4. *The Hydrolysis of Arylsulphuric Acids.** *Part I.*

By G. Norman Burkhardt, W. G. Kenneth Ford, and Eric Singleton.

Potassium phenylsulphate is readily hydrolysed by boiling dilute mineral acid: $SO_2(OPh)(OK) + H_2O \longrightarrow Ph{\cdot}OH + KHSO_4$ (I), but is stable in boiling aqueous solution containing acetic acid and sodium acetate, and also to alkalis up to 150° (Baumann, *Ber.*, 1878, **11**, 1907; Burkhardt and Lapworth, J., 1926, 684). The isomeric potassium nitrophenylsulphates have been shown to be much more readily hydrolysed by mineral acid than either potassium phenylsulphate or the isomeric potassium tolylsulphates (Burkhardt and Wood, J., 1929, 141). The hydrolytic fission of arylsulphates appears, therefore, to be of special interest in that, although it is catalysed by hydrogen ions, yet it is accelerated by the presence of electron-attractive (proton-repulsive) groups in the aromatic nucleus. Also, because substituted phenols can often be prepared more readily than, *e.g.*, the corresponding benzyl chlorides, carboxylic acids, aldehydes, or ketones, the hydrolysis of their sulphuric esters should prove useful in the study of the influence of molecular constitution on reactivity in cases when difficulties of synthesis have limited the use of reactions involving these other materials. The possibility of carrying out the hydrolysis of potassium arylsulphates in water instead of in aqueous alcohol or other mixed solvent is one of the factors which lead to the absence of side reactions in this case.

The hydrolyses were followed, at 48·6° and at temperatures near 80°, by titrating, with alkali, the potassium hydrogen sulphate formed according to equation (I), starting with solutions $M/12$ with regard to potassium arylsulphate and $M/24$ to hydrochloric acid. Potassium phenylsulphate and *p*-nitrophenylsulphate were shown to be salts of strong acids, for, with hydrochloric acid, they had no buffering action detectable by indicator methods in concentrations up to those used in the hydrolysis; potassium sulphate

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* Strictly, aryl hydrogen sulphates; but the historical name is retained.

in similar concentrations showed marked buffering action. If it is assumed, from these observations, that all the potassium arylsulphates which have been examined may be regarded as salts of strong acids, the reaction is represented by equation (II) :

$$\begin{array}{rl} R{\cdot}O{\cdot}SO_2{\cdot}O' + H^{\bullet} + H_2O + K^{\bullet} + Cl' = R{\cdot}OH + & HSO_4' + H^{\bullet} + K^{\bullet} + Cl' \\ & \uparrow\downarrow \\ & H^{\bullet} + SO_4'' \qquad . \ . \ . \ . \quad (II) \end{array}$$

In accordance with this equation, the reaction is of the first order with regard to arylsulphate, and partially autocatalytic in virtue of the increase in hydrogen-ion concentration due to the partial dissociation of the HSO_4' ion formed in the hydrolysis. Satisfactory velocity constants were obtained as described by Burkhardt, Evans, and Warhurst (Part II, succeeding paper), the value of 0·01 being used for the second dissociation constant of sulphuric acid. This corresponds with that found by Dawson, Pycock, and Spivey (J., 1933, 291) in their experiments on the hydrolysis of ethyl acetate in salt-free solution at 25°, and proved sufficiently accurate for the present purpose. Velocity constants were calculated from the expression $k_1 = (dx/dt)/(a + p)(b - x)$, where a and b are the initial concentrations of acid and arylsulphate (mols. per litre) respectively, x is the increase in total acid ($KHSO_4$ produced) in time t (secs.), and p the increased concentration of hydrogen ions due to the dissociation of the acid formed in the hydrolysis.

