RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

January 1963

MECHANISMS OF THE HYDROLYSIS OF AROMATIC SULPHONYL CHLORIDES AND OF ALKYL AND ARYL ARENESULPHONATES

R. V Vizgert

CONTENTS

Introduction 1

1. Substitution in compounds containing sulphonyl or carbonyl groups 1

2. Site of bond rupture on hydrolysis 2

3. Influence of catalyst on the mechanism of hydrolysis 3

4. Influence of the polar effects of substituents on the rate of alkaline hydrolysis of esters 5

   (*a*) Influence of the nature of the acid component and of substituents in the acid component 5

   (*b*) Influence of the nature of the alcoholic component and of substituents in the alcoholic component 8

5. Influence of solvents 11

6. Influence of steric factors on the rate and mechanism of the hydrolysis of the chlorides of carboxylic and sulphonic acids 14

7. Influence of steric factors on the rate and mechanism of the alkaline and aqueous hydrolysis of aryl sulphonates 15

8. Correlation of rate constants for the alkaline hydrolysis of arenesulphonic esters with their structure 17

INTRODUCTION

The reactions of esters involving the carbonyl group, *i.e.* hydrolysis [1-7], alcoholysis [8,9], and ammonolysis [10,11], have been widely discussed in the literature, but considerably less work has been done on the corresponding reactions involving the sulphonyl group: those with sulphonyl chlorides and the esters of aromatic sulphonic acids.

The significance of these reactions in organic chemistry is not limited to the production of dyes [12], drugs [13], surface-active agents [14], insecticides [15], etc. [16] They occupy an important position in the general theory of solvolytic processes. In the present review an attempt will be made to summarise and systematise published information on the hydrolysis of aromatic sulphonyl chlorides and aryl and alkyl sulphonates, and also to compare the specific features of reactions involving the sulphonyl group with the corresponding reactions in which the carbonyl group takes part.

1. SUBSTITUTION IN COMPOUNDS CONTAINING SULPHONYL OR CARBONYL GROUPS

In the carbonyl group an octet is formed by the carbon–oxygen double bond in the

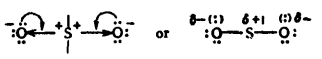


group and by the two covalent bonds linking the carbon with oxygen and with the radical R. Owing to the presence of mobile π electrons and also the great electronegativity of oxygen, the double bond is readily polarised in the direction of the oxygen, so that the electron density is diminished on the carbonyl carbon and increased on the oxygen, which thus forms the negative pole, while the carbon is the positive pole, of the molecular dipole. The electrophilic character of the carbon creates favourable conditions for its attack by nucleophilic reagents; hence most nucleophilic substitution and addition reactions in compounds containing a carbonyl group involve the nucleophilic reagent attacking the carbonyl carbon [17,18].

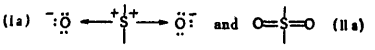
In compounds containing a sulphonyl group the octet rule can be maintained provided that, if two oxygen atoms are linked with the sulphur atom in a sulpho-group by semipolar bonds



the other two bonds (linking the sulphur with oxygen and with the radical R) are covalent. With this distribution of electrons the sulphur is positively charged, which would seemingly facilitate attack by nucleophilic reagents. Actually, the presence of a complete octet hinders this attack. Nevertheless, when it is remembered that the octet rule does not extend to elements of the third and higher periods in the Periodic System, and the sulphur atom can enlarge its octet, the following interpretation is possible for the structure of the $>SO_2$ group



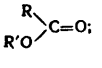
Adoption of the two extreme formulae (Ia) and (IIa):



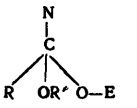
does not, of course, represent the actual distribution of electrons, and is useless for predicting reactivity.

Recently the presence of a semipolar bond in these compounds has been denied on the basis of the following results. The S–O interatomic distances in the $>SO_2$ group have been found to be 1.432 Å, which approximates to the length of a double bond, while those of an S–O single bond in the group S–O–R are 1.7 Å; this is attributed[19] to the formation of a π bond by the 3*d* orbitals of the sulphur atom. On the other hand, the Hammett constant σ for the *p*-SO_3 group is similar to the values obtained for other *para*-substituents (the p*K* relates to the ionisation of a proton in the substituent groups, not the SO_3H, in substituted benzenesulphonic acids), which suggests that conjugation occurs also in sulphonate ions, and that the sulphur atom in sulphonic acids can expand its octet to a decet or a dodecet[20,21]. However, the tendency to such expansion is slight, since compounds containing the $>SO_2$ group do not yield enolic forms[22]. Consequently the sulphur in the SO_2 group is positively charged, its shell of valence electrons contains vacant orbitals, and like carbonyl carbon it can undergo nucleophilic attack, although to a considerably smaller extent. Thus, whereas the carbonyl group readily adds on anions or molecules having lone pairs of electrons, such reactions are difficult with the sulphonyl group.

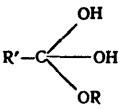
The second difference lies in peculiarities associated with the formation of the transition state. A reactant carboxylic ester molecule has a planar structure of the type:



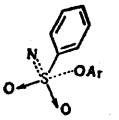
as the nucleophilic reagent approaches, all three substituent groups move closer and, at the instant of formation of the intermediate, yield a tetrahedral structure, with electrophilic reagents adding on to the oxygen, and nucleophilic reagents to the carbon



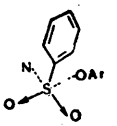
If the resultant splits off a simple molecule and gives a functional group with a double bond, this does not affect the kinetics, since the slowest process is the addition. Bender showed that the intermediate product is tetrahedral[23] in alkaline and in acid hydrolysis:



The sulphur in a sulphonyl group is coordinatively saturated, and it is therefore difficult to imagine the formation of an intermediate product by addition of a nucleophilic species to the sulphur atom. If, however, reactions involving the sulphonyl group are accomplished in a single transition state, the bonds can probably be distributed in two possible ways: (*a*) the attacking and the eliminated groups are in the same plane as the sulphur and oxygen atoms:



or (*b*) the attacking and the eliminated groups are in a plane perpendicular to the O ← S → O plane



Changes in bond angle then require considerable amounts of energy.

Finally, the third difference between compounds containing sulphonyl and carbonyl groups consists in the different polarities of the S–Cl and C–Cl bonds in sulphonyl and acyl chlorides respectively, of the S–OAr and C–OAr bonds in aryl sulphonates and benzoates, and of S–OAlk and C–OAlk bonds in alkyl sulphonates and benzoates. All these factors should produce differences with respect to catalysts, and in the steric effects of substituents, in the influence of the polarity of the solvent and the nucleophilic character of reagents on the rate of hydrolysis, and hence should be shown also in reaction mechanisms.

2. SITE OF BOND RUPTURE ON HYDROLYSIS

The hydrolysis of esters may take place either by an acyl–oxygen[24-27] or by an alkyl–oxygen[28-34] mechanism, more rarely by both mechanisms at the same time[35-38]. The mechanism of hydrolysis is substantially affected by the electronegativity of R and R′ in the ester R.COOR′, and

also by the presence of substituents which cause steric hindrance at the point where reaction occurs[29,39,40]. Esters formed by carboxylic acids with primary aliphatic alcohols, substituted benzyl alcohols, and phenols are hydrolysed by an acyl–oxygen mechanism[41–44]. An alkyl–oxygen mechanism is favoured by increasing the strength of the acid[36] and by introducing electron-donor groups into R′, which increase the stability of its ionic carbonium form, as is the case with the esters of tertiary alcohols[45]. The question of the site of bond rupture is settled unambiguously by isotopic and stereochemical methods.

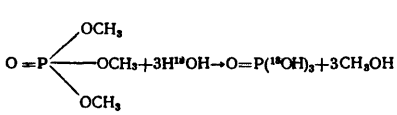
Use of water containing heavy oxygen in the study of the hydrolysis of alkyl and aryl sulphonates has enabled the site of bond rupture to be established with certainty: in the former case it is the alkyl–oxygen bond which is broken[46], and in the latter case the bond linking sulphur with the oxygen of the phenoxy-group[47,48]. Investigation of the reactivities of alkyl and aryl sulphonates in other nucleophilic substitutions, such as their reactions with amines, alkoxides, etc., also indicates the presence not only of different labile bonds but also of different reactive centres, in the first type of compound the carbon atom of the alkyl group, and in the second the sulphur atom of the sulpho-group[49–56].

3. INFLUENCE OF CATALYST ON THE MECHANISM OF HYDROLYSIS

The kinetics of the saponification of esters by acid hydrolysis is complicated by the effect of the acid formed during hydrolysis[57,58]. In hydrolysis in acid medium it is the cation of the protonated form of the ester $RCOOHR^+$ which reacts[59,60]. This is supported by the presence of an *ortho*-effect in the hydrolysis of substituted phenyl acetates in the presence of an acid catalyst[61]. Bender was able to show that, in the acid hydrolysis of ethyl benzoates in the presence of $H_2{}^{18}O$, the rate of oxygen exchange is 20% of that of hydrolysis, and hence that a true intermediate, not a transition complex, is formed[23]. In several cases, however, no strict proportionality is observed between $\log k$ and the Hammett acidity function, the reaction velocity being proportional to the acid concentration, which indicates that the intermediate compound is very complex. The reaction is probably bimolecular, rapid addition of H^+ to the oxygen of the ester first taking place, followed by the rate-determining stage of the reaction in which the carbon atom is attacked by water molecules.

Alkyl–oxygen and acyl–oxygen bonds are not affected in the same manner by the use of acid and alkaline catalysts. In saponification with alkalis it is mainly the latter type of bond which is cleaved; hydrolysis in neutral and acid media favours rupture of the alkyl–oxygen bond.

It has been shown by an isotopic method that the alkaline hydrolysis of trimethyl phosphate involves fission almost exclusively of P–O bonds:



$$O=P(OCH_3)_3+3H^{18}OH \rightarrow O=P(^{18}OH)_3+3CH_3OH\ .$$

In contrast, the acid-catalysed or autocatalytic hydrolysis of trimethyl phosphate is accompanied by bond cleavage in both the possible ways, 30% at the expense of P–O and 70% at the expense of C–O bonds[62,63].

The effect of substituents in the acid hydrolysis of carboxylic esters is slight and shows little regularity[27].

