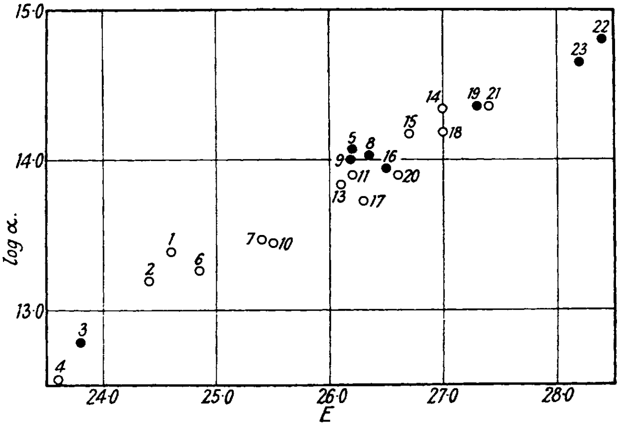
The graph of log $k_{78\cdot 7^{\circ}}$ against E (compare Hinshelwood and Williams, J., 1934, 1079) for the data in this investigation (Fig. 2) shows that, although the points for the hydrolysis of the various phenylsulphates deviate considerably from a straight line, yet they lie in a zone in such a way as to show clearly that the substituents affect the rate of this hydrolysis principally by altering the value of E, while the deviation from a standard slope (2·3RT) indicates a well-marked tendency for α to increase with increasing E. The changes in α tend to compensate the effect of changes in E, as will generally be the case when variations of α are considerable, and this is relevant to the consideration of the significance of the results (cf. Ingold and Nathan, this vol., p. 222). Although the constants vary by little more than one power of 10, the activation energies cover a range of 4800 cals., as compared with ranges of 5900 for the interaction of benzoyl chloride with a series of substituted anilines (Hinshelwood and Williams, *loc. cit.*) and 5500 for the alkaline hydrolysis of a series of substituted benzoic esters (Ingold and Nathan, *loc. cit.*). The differences between the activation energies for the unsubstituted substances and their *p*-nitro-derivatives are 2400, 4450, and 3200 cals. in the three reactions respectively.

Fig. 3, representing the relation between log α and E, expresses the same conclusion directly, and indicates how far these results accord with a linear relationship between log α and E. The existence of such a relationship accounts for the fact that an approximately linear plot is obtained for log k ($=$ log $\alpha - E/RT$) for this reaction against log k for reactions for which only E varies significantly. Similar relationships have been observed for a few other reactions (cf. Moelwyn-Hughes, *op. cit.*, p. 167), and are required to account for the frequent occurrence of linear relationships between the logarithms of dissociation and velocity constants.

If the hypothesis of Evans, Morgan, and Watson (J., 1935, 1168) is applied to our results, it is necessary to regard the attachment of the hydrogen-ion catalyst as connected with α, and another stage of the process, simultaneous or consequent, as determining the activation energy, since proton-repulsive groups lead to low values of α and E, the inverse of their case.

The results recorded here do not appear to fall precisely into any of the categories indicated by Hughes, Ingold, and Shapiro (this vol., p. 228) as likely to show variations of α, although they could be included by a slight further development. It is to be noted also that the *o*-substituted derivatives do not show any abnormal distribution in the graphs of log α against E (Fig. 3), except in so far as both terms tend to be high in a majority of the cases examined. Hence, one must conclude that such local effects as arise in *o*-substituted phenylsulphates do not lead to any increased predominance of the α term. As these authors emphasise, predominant variations in the α term are commoner with saturated than with unsaturated compounds. However, of the reactions which have been studied in the aliphatic series, a large number are of the negative ion interchange type or are catalytic processes, and both these classes of reaction tend to show important variations in the α term.

Fig. 3.



Numbered points correspond with substituents as given in Table III. Black discs refer to arylsulphates containing o*-groups.*

The most important feature which emerges from a consideration of the data available appears to be the generalisation that the principles, concerning the effect of structure on reaction velocity and equilibrium, which have been defined in terms of electronic theory apply nearly equally well whether activation energies and heats of reaction alone are affected or α and entropy terms show important or even predominant variations (these terms being determined by the application of the simple form of the Arrhenius equation to velocity constants measured over quite a narrow range of temperature and in the parallel manner for equilibrium). This applies, not only to the qualitative applications of the electronic theory, but also to the corresponding quantitative relationships. The principle stated above, and the parallelism between variations in α and E (which appears to be of wide application), suggest that it is necessary to regard electron availability as influencing free energy directly rather than activation energy, as hitherto (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1936, 32, 1333).

The preparation of the phenols and arylsulphates and the details of the hydrolysis are given in the following paper.

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