Up to half reaction and in the concentrations used, the values of $(a + p)$ obtained by this method correspond closely with the dissociation of a fixed fraction of the potassium hydrogen sulphate produced according to equation (I), and for the standard concentrations used, good constants were also obtained using the integrated form of the equation $dx/dt = k_2(a + x/5{\cdot}5)(b - x)$, *viz.*, $k_2 = [2{\cdot}303/t(a + b/5{\cdot}5)] \log b(a + x/5{\cdot}5)/a(b - x)$. The agreement of the constants obtained by these two methods was satisfactory; *e.g.*, for potassium phenylsulphate at 48·6° :

Reaction, %	12·5	18·75	25	37·5	50
$k_1 \times 10^5$ (tangents)	8·83	8·93	9·00	9·00	9·03
$k_2 \times 10^5$ (approximate expression)	8·58	8·68	8·85	8·88	8·95

It is now clearly established that the actual rates of reactions, involving suitably related substances and measured under similar conditions chosen on grounds of convenience, are directly related to certain features of the molecular structures of the reactant molecules in a manner which can be expressed in terms of the electronic theories. This applies to substances showing quite small differences in velocity constants in certain cases, including a very wide range of reactions involving groups attached to the benzene ring or to side chains in aromatic compounds. Table I contains the data for a comparison of the velocity constants for the hydrolysis of the substituted phenylsulphates with those for a number of other reactions. The close qualitative relationships are clearly shown. The values relative to each phenomenon rise or fall consistently down each column except those shown in parentheses, most of which relate to *o*-substituted compounds, to which special considerations are known to apply. Comparisons with other reactions are shown in the subsequent discussion of the quantitative relationships (Figs. 1 and 2).

The complete phenylsulphate series (B and C) show clearly that the sulphate group is most readily hydrolysed when it is attached to a position of low electron-availability, and that the rate of hydrolysis decreases with rising electron-availability at the various positions in benzene derivatives (reactions of Class B, Ingold, *Ann. Reports*, 1927, **24**, 155). It is therefore clear that the substituents are not acting in virtue of their influence on the interaction of the phenylsulphate ion and the oxonium ion. This applies whether the reaction proceeds by the type of mechanism represented in equation (III) or by that in (IV), either of which would give a bimolecular form involving phenylsulphate and hydrogen-ion concentrations.

$$Ph{\cdot}O{\cdot}SO_2{\cdot}O' + H_3O^{\bullet} \longrightarrow Ph{\cdot}OH + H_2SO_4 \qquad (III)$$

$$Ph{\cdot}O{\cdot}SO_2O' + H_3O^{\bullet} \rightleftarrows Ph{\cdot}O{\cdot}SO_2{\cdot}OH + H_2O \longrightarrow Ph{\cdot}OH + H_2SO_4 \qquad (IV)$$

(Both these are followed by the equilibria $H_2SO_4 \overset{H_2O}{\rightleftharpoons} H_3O^{\bullet} + HSO_4' \overset{H_2O}{\rightleftharpoons} H_3O^{\bullet} + SO_4''$.)

TABLE I.

A.	B. k (48·6°).	C. k (78·7°).	D. $-CO{\cdot}NH_2$.	E. $-CO{\cdot}NH_2$.	F. $-CH_2Cl$.	G. $-CO_2Et$.
p-NO_2	44·5	12·0	245	6300	7·4	5090
o-NO_2	35·8	8·8	(5·6)		8·4	
m-NO_2	20·5	5·8	204	5300	9·0	3110
m-Cl	16·3				23·7	363
(*o*-OMe)	13·3	4·53				
o-Cl	13·0	4·42	(33·3)	(489)	36	
p-Br	11·5		204	1800	50	242
p-Cl	10·8	3·62	(208)	1800	62	212
m-OMe	10·2	3·40				59
H	8·9	3·35	(217)	944	100	49
m-Me	8·8	3·20	201	752	139	35
o-Me	7·75	2·72	(22·7)	(50·5)	484	
p-Me	6·87*	2·38*	183	623	1060	23
p-OMe	4·50	1·80	131	462		10·5

* The authors are indebted to Mr. C. Horrex and Miss D. Jenkins for these values.