With esters of strong acids, in contrast to those of carboxylic acids, the rate of hydrolysis does not increase in the presence of acid catalysts[36,64–66]. This is probably because the basicity of carboxylic esters is substantially greater than that of sulphonic esters or sulphonyl chlorides. As a result, the concentration of the protonated form of the latter is vanishingly small at low acidities; this is responsible for the absence of acid catalysis. In the vicinity of 100% H_2SO_4, in oleum, and in an H_2SO_4–HSO_3Cl mixture, acid solvolysis of $ArSO_2Cl$ occurs and involves preliminary addition of two protons to the SO_2Cl group[67]. The rate of hydrolysis of ethyl benzenesulphonate is constant at pH 1.4–6.4 and at low alkali concentrations, but increases in proportion to the alkali concentration when this exceeds 0.1 *N*.[68] Therefore the kinetics of the hydrolysis of alkyl sulphonates in acid, neutral, and feebly alkaline solutions obeys a first-order equation.

The hydrolysis of benzenesulphonyl chlorides occurs in a similar manner to that of alkyl benzenesulphonates. The reaction velocity remains constant from pH 1 to 8, and increases sharply at pH 9. In neutral and acid media hydrolysis is produced almost exclusively by unionised water molecules[69,70]. Substituted phenyl esters of benzenesulphonic acid, other than mono- and di-nitrophenyl benzenesulphonates, are not hydrolysed at all in neutral and weakly acidic media[71]. Thus, phenyl benzenesulphonate does not yield even traces of phenol when heated in 60% aqueous dioxan at 120° for 3 weeks[72]. Hence, whereas the hydrolysis of carboxylic esters is accelerated by acid and alkaline catalysts, the rate of hydrolysis of alkyl and aryl sulphonates is independent of the hydrogen-ion concentration.

In spite of the apparent similarity between alkyl and aryl sulphonates, they differ fundamentally in their behaviour in neutral and weakly alkaline media. Whereas the rate of hydrolysis of alkyl sulphonates increases slowly and progressively with increase in alkalinity of the medium, the rate of hydrolysis of aryl sulphonates increases sharply under these conditions.

In the absence of bases, the hydrolysis of alkyl benzenesulphonates occurs according to the equation[49]

$$RSO_2OAlk+H_2O \rightarrow RSO_3OH+AlkOH$$

and obeys the first-order law:

$$\frac{dx}{dt} = k\,(a-x),$$

where $a-x$ is the concentration of the ester.

In the presence of bases, the hydrolysis of alkyl benzenesulphonates occurs according to the equation[73]:

$$RSO_2OAlk+OH^- \rightarrow RSO_2O^-+AlkOH\ ,\quad (R=C_6H_5)$$

and obeys the kinetic equation:

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x)(b-x),$$

where $a-x$ is the ester concentration, $b-x$ the hydroxide-ion concentration, k_1 the first-order rate constant, and k_2 the rate constant of the bimolecular reaction. If relatively high alkali concentrations are used, the neutral hydrolysis can be neglected. Thus for ethyl benzenesulphonate in 0.01 *N* NaOH, $k_2 = 0.0730$ litre mole^{-1} sec^{-1}, and at this temperature $k_1 = 0.000482$ sec^{-1} (in aqueous–alcoholic medium). The activation energies of alkaline and neutral

hydrolysis differ little from one another (21 120 and 22 030 cal mole^{-1}). For ethyl *m*-nitrobenzenesulphonate in 0.033 *N* NaOH $k_2 = 5.7 \times 10^{-3}$ litre mole^{-1} sec^{-1} and $k_1 = 5.23 \times 10^{-5}$ sec. The activation energies for neutral and alkaline hydrolysis of this ester are also quite close to one another, 19 570 and 18 270 cal mole^{-1}.[74] The values given here for k_2 and k_1 were calculated independently of one another, and therefore k_2 includes both alkaline and neutral "aqueous" hydrolysis. In order to calculate k_2 for alkaline hydrolysis alone, a method of graphical differentiation can be used, where

$$k_2^1 = \frac{dx/dt - k_1(a-x)}{(a-x)(b-x)},$$

for ethyl *m*-nitrobenzenesulphonate $k_2^1 = 0.00081$ and $k_2 = 0.00114$ litre mole^{-1} min^{-1}. A graph of the variation of x with t shows that under these conditions the "aqueous" hydrolysis accounts for 30% of the total change in concentration of the compound.

Tommila and Lindholm[49] note also that, in the solvolysis of ethyl benzenesulphonate (in water, methanol, or ethanol), the activation energy is constant (~ 22 000 cal) and the differences in reaction velocities are produced solely by a change in the frequency factor, the logarithm of which varies between 11.22 and 9.5. This can probably be attributed to the absence of any displacement of electrons in the SO_2 group under the influence of the field of the hydroxide ion or the water dipoles, since the corresponding carboxylic esters show an appreciable difference in activation energy with change in polarity of the medium or in the nature of the catalyst.

Aryl sulphonates are hydrolysed only in the presence of alkaline catalysts, according to the equation[74]

$$ArSO_2OAr' + 2OH^- \rightarrow ArSO_3^- + Ar'O^- + H_2O,$$

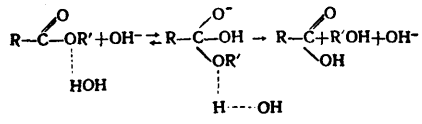
the reaction following a second-order expression which takes into account the double consumption of alkali

$$\frac{dx}{dt} = k(a-x)(b-2x).$$

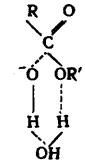
The activation energy E and the frequency factor A for hydrolysis in alkaline aqueous dioxan solution are lower with phenyl benzenesulphonate than with the corresponding ethyl ester (17 860 cal mole^{-1} and log A = 8.66 compared with 19 070 cal mole^{-1} and 9.65), providing a further indication of different mechanisms of hydrolysis with these esters.

According to Hinshelwood *et al.*[2] the activation energy is affected by two factors, the necessity for (1) overcoming the repulsion between the ester molecule and the OH^- ion, and (2) weakening the original bonds (deflecting them from the normal position to the configuration in the transition state).

In the alkaline hydrolysis of carboxylic esters repulsion is least at the carbonyl carbon, and the hydroxide ion attacks this atom, since repulsion is weak, and the activation energy comparatively low. A diminution in activation energy is also favoured by addition of water molecules and formation of an intermediate complex, which probably precedes addition of the OH^- ion[2-4]:



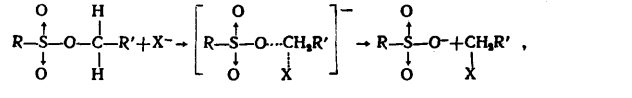
It has recently been suggested that in the transition state an ester molecule, a water molecule, and a hydroxide ion form a six-membered ring. Such an active complex, in which bonds which are being broken alternate with bonds which are being formed, is produced more easily if an alternation of charges on the ions and on the polar bonds is achieved. This additional electrostatic effect lowers the energy of repulsion and favours the formation of cyclic transition complexes[75,76]:



Nucleophilic substitution occurs quite differently in benzenesulphonic esters. Nucleophilic attack on the sulphur atom in the $>SO_2$ group is difficult, although the atom is positively charged. The latter tends to draw off the electrons in the chain towards itself: S ← O ← C; as a result, the alkyl carbon acquires a weak positive charge, and the hydroxide ion adds on to this atom. However, the attraction between the negative ion and the carbon atom is weak, and consequently the activation energy and the frequency factor for the hydrolysis of alkyl sulphonates are far higher than for the corresponding carboxylic esters. In the alkaline hydrolysis of ethyl benzoate in water, for example, E = 12 700 cal and log A = 7.76, while with ethyl benzenesulphonate in water E = 21 100 cal and log A = 12.70.[61] On the other hand, the entropy of activation is less negative with alkyl sulphonates (-10 cal deg^{-1} mole^{-1}) than with ethyl benzoate (-24.9 cal), indicating different degrees of strain in the structures in the transition state.

Whereas in the alkyl sulphonates the transition state has a free, unstrained structure, in the carboxylic esters there is a rigid structure, associated with a redistribution of electron density in the carboxyl group in the transition state.

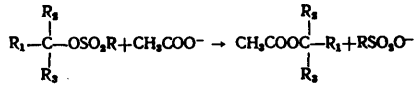
The hydrolysis of alkyl benzenesulphonates is bimolecular, takes place in one step, and, in conformity with Hughes and Ingold's terminology, is an S_N2 reaction[77]



where X = OH^-, $C_2H_5O^-$, or other nucleophilic reagent.

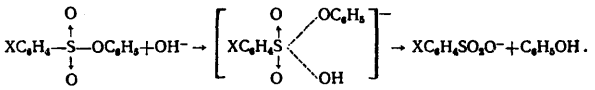
It is probable that solvolysis takes place by the same mechanism[78,79].

Reaction of alkyl sulphonates with alkali-metal carboxylates occurs by an S_N2 mechanism with Walden inversion[80,81]:



With phenyl benzenesulphonates the difficulty of nucleophilic attack by the OH^- ion on the phenyl group results in

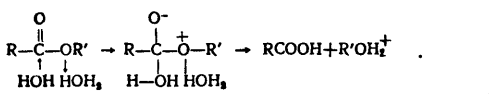
hydrolysis occurring by its attack on the sulphur atom, and perhaps corresponding to the transition state[71,72]



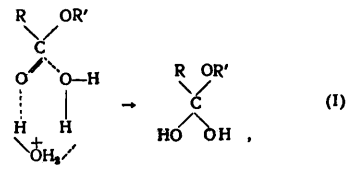
In contrast to the alkyl sulphonates, the reaction occurs here by an "acyl"–oxygen mechanism. Whereas with carboxylic esters such a mechanism of hydrolysis depends on the electrophilic character of the carbonyl carbon and the polarity causing rupture of the C–O bond, with benzenesulphonic esters it depends on the electrophilic character of the sulphur and on the polarity of the S–O bond, which, incidentally, is greater in the aryl sulphonates than in the alkyl sulphonates. Aryl sulphonates provide convenient subjects for studying the mechanism of hydrolysis, since both of these factors can be varied by varying the nuclear substituents in the phenol and in the benzenesulphonic acid. Rupture of the S–O bond was established in an isotopic investigation[48] of the alkaline hydrolysis of phenyl *p*-nitrobenzenesulphonate, nitrophenyl benzenesulphonate, 2,4-dinitrophenyl *o*-nitrobenzenesulphonate, and 2,4-dinitrophenyl toluene-*p*-sulphonate and of the neutral hydrolysis of the latter two esters and also of 2,4-dinitrophenyl benzenesulphonate.