Col. A. The substituents are arranged in the order of their influence on the phenylsulphate hydrolysis.
,, B. Velocity constants (× 10^5) at 48·6° for the hydrolysis of the substituted phenylsulphates.
,, C. ,, ,, (× 10^3) at 78·7° ,, ,, ,, ,, ,, calculated from measurements at various temperatures from 76·7° to 82·5°.
,, D. Velocity constants (× 10^4) at 100° (time in mins.) for the acid hydrolysis of the substituted benzamides (Reid, *Amer. Chem. J.*, 1900, **24**, 403).
,, E. As D, but for alkaline hydrolysis.
,, F. Relative velocity constants for the hydrolysis of the substituted benzyl chlorides (CH_2PhCl = 100) at 83° (Olivier, *Rec. trav. chim.*, 1923, **42**, 775; Olivier and Berger, *ibid.*, 1927, **46**, 605).
,, G. Velocity constants (× 10^4) at 30° (time in mins.) for the alkaline hydrolysis of the substituted ethyl benzoates (Kindler, *Annalen*, 1926, **450**, 1; 1927, **452**, 90).

In (III), electron-attractive (proton-repulsive) substituents in the phenylsulphate would resist combination with the oxonium ion, and in (IV), such groups would tend to increase the dissociation and thereby reduce the concentration of the intermediate neutral complex. Hence, the substituents must be regarded as acting mainly by their effect on other factors in the molecular breakdown by either mechanism. A similar conclusion applies to the acid hydrolysis of substituted benzamides (D). The phenylsulphate breakdown apparently involves the fission of the oxygen–sulphur bond (V) and *not* the carbon–oxygen bond (VI) because, with phenylsulphates, no phenylating properties have been detected analogous to the alkylating properties of the alkylsulphates (VII) which indicate carbon–oxygen breakdown in that series. The well-known difficulty of breaking the bond between the aromatic nucleus and oxygen makes this mechanism probable. On the other hand, alkaline hydrolysis, which is observed at 100° with *o*- and *p*-nitrophenylsulphates only (Burkhardt and Wood, *loc. cit.*) and is much slower than any of the acid hydrolyses, may take place by the fission of the carbon–oxygen bond in a reaction analogous to the alkaline hydrolysis of *o*- or *p*-chloronitrobenzene.

$$\mathrm{Ph{\cdot}O}\vdots\mathrm{SO_2{\cdot}OK}$$

(V.)

$$\mathrm{Ph}\vdots\mathrm{O{\cdot}SO_2{\cdot}OK}$$

(VI.)

$$\begin{array}{r}\mathrm{Et}\vdots\mathrm{O{\cdot}SO_2{\cdot}OK}\\ \mathrm{Ph{\cdot}NH}\vdots\mathrm{H}\phantom{{\cdot}SO_2{\cdot}OK}\end{array}$$

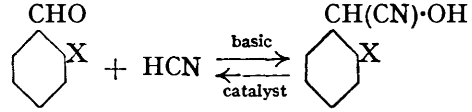
(VII.)

In that it is catalysed by hydrogen ions and yet accelerated by electron-attracting substituents, the acid hydrolysis of substituted benzamides is analogous to the phenylsulphate hydrolysis, but it contrasts with this in showing most marked steric effects when *o*-substituents are present (Table I). The alkaline hydrolyses of benzamides and benzoic esters are also subject to typical strong steric effects. The benzyl chlorides resemble the phenylsulphates in that the *o*-substituents considered here show little or no steric effect (Olivier, *Rec. trav. chim.*, 1926, **45**, 296). In all these reactions the bond next but one to the nucleus is broken (VIII*a*, *b*, *c*, *d*), and this differentiation into strongly and slightly sterically hindered classes is significant. In the former class, the approach of the ion or molecule of the other reactant to the atom next to the nucleus is clearly involved, and as it appears that even small *o*-substituents always make this more difficult, the other cases apparently do not require such a mechanism as part of the rate-regulating process. In the case of the benzyl chlorides, the ionisation of the halogen which regulates the rate

$\mathrm{Ph{-}CH_2}\vdots\mathrm{{-}Cl}$ (VIII*a*.) $\mathrm{Ph{-}O}\vdots\mathrm{{-}SO_2{-}OK}$ (VIII*b*.) $\mathrm{Ph{-}CO}\vdots\mathrm{{-}OEt}$ (VIII*c*.) $\mathrm{Ph{-}CO}\vdots\mathrm{{-}NH_2}$ (VIII*d*.)

should be independent of the approach of water to the methylene group (compare Polanyi and Ogg, *Trans. Faraday Soc.*, **1935**, **31**, **604**), and similarly, the mechanism of the phenylsulphate hydrolysis would appear not to involve the attack of the reagent on that part of the sulphate group which is within the sphere of steric influence of small *o*-substituents.

It must be noted, however, that this conclusion is rendered less certain by the demonstration by Lapworth and his collaborators that steric hindrance cannot be satisfactorily regarded as a simple obstruction phenomenon in the *o*-substituted benzene derivatives. Lapworth and Manske (J., **1928**, **2533**) showed that an abnormally high percentage of cyanohydrin was formed in the equilibrium between *o*-substituted benzaldehydes and hydrogen cyanide (IX) in spite of the necessity for the attachment of the cyanide ion to the carbonyl carbon atom. This indicated that the influence of *o*-substituents on these



(IX.)

equilibria could not be treated on the classical lines (Flürscheim, J., **1909**, **95**, **718**), and it was suggested that direct interaction between the two *o*-groups must be involved. In continuation of this work, Mr. Glyn Owen and others (unpublished) have shown that the formation of cyanohydrins is also abnormally *fast* with *o*-substituted benzaldehydes. This imposes a hitherto unsuspected reservation on the application of steric considerations to kinetics, and the results of a study of steric effects on the arylsulphate hydrolysis will be communicated shortly.

Quantitative Relationships.—In Fig. 1 it is shown that some of the relationships represented in Table I are remarkably quantitative (Burkhardt, *Nature*, **1935**, **136**, 684). As abscissæ are plotted the logarithms of the dissociation constants of a series of substituted benzoic acids, so that these act as a reference series for the other phenomena, and as ordinates the logarithms of the velocity constants for four of the reactions represented in Table I in which the organic reactants contain the same substituents as the benzoic acids with which they are being compared. The straight-line relationship is fully supported or these phenomena although the larger deviations are all beyond experimental error and their significance will require separate discussion. The choice of the dissociation constants of the benzoic acids as reference series is arbitrary, but it shows that the velocity relationships which could have been illustrated against a velocity reference series can also be quantitatively related to ionisation equilibria.

Hammett and Pfluger (*J. Amer. Chem. Soc.*, **1933**, **55**, 4079) observed a similar relationship between the dissociation of various carboxylic acids and the rate of reaction of their methyl esters with trimethylamine, $\mathrm{R{\cdot}CO_2Me + NMe_3 \longrightarrow R{\cdot}COO'\}NMe_4^{\cdot}}$, but they considered the reaction exceptional in showing this relationship.* In that they were able to include, on a single straight line, the constants for aliphatic and *o*-substituted aromatic acids and esters as well as *m*- or *p*-substituted derivatives, their conclusion was well sub-

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* Since this paper was written and a summary published (Burkhardt, *Nature, loc. cit.*), Hammett (*Chem. Reviews*, 1935, **17**, 125) has extended the scope of the relationship observed by him and Pfluger (*loc. cit.*) to include a wide variety of pairs of closely related phenomena, including, as one pair, the logarithms of the dissociation constants of the substituted benzoic acids against the logarithms of the rates of hydrolysis of the benzoic esters (curve E, Fig. 1). Since he stresses closely related phenomena, the present extension to include reactions less clearly related on *a priori* grounds is largely complementary to his, and requires a still wider explanation. Each of the curves in Fig. 3 provides another example of the type of relationship which he discusses.

stantiated. It has, however, been widely recognised that *o*-substituents in the aromatic series, and particularly α- and β-substituents in the aliphatic series, bring in quite special factors * operating to very different degrees in different reactions. It therefore becomes reasonable to consider, first, *m*- and *p*-substituted derivatives, and for these the linear logarithmic relationship is found to hold between a wide variety of reactions and consequently would appear to have a more general significance than follows from its application to a single pair of closely related phenomena.

Watson and his collaborators have plotted, against the dipole moments of monosubstituted benzene derivatives, the logarithms of both the dissociation constants of the benzoic and phenylacetic acids containing the same substituents, and those of velocity constants (or derived activation energies) for a variety of side-chain reactions (Nathan and Watson, J., 1933, 893, 1248; Evans, Morgan, and Watson, J., 1935, 1174; Dippy and Watson, *J. Soc. Chem. Ind.*, 1935, **54**, 735). Smooth curves were obtained for the majority of *m*-derivatives, and their form is very similar for the different phenomena. This is in accord with the existence of a direct relationship between the logarithms of the different velocity and dissociation constants for these *m*-derivatives.