In the alkaline hydrolysis of phenyl benzenesulphonate (on being heated with KOH in a dioxan–$H_2{}^{18}O$ mixture at 90° for 1 h) no exchange of ^{18}O with the oxygen atoms in the ester takes place. These results indicate that the reactions under investigation do not involve the intermediate addition of the OH^- ion to the sulphur atom, but are reactions of type S_N2 occurring by a synchronous one-step mechanism[48]. In this respect the phenyl benzenesulphonates resemble the phenyl benzoates. Whereas when the OH^- ion attacks the carbonyl carbon in ethyl benzoate an intermediate product is formed with a life corresponding to the molecule and a period of existence comparable with the collision period[28], with phenyl benzoate no isotopic oxygen is detected in the unchanged molecule, and the reaction probably takes place by a synchronous mechanism, which facilitates an increase in polarity of the C–O bond[82].

In the acid hydrolysis of carboxylic esters, the proton combines with the ethereal oxygen, and the second step results in addition to the carbonyl carbon of an OH^- ion from the water[57]:

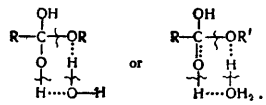


Syrkin gives convincing arguments against the above scheme for acid hydrolysis. It is not clear how the desolvation of H_3O^+ aq, which requires much energy, is compensated for, and it is difficult to understand why the proton adds on to the ethereal and not the carbonyl oxygen, which has a larger negative charge. The possibility of redistributing the *p*-electrons of the oxygen gives the carbonyl oxygen a partial negative charge, while the ether oxygen has a partial positive charge, so that the proton probably adds on to the former, while the hydroxyl from water adds on to the more positive carbonyl carbon[75] according to the scheme:



(I)

with subsequent addition of a water molecule or H_3O^+



Such a six-membered mechanism is, in the opinion of its authors, free from the defects of earlier schemes.

The presence of the intermediate compound (I) was demonstrated by the work of Bender[28].

The absence of double bonds in benzenesulphonic esters makes impossible the displacement of electrons necessary for both the above processes; therefore the hydrogen ion has no catalytic effect on the hydrolysis of alkyl and aryl sulphonates.

4. INFLUENCE OF THE POLAR EFFECTS OF SUBSTITUENTS ON THE RATE OF ALKALINE HYDROLYSIS OF ESTERS

(*a*) Influence of the Nature of the Acid Component and of Substituents in the Acid Component

The influence of substituents, transmitted through the benzene ring[74] to the sulpho-group, follows, according to results obtained for the alkaline hydrolysis of alkyl and aryl sulphonates[74] and also the "aqueous" hydrolysis of aromatic sulphonyl chlorides[83], the general rules. Electrophilic substituents increase, whereas electron-donor substituents decrease, the rates of hydrolysis of alkyl and aryl sulphonates and of aromatic sulphonyl chlorides[50,83] (see Table 1).

TABLE 1. Rate of hydrolysis of alkyl and aryl sulphonates and of aromatic sulphonyl chlorides (70% dioxan–water solution).

Substituent X	Aryl sulphonates $XC_6H_4SO_3OC_6H_5$			Ethyl sulphonates $XC_6H_4SO_2OC_2H_5$			Aromatic sulphonyl chlorides $XC_6H_4SO_2Cl$		
	$10^3 k_{20}$	E	$\log P_z$	$10^3 k_{20}$	E	$\log P_z$	$10^3 k_{20}$	E	$\log P_z$
4-CH_3O	0.076	19260	8.92	0.248	20880	10.49	22.6	14550	6.20
4-CH_3	0.145	18650	8.78	0.291	20150	10.10	24.5	13810	5.74
H	0.374	17860	8.66	0.596	19070	9.65	34.3	13430	5.30
4-Cl	1.120	17190	8.72	1.445	18800	9.88	49.7	12310	5.02
4-Br	1.128	17060	8.60	1.440	18270	9.52	49.1	12310	5.05
4-NO_2	26.3	13160	7.40	6.52	17710	9.80	k_{20}=123.3	10350	4.56
3-NO_2	11.44	15200	8.35	5.45	18270	10.10	128.7	11000	4.55
2-NO_2	7.34	16340	8.92	14.08	18580	10.72	45.3	13580	5.87
2.5-Cl_2	2.97	17030	9.00	5.92	18240	10.12	34.17	12870	5.25

A similar order for the effect of substituents is observed in the hydrolysis of esters formed by bishydroxyphenyl sulphone with substituted benzenesulphonic acids [72,84,85] (see Table 2).

The units of the rate constants for the alkaline hydrolysis of alkyl and aryl sulphonates are litres $mole^{-1}$ sec^{-1}; the rate constants for the hydrolysis of aromatic sulphonyl chlorides are measured in sec^{-1}.

In the bimolecular reaction the substituents increase the activation energy in the same sequence ($4\text{-}NO_2 < 4\text{-}Cl <$ $< 4\text{-}Br < 4\text{-}CH_3 < 4\text{-}CH_3O$) as that in which they increase the electron density at the point of reaction.

However, although the effects of different substituents on the rates of hydrolysis of ethyl and aryl sulphonates and of benzenesulphonyl chlorides are in the same order, their relative magnitudes differ for the two reactions. Phenyl benzenesulphonate is saponified more slowly than the corresponding ethyl ester. Introduction of chlorine or bromine in the *para*-position has some effect in levelling out the rates of hydrolysis of esters formed by the two types of alcohol. Introduction of a *p*-methoxy-group diminishes the rates of hydrolysis of the ethyl and phenyl esters by factors of 2.3 and 5 respectively. When a nitro-group is introduced into the *meta*- and especially the *para*-position, the rate of hydrolysis of the phenyl esters begins to exceed that of the ethyl esters (introduction of NO_2 in the *para*-position increases the rates of hydrolysis by factors of 70 and 11.5 respectively). With two nitro-groups, in positions 3 and 5, the phenyl ester is saponified six times as rapidly as the corresponding ethyl ester. These results show that substituents in the acid component exert a greater influence on the rate of hydrolysis of phenyl esters than of ethyl esters.

The variation in the activation energy and the preexponential factor support the above suggestion. Their values are lower, and vary within wider limits, with the phenyl than with the ethyl esters. The lowest values are obtained with the *p*-nitro-derivatives, 13 160 and 7.4 respectively for the aryl sulphonates, and 17 710 and 9.8 for the ethyl sulphonates; the highest values are observed with the methoxy-derivatives, 19 260 and 8.92 for the aryl sulphonates, and 20 880 and 10.49 for the ethyl sulphonates. The wide variations in activation energies and preexponential factors with the aryl sulphonates are a consequence of the greater influence of the nature of substituents in the acid component on the rate of hydrolysis in the case of aryl sulphonates compared with ethyl sulphonates.

The difference in the influence of the orientation of substituents on the rates of hydrolysis of ethyl and aryl sulphonates is especially marked with *ortho*-substituents. Ethyl *o*-nitrobenzenesulphonate is saponified twice as rapidly as the corresponding *para*-derivative, while phenyl *o*-nitrobenzenesulphonate is saponified at one-quarter of the rate for the corresponding *p*-nitrobenzenesulphonic ester. The effect of the position of the nitro-group on the rate of hydrolysis of the ethyl esters can be represented by the following sequence:

$$o\text{-}NO_2 > p\text{-}NO_2 > m\text{-}NO_2 > H;$$

for the phenyl esters the sequence is different:

$$p\text{-}NO_2 > m\text{-}NO_2 > o\text{-}NO_2 > H.$$

2,5-Dichlorobenzenesulphonic esters are saponified more rapidly than the corresponding unsubstituted esters, the increase in rate of hydrolysis being particularly great with the ethyl ester, and ethyl 2,5-dichlorobenzenesulphonate being saponified twice as rapidly as the corresponding phenyl ester. Thus introduction of substituents into the *ortho*-position, compared with the *meta*- and *para*-positions, facilitates hydrolysis of ethyl sulphonates and hinders that of aryl sulphonates.

It is interesting that the effect of *ortho*-substituents on rate of hydrolysis shows the same trend with aryl sulphonates as with aromatic sulphonyl chlorides and carboxylic esters, as is evident from Table 3. Ethyl *o*-nitrobenzoate and phenyl *o*-nitrobenzenesulphonate are saponified more rapidly than the unsubstituted esters, but considerably more slowly than the *m*- and especially the *p*-nitro derivatives (see Table 3).

The effect of *meta*- and *para*-substituents in benzenesulphonic acid on the rate of alkaline hydrolysis of the aryl sulphonates is in the same order as with the benzoic esters [86,87] (see Table 4).

Thus aryl sulphonates exhibit greater resemblances to carboxylic esters than to ethyl sulphonates, which confirms the different mechanisms of hydrolysis with alkyl and with aryl sulphonates. In the former case the reactive centre is the carbon of the alcohol radical, and in the latter the

TABLE 2.

Acid $p\text{-}XC_6H_4SO_2OH$	10^3k_{20}	10^3k_{90}	E	log P_z
H	3.10	15.45	15420	8.64
p-Cl	4.42	21.70	15400	8.80
p-Br	3.84	18.19	15100	8.49
m-NO_2	38.8	171.20	14000	9.33

TABLE 3. Effect of the position of the nitro-group in the benzene nucleus on the rate of hydrolysis of aromatic sulphonyl chlorides, aryl sulphonates, and ethyl carboxylates and sulphonates (values of 10^5k_{50}).

Substituent X	H	*m*-NO_2	*p*-NO_2	*o*-NO_2
$C_6H_4SO_2Cl$ [80]	34.2	128.7	—	45.3
$C_6H_4SO_2OC_6H_5$	37.4	1144.0	2630.0	734.0
$C_6H_4CO_2C_2H_5$	55.0	3110.0	5090.0	334.0
$C_6H_4SO_2OC_2H_5$	56.9	545.0	652.0	1408.0

TABLE 4. Effect of orientation of substituents in benzenesulphonic acid on rate of alkaline hydrolysis of aryl sulphonates (10^3k_{50}, litre $mole^{-1}$ min^{-1}).

Substituent X	$p\text{-}XC_6H_4SO_2OC_6H_5$	$m\text{-}XC_6H_4SO_2OC_6H_5$
NH_2	0.0027	0.034
CH_3O	0.015	0.142
CH_3	0.030	0.055
H	0.078	0.078
Cl	0.233	0.525
NO_2	5.50	2.27

sulphur atom of the sulpho-group. In the aryl sulphonates the substituent in the benzene ring will be considerably closer to the reactive centre, the sulphur atom of the sulpho-group, and therefore its effect on the rate constant of hydrolysis, the activation energy, and the preexponential factor will also be more strongly developed than in the alkyl sulphonates. The shift in the reactive centre from the carbon of the alcoholic radical (in alkyl sulphonates) to the sulphur of the sulpho-group (in aryl sulphonates) also explains the difference in the effect of substituents in the *ortho*-position. *ortho*-Substituents exert a retarding influence on the hydrolysis of aryl sulphonates, aromatic sulphonyl chlorides, and carboxylic esters, where the reactive centre, the sulphur of the sulpho-group and the carbon of the carboxyl group, are directly linked to the benzene ring; and they increase the rate of hydrolysis of ethyl sulphonates, in which the reactive centre is somewhat remote. The decrease in rate of hydrolysis observed in the former case is due to the presence of an *ortho* effect, whereas in the latter case the *ortho* effect is absent.