To illustrate further the application of the linear logarithmic relationship, a number of other reactions are represented in Fig. 2 against the same reference series as was used in Fig. 1. The curve (H) for the hydrolysis of the substituted cinnamic esters, considered in conjunction with that for the benzoic esters (G) in Fig. 1, shows that the same influences from the substituents operate on the hydrolysis of the carbethoxyl group with the same relative effectiveness as compared with one another, whether the group is attached directly to the benzene nucleus or separated from it by the CH⁚CH group in the cinnamic side-chain. The slope of curve G being 2·5 and that of curve H 1·25, it can be stated that the introduction of the CH⁚CH group into the side-chain diminishes the effectiveness of *m*- and *p*-substituents by 50%. For the same reaction (hydrolysis of the carbethoxyl group by alkali) measured in the two series at the same temperature, this conclusion appears to be satisfactory in the unqualified form.

The iodine–chlorine interchange (curve I) brings in yet another type of reaction and a further indication of the persistence of the quantitative relationship at the end of a side chain, which in this case is saturated. The dissociation constants of the phenylacetic acids (curve K; all the other curves represent velocities) indicate the same persistence of the relationship along a side chain and its application to another dissociation equilibrium. The bromination of acetophenones (J) and the acid hydrolysis of the benzamides (D) are representative of reactions for which the straight-line relationship apparently fails: the former curve has a minimum at the *m*-nitro-derivative (or, alternatively, *p*-nitroacetophenone constitutes the sole anomaly), and the latter shows a marked **S** form which occurs also, but less markedly, in the phenylsulphate points (B, Fig. 1). Many reactions may be expected to deviate farther still. In general, reactions and particular substituents which have required special treatment on the simpler forms of electronic theory will fail to fall on straight lines when plotted against any of the phenomena which show the linear relationship. Shoppee (J., 1931, 1225), discussing a group of such reactions, plotted the free-energy change in the benzaldehydecyanohydrin equilibrium (Lapworth and Manske, *loc. cit.*) against the logarithms of the velocity constants for the alkaline hydrolysis of the benzoic esters (Kindler, *loc. cit.*) and obtained a smooth curve with a maximum.

The results given in Figs. 1 and 2 show that the linear logarithmic relationship is of very wide application in the case of *m*- or *p*-substituted derivatives, and in its simplest form, it is clearly much more satisfactorily applicable to remote substitution, of which the *m*- and *p*- cases have been most extensively studied, than to other types of structural change. The present communication is primarily concerned with this type of substitution, but a few preliminary observations on the further applicability of the logarithmic relationship may be recorded.

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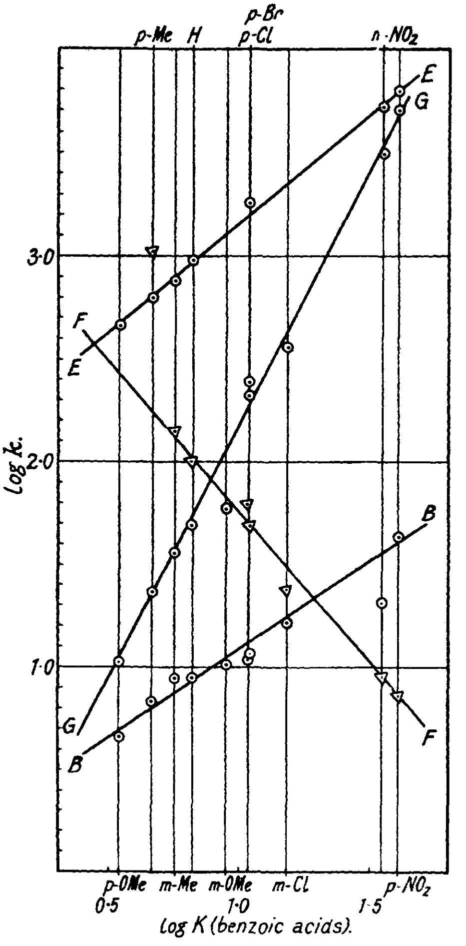
* As was emphasised above (p. 20), these factors are more complex than a simple steric hindrance. They include, *e.g.*, chelation and resonance phenomena, which are often peculiar to groups close to one another.

In a number of cases, similar plots of the logarithms of velocity constants against those of dissociation constants give, for the limited data available, straight lines for *o*-derivatives, but these are displaced from the *m*-, *p*-curves by amounts corresponding to the effects peculiar to the *o*-derivatives, and major deviations are commoner than in the *m*-, *p*-series; *e.g.*, the abnormally high rate of hydrolysis of potassium *o*-methoxy-

FIG. 1.



Ordinates for curves.

B . . . log (k × 10^5) *for acid-catalysed hydrolysis of the substituted potassium phenylsulphates at* 48·6°.

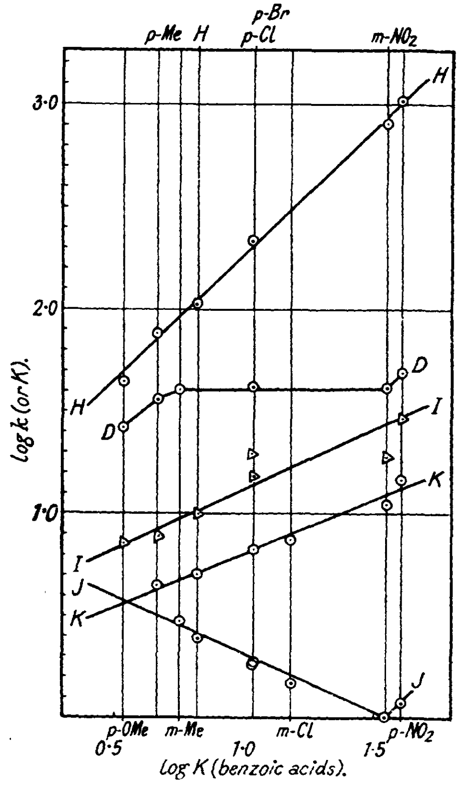
E . . . log (k × 10^4) *for alkaline hydrolysis of the substituted benzamides at* 100° (*Reid*).

G . . . log (k × 10^4) *for alkaline hydrolysis of the substituted ethyl benzoates at* 30° (*Kindler*).

F . . . log k *for hydrolysis of the substituted benzyl chlorides by aqueous alcohol at* 83° (*Olivier*).

Abscissæ: *log* K (*benzoic acids*) . . . *logarithms of the dissociation constants* (× 10^5) *of the substituted benzoic acids, taken from Landolt–Börnstein or International Critical Tables except the values for* o- *and* p-*chloro- and* p-*bromo-benzoic acids* (*Dippy and Williams*, J., 1935, 343).

FIG. 2.



Ordinates for curves.

H . . . log (k × 10^3) *for alkaline hydrolysis of the substituted ethyl cinnamates at* 30° (*Kindler*).

D . . . log (k × 10^4) *for acid hydrolysis of the substituted benzamides at* 100° (*Reid*).

I . . . log (k × 10^2) *for reaction*
$KI + C_6H_4X{\cdot}S{\cdot}[CH_2]_2{\cdot}Cl$
in acetone at 55° (*Baddeley and Bennett*, J., 1933, 261).

J . . . log (k × 10) *for bromination of substituted acetophenones at* 25° (*Evans, Morgan, and Watson*).

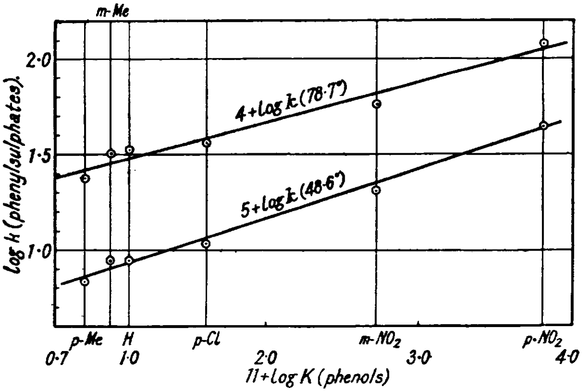
K . . . log (K × 10^5) *of the substituted phenylacetic acids* (25°) (*Dippy and Williams*, J., 1934, 161, 1888).

phenylsulphate * and the abnormally low dissociation constant of *o*-phthalaldehydic acid will lead to anomalies in any plot involving either of these two substances. In relating reactions which are similarly or not markedly affected by factors due to the close proximity of the groups, curves for *m*- and *p*-derivatives should be found to include the *o*-derivatives also.