Although in the case of alkyl and aryl sulphonates and aromatic sulphonyl chlorides a parallelism is observed between rate of hydrolysis and strength of acid (Figs.1 and 2), such parallelism is not observed with esters of acids belonging to different classes of organic acids and differing in strength — acetic, benzoic, and benzenesulphonic acids[72,88] (see Table 5).

In the above series of acid components, the greatest rate of hydrolysis is shown by acetic esters, and the lowest by benzenesulphonic esters

$$CH_3COOH > C_6H_5COOH > C_6H_5SO_2OH.$$

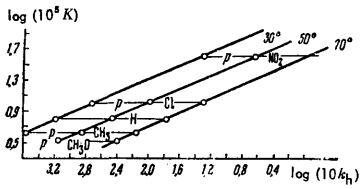


Fig. 1. Linear relations between dissociation constants of substituted benzoic acids and hydrolysis constants of the phenyl esters of the substituted benzenesulphonic acids.

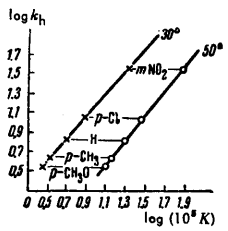


Fig. 2. Linear relations between hydrolysis constants of sulphonyl chlorides and dissociation constants of the corresponding acids.

TABLE 5. Alkaline hydrolysis of ethyl esters.

Acid component	$10^3 k_{18}^*$	$10^3 k_{30}$	$10^3 k_{80}$	E
Acetic	13.2	46.3	—	14450
Benzoic	1.47	5.52	—	15400
Benzenesulphonic	—	0.213	1.09	1600

* k in litre mole^{-1} sec^{-1}.

Within each series, there is a linear relation between hydrolysis rate constant and dissociation constant[42,88] (see Table 6).

The ionisation constants of the acids form to some extent a basis for assessing polar effects on the hydrolysis rate constant. An increase in strength of the acid forming the ester should diminish the stability of its ether bond.

The absence of a correlation between acid strength and rate of hydrolysis in benzoic and benzenesulphonic esters is due to the different mechanisms of hydrolysis and especially to different reactive centres, the carbonyl carbon in the first case and the alkyl carbon in the second.

Let us examine the reasons for deviations from this rule in acetic and benzoic esters. Conjugation between the π electrons of the benzene ring and of the carbonyl group, $\pi\pi$ conjugation, tends to stabilise the carboxylate ion, and thereby facilitates the splitting off of a proton from benzoic acid. Since in the alkaline hydrolysis of carboxylic esters the transition state is saturated, and there is no considerable conjugation with the functional group, the activation energy of hydrolysis for benzoic esters can be expected to exceed that for acetic esters by the stabilisation energy due to the conjugation



in the former esters. It is the presence of this conjugation which diminishes the susceptibility of the carbonyl carbon to nucleophilic attack.

Although, therefore, the phenyl group represents a system of conjugated σ and π bonds, is electron-accepting, and should tend to weaken the C–O bond, *i.e.* favour hydrolysis, benzoic esters are hydrolysed by alkalis more slowly than the corresponding acetic esters. Exactly the same situation occurs with cinnamic and crotonic esters[89]. The

TABLE 6. Effect of acid strength on rate of hydrolysis of esters $RCOOC_6H_5$.

R	Hydrolysis rate constant[42], $10^3 k_{18}$	Acid dissociation constant[42], $10^6 K_{25}$
H	rapidly saponified	214.2
CH_3	245.4	18.0
C_2H_5	150.0	13.4
C_6H_5	22.3	63.0
$C_6H_5CH_2$	605.0	56.6
$C_6H_5CH_2CH_2$	165.0	22.7

steric effect of the phenyl ring is slight, and therefore the appreciably lower rates cannot be due to this cause. Removal of the benzene ring from the carbonyl carbon destroys the conjugation, and an increase in rate of hydrolysis is observed in phenylacetic and phenylpropionic esters owing to the favourable inductive effect[42].

The effect of remoteness of the phenyl radical from the carbonyl carbon on rate of hydrolysis can be determined by calculating the transfer factor of the effect.

From the ratio of the rate constants for the hydrolysis of

$$C_6H_5COOC_6H_5\ (k_1),\quad C_6H_5CH_2COOC_6H_5\ (k_3),\quad C_6H_5CH_2CH_2COOC_6H_5\ (k_5),$$

to the rate of hydrolysis of phenyl acetate k_4 we have $k_1 : k_4 = 0.09$. The ratio is less than unity owing to conjugation; the transfer factor of the effect is 2.47 for phenylacetic acid, and 1.27 for phenylpropionic acid.

When conjugation between the benzene ring and the carbonyl group of the ester is impossible, as with a phenylacetic, alkaline hydrolysis is more rapid than with the corresponding acetic ester (Table 6). This result can be regarded as evidence of the great capacity of the phenyl group for withdrawing electrons. The phenylpropionic ester shows a decrease in the transfer factor owing to weakening of the inductive effect of the benzene ring. The inductive effect of a substituent is approximately halved by the introduction of the methylene group.

Esters of substituted benzoic acids show complete parallelism between the dissociation constants of the acids and the reactivity of the ester link[90,91].

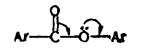
Comparison of the rate constants for the alkaline hydrolysis of phenyl methanesulphonate[82] $k_1 = 0.555$ litre mole^{-1} × × sec^{-1} and phenyl toluene-*p*-sulphonate $k_2 = 0.191$ litre × × mole^{-1} sec^{-1} shows no great decrease in rate of hydrolysis due to introduction of the benzene ring. The ratio of the rate constants $k_1 : k_2 = 3$, whereas the corresponding ratio for phenyl acetate and benzoate is 14. The small difference between the rates of hydrolysis of the sulphonic esters shows either that the benzene ring is not conjugated with the sulphonyl group or that the initial and transition states have the same structure. The slight decrease in rate of hydrolysis can be attributed to the steric effect of the ring. The hydrolysis rate constants of the chlorides of carboxylic acids (acetyl and benzoyl chlorides) vary in conformity with the same rules as were observed with carboxylic esters. Different relations are observed with the sulphonyl chlorides: the hydrolysis rate constant of benzenesulphonyl chloride is $10^4 k_{30} = 4.33$, while the value for methanesulphonyl chloride[92] is $10^4 k_{30} = 1.5$ sec^{-1}: here introduction of a benzene ring does not diminish but increases the rate of hydrolysis, probably owing to the predominant influence of the polarity of the S–Cl bond, not of the nucleophilic character of the sulphur, on the rate of hydrolysis of aromatic sulphonyl chlorides.

(*b*) Influence of the Nature of the Alcoholic Component and of Substituents in the Alcoholic Component

The rate of hydrolysis of carboxylic esters is governed mainly by the electrophilic character of the carbonyl carbon. Increase in the electronegativity or acidic properties of the alcohol radical as a result of the inductive effect enhances the electrophilic character of the carbonyl carbon in the ester and thereby facilitates the addition of OH^- ions[42,93,94].

The alcoholic components arrange themselves in the following sequence with respect to their effect on the rate of alkaline hydrolysis of the acetic and benzoic esters: $C_2H_5OH < C_6H_5CH_2CH_2OH < C_6H_5CH_2OH < C_6H_5OH < < HOC_6H_4SO_2C_6H_4ONa < HOC_6H_4SO_2C_6H_5$.

The difference in the rates of hydrolysis of ethyl benzoate (k_4) and phenyl benzoate (k_1) can be attributed to the electronic effect of the phenyl radical. The ratio is $k_1 : k_4 = 22.3 : 1.47 = 15$. With the benzyl ester this ratio is 1.67, while with the phenethyl ester it approaches unity: *i.e.* the electronic effect of the phenyl ring on the carbonyl carbon is almost completely extinguished when they are separated by two methylene groups. The large transfer factor for the phenyl radical is probably due to the influence of the inductive effect and the conjugation effect:



In the benzyl and phenethyl esters the alcoholic components are not involved in the conjugation, and only a slight inductive effect is developed.

A change in the nature of the alcoholic component in esters formed by benzenesulphonic acid with aliphatic alcohols affects not only the rate but also the mechanism of the reaction. If R in the ester $XC_6H_4SO_2OR$ is derived from a primary alcohol, reaction takes place by an S_N2 mechanism[49,74]; if R represents the radical of a benzyl[95], cycloalkyl[96], or a secondary or tertiary aliphatic alcohol, hydrolysis takes place by an ionic mechanism[97]. Alkyl benzenesulphonates in some respects resemble alkyl halides. The alkaline hydrolysis of methyl and ethyl halides in aqueous acetone or alcohol is mainly an S_N2 reaction, whereas isopropyl and t-butyl halides undergo hydrolysis in two steps by an S_N1 mechanism[20,21,98–100].

A study of the kinetics of the hydrolysis of methyl, ethyl, n-propyl, and isopropyl benzenesulphonates in aqueous solution showed that reaction velocity increases in the series[49]

$$\text{n-propyl} < \text{methyl} = \text{ethyl} < \text{isopropyl}.$$

The rate of hydrolysis of isopropyl benzenesulphonate in aqueous acetone or in aqueous dioxan is independent of the concentration of OH^- ions, and remains constant in alkaline, neutral, and acid media. The reaction velocity is governed by fission of the C–O bond:

$$RSO_2OCH(CH_3)_2 \rightarrow [RSO_2O^{-\delta} \ldots CH^{+\delta}(CH_3)_2] \rightarrow$$

$$\rightarrow RSO_2O + \overset{+}{C}H(CH_3)_2 \quad \text{(slow)},$$

$$(CH_3)_2\overset{+}{C}H + HOH \rightarrow (CH_3)_2CHOH + H^+ \rightarrow \text{(rapid)}.$$

s-Butyl benzenesulphonate behaves similarly.

The activation energy in the hydrolysis of sulphonic esters RSO_2OCH_2R' is determined mainly by the repulsion between the attacking reagent (OH^- or H_2O) and the alkyl carbon atom.

When R' = H, repulsion is insignificant, and reaction occurs by an S_N2 scheme. When, however, the energy of repulsion is significant, reaction takes place by an S_N1 mechanism. In conformity with this, the S_N1 mechanism

usually requires a greater activation energy than does S_N2 for similar molecules. The frequency factor is greater for the former than for the latter type of process. Introduction into the alkyl radical of substituents which increase the negative charge on carbon favours the unimolecular and hinders the bimolecular mechanism.

If R′ is an aryl radical, as in the hydrolysis of substituted benzyl toluene-*p*-sulphonates [101] $CH_3C_6H_4SO_2OCH_2C_6H_4X$ in 76.6% aqueous acetone (values of 10^5k_{25} in sec^{-1} for various substituents X are: *p*-NO_2 0.224, *m*-Br 0.880, *p*-Br 4.30, *m*-CH_3O 6.50, H 11.0, *m*-CH_3 19.7, *p*-CH_3 310.0, *p*-CH_3O 480.0), reaction occurs by the S_N1 mechanism and obeys a first-order equation.

The influence of the electronic nature of the substituents and the polarity of the medium on the rate of hydrolysis of benzyl toluene-*p*-sulphonates confirms the presence of an S_N1 ionic mechanism, in which the polarity of the C–O bond plays the decisive part. Therefore substituents which increase the electron density at the site of the reaction accelerate the reaction, while those which diminish the electron density retard the reaction.

The value of ρ for solvolysis is -2.2. The minus sign indicates a more complete intermediate dissociation of the C–O bond than in the solvolysis of $C_6H_5CH_2Cl$ (ρ = -1.33), which is probably linked with the greater solvation of the toluene-*p*-sulphonate ion compared with the chloride ion. Values of σ for all substituents other than *p*-CH_3 and *p*-CH_3O (σ = -0.65 and -2.5 respectively) coincide with those calculated earlier. The discrepancies are due to stabilisation of the $ArCH_2^+$ ion in the intermediate state by the supply of electrons from the *p*-CH_3 and *p*-CH_3O groups.

The solvolysis of cycloalkyl toluenesulphonates containing rings of different sizes (n = 4–15) also passes through a stage of slow ionisation of the toluene-*p*-sulpho-group [96].

Replacement of an alkyl by an aryl radical in the alcoholic component of benzenesulphonic esters fundamentally changes not only the reaction mechanism but also the point of attack. The sulphur atom in the sulpho-group then becomes the reactive centre, and the reaction becomes bimolecular with an S_N2 mechanism (see Table 7).

Alcoholic components arrange themselves in the following sequence according to rate of hydrolysis: C_6H_5OH < < C_2H_5OH < *pp′*-$HOC_6H_4SO_2C_6H_4ONa$ < *p*-$HOC_6H_4SO_2C_6H_5$.

This sequence corresponds to increasing acidity of the reactants with the exception of phenyl benzenesulphonate, which, because of the change in reaction mechanism on passing from alkyl to aryl sulphonates, does not fit into this order. The esters of the di- and mono-hydroxy derivatives of diphenyl sulphone show a further diminution in the stability of the ester link to hydrolysis.

The alcoholic components arrange themselves in the following sequence with respect to the rate of hydrolysis of the carboxylic esters (acetates and benzoates): C_2H_5OH < < C_6H_5OH < $HOC_6H_4SO_2C_6H_4ONa$ < $HOC_6H_4SO_2C_6H_5$, *i.e.* in order of increasing acidic properties. The phenyl esters showed no deviation from this sequence, in conformity with the common mechanism of hydrolysis of these esters.

Substituted phenyl benzenesulphonates show a complete parallelism between the acidity of the alcoholic components and the rate of hydrolysis.

Electrophilic and nucleophilic substituents affect the rate of hydrolysis in the same sense, independently of their orientation in the benzene ring of the phenol or of the benzenesulphonic acid (Table 8 collates the rate constants for the hydrolysis of aryl sulphonates with the dissociation constants of the substituted phenols).

Although the order of the effect of different substituents is the same, the relative magnitude of the effect for each substituent depends on whether it is located in the benzene ring of the acid or of the alcoholic component. Electrophilic substituents (*p*-Cl, *p*-NO_2) exert a greater influence on the rate of hydrolysis of aryl sulphonates when they are located in the phenolic ring (see Table 8). The influence of electron-donor substituents transmitted through the benzene ring of the phenol is weaker than that of the same substituents in the benzenesulphonic acid. If it is assumed that the reactive centre in the hydrolysis of aryl sulphonates is the sulphur atom in the sulpho-group, the greater effect of electrophilic substituents in the benzene ring of the phenol can be explained either by the presence on the oxygen of two pairs of *p*-electrons conjugated with the electrons of the benzene ring or by a considerable increase in polarity of the S–O bond. The variation in the activation energy and the frequency factor corresponds to the changes observed in the rate constant. The influence of substituents in the *ortho*-, *meta*-, and *para*-positions develops differently depending on whether the benzene ring is in the acid or the alcoholic component.

In esters formed by benzenesulphonic acid and a substituted phenol the influence of a nitro-group on the rate of

TABLE 7. Alkaline hydrolysis of benzenesulphonic esters $C_6H_5SO_2OR$, having different phenolic components, in 70% dioxan–water solution [85].

R	$10^3k^*_{50}$	10^3k_{50}	log P_z	E
C_2H_5	0.213	1.09	7.88	16000
C_6H_5	—	0.43	—	—
$C_6H_4SO_2C_6H_4OH$	3.10	15.45	8.64	16500
$C_6H_5SO_2C_6H_4$	4.92	23.25	8.10	15100

* k in litre $mole^{-1}$ sec^{-1}.

TABLE 8. Effect of the nature of the substituents in the phenyl ring on the rate of alkaline hydrolysis of aryl sulphonates [71] $C_6H_5SO_2OC_6H_4X$.

Substituent X	$10^3k^*_{50}$	log P_z	E	Dissociation constant K
2-CH_3	0.129	10.24	20900	$6.3\cdot10^{-11}$**
4-CH_3	0.184	8.78	18500	$6.7\cdot10^{-11}$
3-CH_3	0.263	8.82	18300	$9.8\cdot10^{-11}$
H	0.374	8.66	17900	$1.0\cdot10^{-11}$
4-Cl	2.47	8.77	16700	
3-NO_2	31.50	8.95	15400	$5.3\cdot10^{-9}$
4-NO_2	76.65	9.23	15300	$9.6\cdot10^{-9}$
2-NO_2	134.90	8.95	1000	$7.5\cdot10^{-8}$

* k in litre $mole^{-1}$ sec^{-1}.

** See Ref. 102.

hydrolysis varies in the following sequence: o-NO_2 > > p-NO_2 > m-NO_2; whereas a different order is found in esters of phenol with a substituted benzenesulphonic acid: p-NO_2 > m-NO_2 > o-NO_2. Thus a nitro-group in the *ortho*-position in the benzenesulphonic acid diminishes the rate of hydrolysis of aryl sulphonates and aromatic sulphonyl chlorides, whereas a nitro-group in the *ortho*-position in phenol has a favourable influence, exhibiting only its electronic effect, and producing no steric hindrance.

The influence of substituents, transmitted through the benzene ring of benzoic acid, on the rate of hydrolysis of ethyl and phenyl benzoates is far greater than their influence in the benzene ring of phenol: *i.e.* the observed regularity is opposite to that found for aryl benzensulphonates (see Table 9).

Introduction of a p-NO_2 group into benzoic acid increases the rate of hydrolysis of a benzoate by a factor of 85, but a p-NO_2 group in phenol increases the rate of hydrolysis of the phenyl ester by a factor of only 15. Yet introduction of this group into a benzenesulphonic acid increases the rate of hydrolysis of a phenyl benzenesulphonate by a factor of 70, while the corresponding factor for its introduction into the phenol is 205.

Such a difference in the effect of substituents in the alcoholic component on the rates of hydrolysis of carboxylic and of benzenesulphonic esters results from the difference in the mechanism of their hydrolysis. The reactivity of carboxylic esters is influenced by the electrophilic character of the carbon, which facilitates the approach of the OH^- ion and increases the polarity of the C–O bond undergoing rupture. The reactivity of sulphonic esters depends on the electrophilic properties of the sulpho-group and the polarity of the S–O bond undergoing rupture. Since substituents have a greater effect when present in the acid component than in the alcoholic component of carboxylic esters, the main factor influencing the rate and activation energy of the hydrolysis of such esters is the electrophilic character of the carbon. In benzenesulphonic esters the greater effect of substituents in the phenolic moiety indicates that it is the polarity of the S–O bond which governs the reaction velocity. The more polar the bond, the more readily is it ruptured, which also facilitates a synchronous mechanism of S_N2 type.

Thus the hydrolysis of carboxylic esters can be regarded as a nucleophilic addition, since the reaction velocity will be governed by addition to the carbonyl carbon; whereas the hydrolysis of benzenesulphonic esters is rather a nucleophilic substitution, since the rate depends mainly on the stability of the S–O bond under synchronous reaction conditions.

TABLE 9. Rate of alkaline hydrolysis of phenyl acetates and ethyl benzoates [90].

Substituent X	$XC_6H_4OCOCH_3$ 10^2k_{25}	$C_2H_5OCOC_6H_4X$ 10^2k_{25}
H	53.7	0.2891
m-CH_3	38.83	0.1686
p-CH	31.91	0.1142
m-NO_2	549.00	13.65
p-NO_2	805.0	24.63
p-NH_2	28.15	0.0864

Introduction of more than one nitro-group, whether in the acid or in the alcoholic component, gives a considerable increase in rate of alkaline hydrolysis compared with the mononitrated esters [58,66,103]. The increase in rate of hydrolysis is especially noticeable when two nitro-groups are introduced into the phenolic component (see Table 10).

In order to compare the effect of two nitro-groups in the benzenesulphonic acid with the effect of the same groups in the phenol, it is useful to calculate the transfer factor of the electronic effect of substituents at different ends of the system, from the ratios of the hydrolysis rate constant of phenyl 2,4-dinitrobenzenesulphonate (k_2) to that of the unsubstituted phenyl benzenesulphonate (k_1) and the ratio of that of 2,4-dinitrophenyl benzenesulphonate (k_3) to k_1

$$f_1 = \frac{k_2}{k_1} = \frac{183}{0.06} = 3050; \quad f_2 = \frac{k_3}{k_1} = \frac{880}{0.06} = 14\,300; \quad f_2 : f_1 = 4.7 .$$

Similarly, for the p-mononitro-derivatives

$$f_3 = \frac{k_4}{k_1} = \frac{6.79}{0.06} = 113; \quad f_4 = \frac{k_5}{k_1} = \frac{15.9}{0.06} = 265; \quad f_4 : f_3 = 2.3 .$$

The relatively high value of f_2 compared with f_1 is due to the operation of two factors, firstly the increase in polarity of the S–O bond, and secondly the presence of an *ortho* effect in phenyl 2,4-dinitrobenzenesulphonate. The latter effect is confirmed also by the considerably higher activation energy of hydrolysis (by 5000 cal) in phenyl 2,4-dinitrobenzenesulphonate compared with 2,4-dinitrophenyl benzenesulphonate.