Apart from closely related phenomena such as those compared by Hammett and Pfluger, it appears that changes of structure such as have been studied in the aliphatic series do not commonly give similar linear relationships. Some examples give smooth non-linear curves which can be interpreted, but others show no simple relationship at all.

In considering the physicochemical explanation of the linear relationships, it is convenient to examine phenomena as closely related as possible, as did Hammett and Pfluger. Fig. 3 shows the relationship between the logarithms of the rates of hydrolysis of the substituted potassium phenylsulphates at two temperatures and the logarithms of the dissociation constants of the corresponding phenols. Here the points lie somewhat closer to the straight line than those in the benzoic acid reference series in Fig. 1; particularly is this true of the points for the *m*-nitro-derivatives. Similar though smaller deviations are to be noticed with *m*-nitro-derivatives in Fig. 2, and a consideration of the removal of anomalies by altering the reference series provides one approach to the explanation of the larger deviations from the linear relationships.

FIG. 3.



We are indebted to Professor Polanyi for drawing our attention to the explanation of the relationship between the rates of the acid-catalysed hydrolysis of the phenylsulphates and the dissociation of the corresponding phenols provided by the discussion of Horiuti and Polanyi (*Acta Physicochemica, U.R.S.S.*, 1935, **2**, 505).

The curve in Fig. 3 corresponding to the higher temperature is the less steep, as is to be anticipated if substitution mainly affects the activation energy, the slopes being 0·26 at 48·6° and 0·21 at 78·7°, a fall of 20% for a rise of temperature from 321·6° to 351·7° Abs. This variation complicates the use of slopes as a measure of the sensitivity of a reaction to substitution (compare p. 21), and an examination of the significance of the linear relationship in terms of energetics is required to elucidate this problem.

It may be noted that the results for the substituted potassium phenylsulphates given in Table II (derived from the constants to two temperatures by the application of the Arrhenius equation, $k = \alpha e^{-E/RT}$) indicate fairly definitely a rise in α from the most rapidly hydrolysed derivatives to the slowest, and a corresponding fall in the temperature-sensitive term, the effect of changes in the activation energy predominating (Burkhardt, *J. Inst. Chem.*, 1933, 301).

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* This is the only anomaly in the phenylsulphate series. The value is anomalous whether it is considered from the point of view of the electronic theory, or on analogies with other isomerides and the influence of methoxyl in other reactions, or as it concerns the linear relationship. No explanation has been established. The effect might be accounted for by (*a*) the basicity of the methoxyl group, (*b*) the stabilisation of a single bond between the groups, or (*c*) direct interaction of the two groups.

TABLE II.

Substituent.	p-NO$_2$.	o-NO$_2$.	m-NO$_2$.	o-Cl.	p-Cl.	m-OMe.	H.	m-Me.	o-Me.	p-Me.	p-OMe.
$k_{48\cdot6^\circ} \times 10^5$	44·5	35·8	20·5	13·0	10·8	10·2	8·9	8·8	7·75	6·80	4·50
E (kg.-cals.)	24·7	23·8	24·8	26·2	26·2	26·1	27·0	26·7	26·5	26·6	27·4
$\alpha \times 10^{-14}$	0·24	0·06	0·18	0·10	0·30	0·68	2·4	1·5	0·88	0·79	2·3

The analysis in terms of the Arrhenius equation, which is developed elsewhere, follows the current methods. On the other hand, the existence of the linear logarithmic relationship and a parallelism between the α and the E terms (compare Burkhardt, *Nature, loc. cit.*) suggests a direct consideration of the influence of substitution on the logarithms of velocity and equilibrium constants, *i.e.*, on free energies (Burkhardt, *ibid.*). According to the transition-state method, as used by Evans and Polanyi (*Trans. Faraday Soc.*, **1935**, **21**, 875) or by Wynne-Jones and Eyring (*J. Chem. Physics*, **1935**, **3**, 492), the velocity constant of a reaction is determined by the equilibrium between the initial and the transition state; log k (velocity) is directly related to the free-energy change in this process as log K (equilibrium) is to the total free-energy change in dissociation, and the linear relationships described above may be stated as follows in terms of the transition-state conception.