With regard to the effect of orientation on the rate of hydrolysis of aryl sulphonates, the following sequence is obtained for the dinitro-compounds: 2,6 > 2,4 > 2,5 > 3,4. In this case, too, the greatest accelerating effect is exerted by two o-nitro-groups. Thus such groups exert no steric hindrance, which is consistent with an acyl–oxygen mechanism for the hydrolysis of these esters.

TABLE 10. Alkaline hydrolysis of nitro-substituted aryl sulphonates.

Ester	$10^3k_0^*$	10^3k_{15}	E	log P_z	ΔS
$C_6H_5SO_2OC_6H_3(NO_2)_2$-2,4	318.0	996.0	11900	9.02	—19.88
2,4-$(NO_2)_2C_6H_3SO_2OC_6H_5$	38.0	183.0	16400	11.68	
3,5-$(NO_2)_2C_6H_3SO_2OC_6H_5$	1.45	5.8	14400	8.67	
2-$NO_2C_6H_4SO_2OC_6H_3(NO_2)_2$-2,4	2450	—	—	—	—
2,4-$(NO_2)_2C_6H_3SO_2OC_6H_4NO_2$-2					
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-2,6	1980	—	—	—	—
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-2,4	1170	—	—	—	—
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-2,5	702	2310	12400	9.77	—16.41
4-$ClC_6H_4SO_2OC_6H_3(NO_2)_2$-3,4	178	560	11990	8.85	—20.67
4-$ClC_6H_4SO_2OC_6H_3$—2-NO_2-4-Cl	44.2	183	14800	10.49	—13.14
4-$ClC_6H_4SO_2OC_6H_3$—2-Cl-4-NO_2	36.7	144	14200	9.97	—15.56
4-$ClC_6H_4SO_2OC_6H_3$—2-Cl-3-NO_2	12.6	63.5	16800	11.53	— 8.43
$C_6H_5SO_2OC_6H_3(NO_2)_2$-2,6	737	2200	11400	8.98	—20.05
2,4,6-$(CH_3)_3C_6H_2SO_2OC_6H_3(NO_2)_2$-2,6	168	631	13800	10.27	—14.17
4-$CH_3C_6H_4SO_2OC_6H_3(NO_2)_2$-2,4	182	382	12800	9.28	—18.75
2,4,6-$(CH_3)_3C_6H_2SO_2OC_6H_3(NO_2)_2$-2,4	84.2	306	13600	9.82	—16.19

* k in litre $mole^{-1}$ sec^{-1}.

The influence of several different substituents on k, E, and P_z does not show the strict regularity characteristic of single *para*-substituents. In this case relations are complicated by variation not only in the nature of the substituents but also in their position. With each individual ester, however, variation in the rate constant depends on the activation energy, the reaction velocity increasing when the latter decreases. The temperature-independent factor P_z increases with increase in activation energy.

The entropy of activation is very negative, fluctuating between -13 and -20 cal deg^{-1} mole^{-1}, which approaches the entropy of activation for the hydrolysis of benzoic esters (-24.9) and differs from the corresponding value for ethyl benzenesulphonates (-10 cal deg^{-1} mole^{-1}). Such a difference in entropy of activation is caused by differences in the electron distribution on formation of the transition structures. The more negative the entropy of activation, the more polar is the active complex. With aryl sulphonates there is a rigid structure, associated with the electron distribution and with a change in solvation on formation of the transition state.

Introduction of methyl groups into benzenesulphonic acid, which decrease the positive charge on the sulphur, diminishes the rate of hydrolysis (Table 10). The introduction of three methyl groups in the 2,4,6-positions, which produce steric hindrance to the hydrolysis of esters, slows down the hydrolysis of sulphonates far less than could have been expected.

5. INFLUENCE OF SOLVENTS

With most nucleophilic substitutions, increasing the polarity of the medium increases the rate of hydrolysis, since it tends to increase the charge at the site of reaction.

The total activation energy includes the energy of bond rupture E_B and the repulsion energy E_x. If the dielectric constant ϵ is infinite, E_x falls to zero.

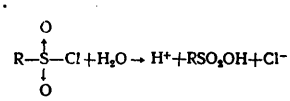
The relation between activation energy and dielectric constant can be expressed by the equation:

$$\epsilon = E_B + (E_x/E_{\epsilon_0}).$$

Thus the hydrolysis of esters is most rapid in water; organic solvents, such as ethanol, acetone, dioxan, etc., diminish the reaction velocity to a greater or lesser extent[39,104-110]. At the same time, the rate constant depends on the molecular structure of the solvent and not on its macroscopic properties[96]. As a result, the empirical relation established between activation energy and dielectric constant of the solvent represents a special case[80]. However, interaction no doubt occurs between the reactants and the solvent, resulting in the formation of either cyclic complexes[75,76] or solvates[111].

The hydrolysis of sulphonyl chlorides is accelerated by an increase in polarity of the solvent[92,112-114].

Data available on the influence of the nature and position of substituents[74] (Table 1) and also of the polarity of the solvent on rate of hydrolysis indicate that the uncatalysed hydrolysis of substituted benzenesulphonyl chlorides occurs by an S_N2 mechanism, being represented by a pseudounimolecular expression where the solvent molecule is a direct reactant[70]:



and reaction is accomplished by nucleophilic attack on the positively charged sulphur atom.

Whereas for hydrolysis in 70% dioxan–water medium substituents are arranged in the following sequence with respect to their accelerating influence: 4-NO_2 > 2,4,6-$(CH_3)_3$ > H > 2,4-$(CH_3)_2$ > 4-CH_3 > 4-CH_3O, the change in polarity of the medium on passing to 40% dioxan–water solution gives a different sequence[115]: 2,4,6-$(CH_3)_3$ > 4-NO_2 > > H > 2,4-$(CH_3)_2$ > 4-CH_3O > 4-CH_3; the sequence in water is 4-CH_3O > 4-CH_3 > 4-NO_2 > 4-Cl (Fig. 3).

The inductive effect of substituents on the rate of hydrolysis of aromatic sulphonyl chlorides can be estimated by means of Taft's equation: $\log k/k_0 = \rho^\circ\sigma^\circ$,[117] where k and k_0 are the hydrolysis rate constants for the substituted and unsubstituted benzenesulphonyl chlorides respectively, σ° is the inductive constant of the substituents (C_6H_5 being taken as standard, for which $\sigma^\circ = 0$), and ρ° is a constant indicating the sensitivity of the given reaction series to the inductive effect of the substituents. The graph of $\log k$ plotted against the σ° constants is shown in Fig. 4. All the substituents other than 2,4,6-$(CH_3)_3$ and 2,4-$(CH_3)_2$ fit well on the same straight line.

The value of ρ° in Taft's equation is positive and diminishes with increasing proportion of water: for 70, 60, 50, and 40% dioxan–water solutions the reaction constant is 1.33, 1.13, 0.93, and 0.80 respectively. In the cases of 2,4-$(CH_3)_2$ and 2,4,6-$(CH_3)_3$ the reaction constant is negative (-3.44). A large negative value of ρ° indicates a change in mechanism.

Thus the polar and steric effects of these substituents continuously decrease the absolute reaction velocity by the S_N2 mechanism, while the rate by the S_N1 mechanism increases starting from 2,4-$(CH_3)_2$.

Increasing the polarity of the medium (on passing from a 70% dioxan–water solution to water, with a change in dielectric constant from 18 to 80) increases the rate of hydrolysis of all benzenesulphonyl chlorides, but not to the same extent, the factor being 3 in the case of p-NO_2 and 175 for p-CH_3O.

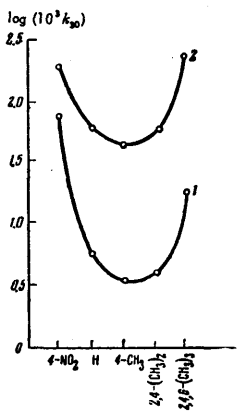


Fig. 3. Effect of the nature and orientation of substituents on the hydrolysis rate constant of substituted benzenesulphonyl chlorides in dioxan–water solutions: 1) 70%; 2) 40%.

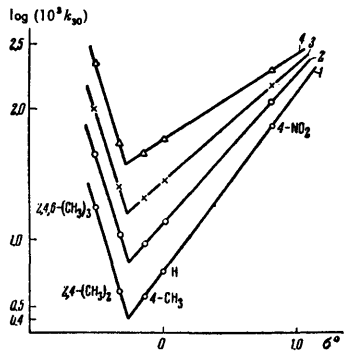


Fig. 4. Dependence of the hydrolysis rate constants of substituted benzenesulphonyl chlorides on σ° in dioxan–water solutions: 1) 70%; 2) 60%; 3) 50%; 4) 40%.

The dependence of log k on the ionising power of the solvent in the Grunwald–Winstein equation is linear, the straight lines lying close together and that for p-nitrobenzenesulphonyl chloride having the lowest slope (Fig. 5).

The Grunwald–Winstein equation is [118]:

$$\log k_{ij}/k_{0i} = m_i \log k_{0j}/k_{00},$$

where k_{ij} represents the rate constant for the hydrolysis of substituted benzenesulphonyl chlorides in different dioxan–water solutions, k_{0i} the corresponding rate constant for hydrolysis in the standard solvent (80% ethanol by volume), k_{0j} the rate constant for the hydrolysis of t-butyl chloride in the given solvent, and k_{00} the corresponding rate constant in 80% aqueous alcohol. The ratio log k_{0j}/k_{00} is denoted by Y and is termed the "ionising power of the solvent". The equation is abbreviated log $k_{ij}/k_{00} = m_i Y$, m_i being a constant depending solely on the nature of the substance. Values of Y can be calculated for any solvent by means of the formula

$$Y = a + bN + cN^2 + dN^3 + eN^4, \qquad (1)$$

where N is the mole fraction of water and a, b, c, ... are correction factors, their values under our conditions being: a = -5.641; b = 15.837; c = 20.374, and d = 13.885. Values of Y calculated by means of Eqn. (1) are listed in Table 11.

The presence of linear relations (Fig. 5) and the increase in the value of m indicate that the hydrolysis of benzenesulphonyl chlorides takes place partly by an S_N1 mechanism, except in the case of the p-nitro-derivative.

The existence of two mechanisms, S_N2–S_N1, in the hydrolysis of aromatic sulphonyl chlorides follows also from a calculation of the number of water molecules associated with the chlorides in the transition state [78]. If the reaction velocity is assumed to be proportional to the nth power of the molar concentration of water, the rate equation will be of the form

$$\frac{dx}{dt} = k\,[a - x]\,[H_2O]^n,$$

whence

$$\log k = \log k_1 + n \log C_{H_2O},$$

$$\log k = n \log [H_2O] + \text{const.}$$

TABLE 11.

Concn. of dioxan–water soln., vol. %	N_{H_2O}	Y
40	0.88	+1.99
50	0.82	+1.33
60	0.75	+0.65
70	0.65	−0.13

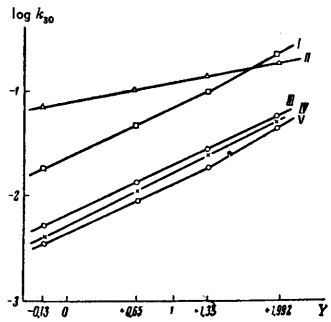


Fig. 5. Dependence of the hydrolysis rate constants on the ionising power Y of the solvent: I) 2,4,6-$(CH_3)_3$; II) 4-NO_2; III) H; IV) 2,4-$(CH_3)_2$; V) 4-CH_3.

The value of n was found from the slope of the plot of log k against the molar concentration of water (Fig. 6).

The reaction is first order with respect to the sulphonyl chloride, but the reaction order with respect to water depends both on the nature of the substituent and on the concentration of dioxan. With p-NO_2 in 70–40% dioxan–water solutions the reaction is first order with respect to water; with the other chlorides in 70–50% dioxan–water solutions the reaction is third order with respect to water, and in 50–40% dioxan–water solutions the reaction order is 4–5.

From these results it follows that, at all dioxan concentrations between 40 and 70%, p-nitrobenzenesulphonyl chloride entraps one molecule of water and is hydrolysed by a bimolecular S_N2 mechanism, which involves nucleophilic attack by the water.

All other sulphonyl chlorides at dioxan concentrations of 60–70% associate with about three water molecules, while in 40% solution four water molecules are closely involved in formation of the transition complex. This last fact indicates the tendency of sulphonyl chloride to react by a mixed S_N2–S_N1 mechanism with the latter predominating in 40% solution.

Values close to three are greater than are required for reaction by an S_N2 mechanism. It is probable that solvation of the sulphonyl chloride molecules by a few water molecules is sufficient to produce the energy required to split the S–Cl bond, and after sufficient extension, one of the water molecules of the solvate layer can react with the sulphonyl group. The transition state is probably formed within a cell made up of four molecules of water and an outer layer of oriented water molecules. Variation in the

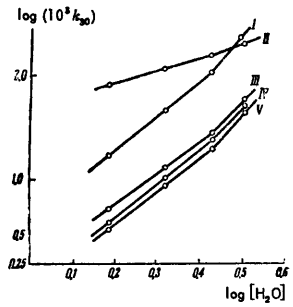


Fig. 6. Relation between log k and log $[H_2O]$: I) 2,4,6-$(CH_3)_3$; II) 4-NO_2; III) H; IV) 2,4-$(CH_3)_2$; V) 4-CH_3.

TABLE 12. Effect of the polarity of the solvent on the rate of alkaline hydrolysis of p-nitrophenyl benzenesulphonate[115].

Content of solvent	$10^3 k^*_{25}$	$10^3 k_{20}$	log P_z	E
vol. %	A. Aqueous dioxan solution			
40	12.80	52.70	8.033	13760
50	13.05	54.00	8.104	13850
60	13.60	57.30	8.225	13990
70	14.00	60.00	8.356	14150
80	17.30	76.60	8.67	14460
wt. %	B. Aqueous acetone solution			
40	9.1	36.5	7.70	13500
50	9.7	40.5	8.01	13900
60	10.1	41.8	8.00	13860
70	12.0	51.6	8.32	12400

* k in litre mole^{-1} sec^{-1}.

nucleophilic character of the reagent shows that trimethylbenzenesulphonyl chloride is very insensitive to change in alkalinity of the medium, which in turn confirms the S_N1 mechanism in this case, involving ionisation according to the scheme:

$$(CH_3)_3C_6H_2SO_2Cl \rightarrow (CH_3)_3C_6H_2SO_2^+ + Cl^- \quad \text{(slow)},$$

$$(CH_3)_3C_6H_2SO_2^+ + H_2O \rightarrow (CH_3)_3C_6H_2SO_2OH + H^+ \quad \text{(rapid)}.$$

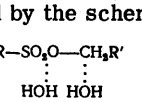
Alkyl benzenesulphonates exhibit a tendency to react more rapidly by the S_N2–S_N1 mechanisms than by either of them separately[74,78,119]. The transition from an S_N2 to an S_N1 mechanism becomes more marked with increasing polarity of the solvent. The effect of the solvent on the uncatalysed hydrolysis of alkyl sulphonates shows a great similarity to the hydrolysis of alkyl halides. The reaction velocity by the S_N1 mechanism increases with increase in the ionising properties of the solvent. With bimolecular reactions the transition from the initial to the intermediate state is linked with the magnitude of the charges, and therefore it depends, nevertheless, on the ionising properties of the solvent, although to a smaller extent. These points have been verified for the alkyl halides and the solvolysis of alkyl sulphonates[34,120–122]. The rate of hydrolysis of isopropyl benzenesulphonate increases steadily with increasing content of water in the solvent: 50° the rate in pure water is 4.3 times that in 17.8% aqueous acetone, and 1000, 10 000, and 73 000 times those in 80, 92.5, and 98% aqueous acetone, respectively.

The influence of the polarity of the medium is considerably less marked in the hydrolysis of ethyl and n-propyl benzenesulphonates. The corresponding factors for the former ester are 2.3, 86, 500, and 1080 respectively. The relation $\log k = n \log [H_2O]$ remains linear when the concentration of acetone in water varies between 0 and 60–70%. The slope of the curve indicates that seven molecules of water are involved in formation of the transition state in the case of t-butyl chloride, six with the corresponding bromide, but only two with ethyl bromide.

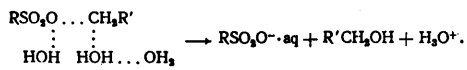
The number of molecules of water involved in the transition state with the alkyl sulphonates is as follows:

Isopropyl benzenesulphonate in	0–50% dioxan	6.0	molecules (n)
	50–90% "	2.6	"
Ethyl benzenesulphonate in	0–50% "	3.6	"
	50–95% "	2.1	"

The value $n = 6$ is characteristic of the S_N1 mechanism in the range 0–50%. Values of 2.1–1.7 for alkyl benzenesulphonates correspond to a medium containing < 50% of water and represent the S_N2 mechanism. In the rate-determining stage of the reaction, one molecule of water forms a bond with the alkyl carbon, while the other forms a hydrogen bond with the oxygen of the O–C group. The transition state can be represented by the scheme:



or



In the case of the S_N1 reaction, experiment shows that six molecules of water are required. They determine the activation energy required to split the C–O bond. A carbonium ion is formed without the participation of the aqueous solvent, and then reacts with one of the water molecules.

The values of 3.6 and 3.8 for an n-alkyl benzenesulphonate are larger than are required for the S_N2 reaction. They show, moreover, that four molecules of water are involved in forming the transition state.

These results can be summarised by stating that ethyl and n-propyl benzenesulphonates react by an intermediate mechanism in solvents having a high water content, and by the S_N2 bimolecular mechanism in solvents containing less than 50% of water. Isopropyl benzenesulphonates undergo hydrolysis by a unimolecular mechanism, but this becomes difficult in solvents containing a small quantity of water.

The influence of the polarity of the medium on the rate and mechanism of the alkaline hydrolysis of aryl sulphonates corresponds to a typical S_N2 mechanism[71,74,115]. Increasing the polarity of the solvent — changing from 80 to 40% dioxan in water solution, and from 70 to 40% acetone in water solution — decreases the rate of alkaline hydrolysis to 1/1.35–1/1.3 of its value. The comparatively slight decrease in rate of hydrolysis of aryl sulphonates with increasing polarity of the medium may be explained (in conformity with Ingold's views) by a decrease in polarity of the reactants in the transition state (compared with the initial state) due to dispersal of the charges[108] (see Table 12).

With each class of compounds a transition from an S_N2 to an S_N1 mechanism can probably be traced for change in polarity of the substituent, in the nucleophilic character of the reagent, and in the ionising properties of the solvent.

6. INFLUENCE OF STERIC FACTORS ON THE RATE AND MECHANISM OF THE HYDROLYSIS OF THE CHLORIDES OF CARBOXYLIC AND SULPHONIC ACIDS

It is of interest to study steric effects in the hydrolysis and solvolysis of benzenesulphonyl chlorides and aryl sulphonates, since this provides an independent approach to establishing the mechanism of hydrolysis with this class of compounds. Depending on the reaction mechanism, the spatial factor may produce either steric hindrance or steric promotion [74,83,115]

Experimental results on the influence of the structure of the initial benzenesulphonyl chloride, the ionising properties of the solvent, and the nature of the reagents on the rate of hydrolysis indicate that trimethylbenzenesulphonyl chloride is hydrolysed by an S_N1 mechanism, whereas the dimethylated compound hydrolyses partly by an S_N2 and partly by an S_N1 mechanism.

Comparison of the relative rates of hydrolysis of substituted benzenesulphonyl chlorides with those of alkyl benzenesulphonates [121] and alkyl halides (Table 13) [20,123,124] shows that aromatic sulphonyl chlorides are similar in some respects to alkyl halides and the alkyl sulphonates. Independently of whether the Alk–Br, Alk–O–S, or $ArSO_2$–Cl bond is broken, the accumulation of electron-donor groups, by creating steric hindrance at the reaction site, in all cases diminishes the reaction velocity by the S_N2 mechanism and favours the S_N1 mechanism.

A change in the nature of the group which is eliminated (Br^-, $C_6H_5SO_2O^-$, Cl^-) has a considerable effect on the absolute rate of substitution, but an insignificant effect on the reaction mechanism. The latter is understandable, since the group which is eliminated completely removes at the same time the previously delocalised electrons, independently of the reaction mechanism. With the alkyl sulphonates and alkyl bromides the minimum rate is shown by the ethyl derivative, but with the alkylated benzenesulphonyl chlorides by the methyl compound (see Table 13).

TABLE 13. Comparison of the relative rate of hydrolysis of substituted benezenesulphonyl chlorides (A) with methyl, ethyl, and isopropyl benezenesulphonates and with the corresponding bromides (B).