> The influence of substituents on the free-energy changes associated with the equilibria between the initial and the transition states, in the reactions considered in respect of velocity, are directly proportional to their influence on the free-energy changes between the initial and the final states in corresponding dissociations.

These relationships may be regarded as developments from Flürscheim's observation of the parallelism between the influence of substituents on aromatic substitution and on the dissociation of the corresponding benzoic acids (J., **1909**, **95**, 725). Most of the data which have been used here have been accounted for on a qualitative basis, either in terms of Flürscheim's theory of valency or, more completely, in terms of the electronic theory which has incorporated the essentials of the earlier view. One of the modifications of the latter treatment which is required by the recognition of their quantitative nature may be stated as follows : Substituents operate with the same relative effectiveness, as compared one with another, on all the phenomena connected by the linear relationship. It is improbable that the temporary effects, to which the substituents may give rise, would influence all the reactions proportionately, and it therefore appears that such effects are not important in those cases where the relationship is followed closely, although they may provide the explanation of some of the individual deviations. In these cases the polarisability of a substituent would only be effective in so far as it became a polarisation in the course of any particular reaction.

The hydrolysis of the potassium arylsulphates and a number of problems concerning the quantitative relationship between reaction velocities and equilibria will be discussed further in the near future.

EXPERIMENTAL.

Velocity Measurements.—10 C.c. of $N/4$-hydrochloric acid were added to 50 c.c. of an $N/10$-aqueous solution of the substituted potassium arylsulphate in a well-stoppered flask in a thermostat (± 0·03° at 48·6°, ± 0·05° at about 80°), both solutions having attained the temperature of the bath before mixing. As soon as possible and also at suitable intervals, samples were removed, run on to ice, and titrated with $N/10$- or $N/20$-alkali, p-nitrophenol being used as indicator and the alkali being standardised in a blank experiment on each occasion. The hydrolyses were carried out at least in duplicate. The delivery jets of the pipettes were bent back into an elongated S alongside the bulb, so that the latter was largely immersed in the thermostat liquid when the meniscus was set; with a standard procedure to regulate drainage, this was satisfactory for the present series of experiments. The pipettes were calibrated at the temperatures concerned. The initial concentration of the acid was obtained by extrapolating the curve back to zero time, that of the phenylsulphate being deduced from the volumes and concentrations of solutions and in some cases checked by complete hydrolysis.

The phenols for the preparation of sulphates were all purchased except m-chlorophenol, which was prepared from m-chloroaniline by diazotisation. The b. p. or m. p. of each was checked, and where necessary the phenol was purified by distillation or crystallisation. The substituted potassium phenylsulphates were prepared by the method of Burkhardt and Lapworth (*loc. cit.*), except that the temperature of the reaction mixture was kept below 35° for the *m*-methyl and the methoxy-derivative to avoid sulphonation (therefore in these cases the solvent was not distilled off), and for the nitro-derivatives Burkhardt and Wood's modification (*loc. cit.*) was used. The products were recrystallised from water or aqueous alcohol, and examined qualitatively for inorganic sulphate and chloride and for the free phenol. Analysis for potassium gave molecular weights within 0·5% of theory in all cases.

To obtain an estimate of the strength of the phenylsulphuric acids, 10 c.c. of *N*/4-hydrochloric acid were added slowly to 25 c.c. of *N*/10-solutions of potassium phenylsulphate, *p*-nitrophenylsulphate, or sulphate and of distilled water, and the p_H values of the solutions were taken at various stages by the B.D.H. capillator. The potassium sulphate showed appreciable buffering; the others were indistinguishable.

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THE UNIVERSITY, MANCHESTER. [*Received, October* 19*th*, 1935.]