A			B	
R	$C_6H_5SO_2Cl$*	R	$C_6H_5SO_2OR$**	RBr***
H	1	CH_3	1	1
$CH_3C_6H_4$	0.76	C_2H_5	0.43	0.76
$(CH_3)_2C_6H_3$	0.98	$(CH_3)_2CH$	4.17	1.46
$(CH_3)_3C_6H_2$	3.80	s-butyl	6.00	

* 50% dioxan–water solution.
** 56% acetone–water solution [70].
*** 50% ethanol–water solution [97].

TABLE 14. Reactions of substituted benzoyl chlorides XC_6H_4COCl with alcohols [126,127].

Substituent X	$\frac{k_{XC_6H_4COCl}}{k_{C_6H_5COCl}}$
H	1.00
o-OCH_3	66.0
o-CH_3	5.2
p-CH_3	0.68
o-NO_2	1.8
p-NO_2	15.6
2,4,6-$(NO_2)_3$	very slow
2,4,6-$(CH_3)_3$	very rapid

Substituted benzenesulphonyl chlorides show greater variations in relative rate constants with change in the nature of the substituent than is the case with alkyl bromides, and smaller than with substituted alkyl sulphonates. It is very probable that the C–O bond in these sulphonates is the most ionic in character, then follows the S–Cl bond in the sulphonyl chlorides, and the least polarised bond is the C–Br linkage in the bromides. Thus nucleophilic substitution at the S atom in benzenesulphonyl chlorides can be effected by S_N2–S_N1 mechanisms, as occurs at a saturated carbon atom [3,4,20,21,57,98,99,108,109,123,124].

Carboxylic acid chlorides are readily hydrolysed, since chlorine has a higher electron affinity than has hydroxyl (or the OR′ group in esters), and the conjugation of the carbonyl which normally occurs in acids and in esters breaks down.

Most reactions of acid halides could occur in two possible ways: (1) addition at the carbonyl carbon, and (2) ionisation [125]:

$$R{-}COCl + CH_3OH \rightarrow R{-}\underset{\displaystyle OCH_3}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}Cl \rightarrow RCOOCH_3 + HCl\,, \qquad (1)$$

$$RCOCl \rightarrow RCO^+ + Cl^- \xrightarrow{CH_3OH} RCOOCH_3 + HCl\,. \qquad (2)$$

Reactions occurring according to Eqn. (1) are confirmed by the steric effects observed in both the hydrolysis and the alcoholysis of acid halides. In substituted benzoyl chlorides all groups (other than *p*-methyl) increase the rate of reaction with alcohols (see Table 14).

In the cases of the methyl and methoxy-compounds, the *ortho*-isomers show considerably higher reaction velocities than do the *meta*- and *para*-isomers. Steric hindrance appears in reactions taking place by an ionic mechanism, and reaches a maximum with 2,4,6-trimethylbenzoyl chloride, which at 0° reacts with methanol too rapidly for the reaction velocity to be measured [126]. Study of the kinetics of the hydrolysis of substituted and unsubstituted benzoyl chlorides in the presence of different amounts of the hydroxide ion in a water–acetone mixture supports still more strongly the possibility of S_N2 and S_N1 mechanisms [128,129]. The latter mechanism is favoured by an increase in the water content of the mixture. 2,4,6-Trinitrobenzoyl chloride hydrolyses mainly by the S_N2 mechanism, whereas 2,4,6-trimethylbenzoyl chloride hydrolyses mainly *via* an ionic stage. Thus whether steric factors impede hydrolysis depends on the mechanism of the latter.

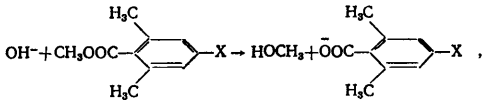
7. INFLUENCE OF STERIC FACTORS ON THE RATE AND MECHANISM OF THE ALKALINE AND AQUEOUS HYDROLYSIS OF ARYL SULPHONATES

The considerable influence of polar effects on the rate of alkaline hydrolysis of substituted phenyl benzenesulphonates shows that movement of electrons from the attacking agent to the displaceable phenoxy-group is not complete in the transition state. Therefore a change in polarity of the replaceable group should affect the reaction velocity[71]. The influence of the polar substituents (Tables 1 and 8) and of the polarity of the medium (Table 12) on the alkaline hydrolysis of aryl sulphonates indicates that such reactions are effected by an S_N2 mechanism[48] and are accompanied by fission of the S–OAr bond.

Investigation of the alkaline hydrolysis of 2,4- and 2,6--dinitrophenyl mesitylenesulphonates in the presence of $H_2{}^{18}O$ also indicates an acyl–oxygen mechanism. With such a mechanism of hydrolysis it is quite obscure why phenyl mesitylenesulphonate is hydrolysed by alkalis only slightly more slowly than is phenyl toluene-*p*-sulphonate, whereas the corresponding mesitylenecarboxylic ester is very difficult to hydrolyse owing to the difficulty of nucleophilic attack on the carbonyl carbon[130].

Although the rate constant for the alkaline hydrolysis of methyl benzoate at 25° is 5.02, the corresponding value for methyl 2,4,6-trimethylbenzoate at 25° is 1.35. Introduction of activating substituents into the *para*-position has little effect on the rate constant.

Alkaline hydrolysis of a methyl 2,6-dimethyl-4-X-benzoate involves attack on the alkyl carbon of the ester group[130]:



the presence of considerable steric hindrance results in a different bond being broken.

Measurement of the dissociation constants of a series of 4-substituted 2,6-dimethylbenzoic acids[131] (in 20 vol.% aqueous dioxan and in 50% aqueous ethanol)[130] shows that the polar effect of the 4-substituent is fundamentally equal to the corresponding effect on the dissociation of the *para*--substituted benzoic acid under the same conditions[132,133]. Thus the dissociation of both series of acids obeys the Hammett equation, the values of ρ being very similar. This shows that dissociation of sterically hindered benzoic acids, in contrast to their hydrolysis, does not disturb the conjugated of the substituted groups with the reactive centre.

The steric effect of methyl groups in the 2,6- and 2,4,6--positions of benzoic esters on their rate of hydrolysis is readily visualised from the structure of the transition complex, in which three substituent groups move to give a tetrahedral structure, the presence of three methyl groups in the benzene ring undoubtedly impeding formation of the intermediate.

It is considerably more difficult to produce a spatial representation for the effect of steric factors on reactions at an unsaturated sulphur atom. In the initial $ArSO_2OAr'$ molecule the valence bonds are probably arranged tetrahedrally, but sulphur, in contrast to carbonyl carbon, is coordinatively saturated, and attack by a nucleophilic reagent can occur in two possible ways, the sulphonyl group being arranged in a plane either coplanar with or perpendicular to that containing the attacking and eliminated groups (see Section 1); this determines whether the sulphonyl group will or will not be conjugated with the benzene ring, and hence whether or not steric hindrance may occur.

Experimentally, introduction of an NO_2 group into phenyl benzenesulphonate *ortho* to the sulpho-group has a retarding influence compared with *para*- or *meta*-substitution, showing that in this case the benzene ring remains coplanar and the *o*-NO_2 group sterically hinders the approach of reagents. The introduction of methyl groups in the 2,4,6--positions of the benzene ring of the acid part in substituted phenyl benzenesulphonates can be expected not only to force the ring out of planarity but also to change the mechanism of hydrolysis.

In order to clear up the anomalous behaviour of the mesitylenesulphonic ester, let us examine the influence of the polarity of the medium and the accumulation of methyl groups in the acyl part of the ester on the rate of hydrolysis of methylated aryl sulphonates (see Tables 15 and 16).

Increasing the polarity of the solvent — on passing from a 70 to a 50% dioxan–water solution — diminishes the rate of hydrolysis of dinitrophenyl and phenyl methylated benzenesulphonates by a factor of 1.7–1.8. The comparatively small decrease in rate of hydrolysis of aryl sulphonates with increase in polarity of the medium may be explained by a diminished polarity of the reactants in the transition state compared with the initial state, due to dispersion of the charges. Furthermore, an increase in polarity of the medium in the alkaline hydrolysis of aryl sulphonates is accompanied by a decrease in activation energy and in the preexponential factor. The dispersion of the charge probably weakens electrophilic character of the sulphur atom, and at the same time the increase in polarity of the solvent increases the polarity of the S–O bond undergoing rupture, thereby diminishing the activation energy.

TABLE 15. Alkaline hydrolysis of dinitrophenyl benzenesulphonates $XC_6H_4SO_2OC_6H_3(NO_2)_2$-2,4 in 70 and 50% dioxan–water medium[115].

Substituent X	70%			50%		
	10^3k_{15}	log P_z	E	10^3k_{15}	log P_z	E
H	996	9.02	11900	560	8.26	11200
4-CH_3	382	9.28	12800	247	8.76	12300
2,4-$(CH_3)_2$	270	9.72	13600	148	9.31	13400
2,4,6-$(CH_3)_3$	301	9.46	13200	176	9.18	13100

TABLE 16. Alkaline hydrolysis of phenyl benzenesulphonates $XC_6H_4SO_2OC_6H_5$ in 70 and 50% dioxan–water medium.

Substituent X	70%	50%
	10^4k_{70}	10^4k_{70}
H	18.97	10.1
4-CH_3	8.0	4.6
2,4-$(CH_3)_2$	7.0	4.1
2,4,6-$(CH_3)_3$	8.0	4.9

Study of the effect of electron-donor groups on the rate of alkaline hydrolysis confirms the presence of an S_N2 mechanism. Aryl methylated sulphonates arranged themselves in the following sequence of decreasing reaction velocity:

$$H > 4\text{-}CH_3 > 2,4,6\text{-}(CH_3)_3 > 2,4\text{-}(CH_3)_2 .$$

The mesitylenesulphonic ester behaves somewhat anomalously (Fig. 7).

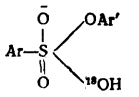
Introduction of three methyl groups, by causing steric hindrance at the site of reaction, gives a slight increase, instead of the expected decrease, in the rate of hydrolysis, which can be explained by the trimethylated benzene ring being forced out of coplanarity, so that nucleophilic attack on the sulphur atom is facilitated.

Introduction of a nitro-group into the phenyl part of the ester has a substantial effect on the rate of alkaline hydrolysis (Tables 15 and 16): phenyl benzenesulphonate is saponified at a rate which is only 1/15 000 of that of the corresponding 2,4-dinitrophenyl ester, providing evidence of the great effect of two nitro-groups on the polarity of the S–O bond.

Of the mono- and di-nitro-substituted phenyl benzenesulphonates only those with a nitro-group in the phenolic part undergo uncatalysed hydrolysis with water. Thus the amounts of 2,4-dinitrophenyl benzenesulphonate and phenyl 2,4-dinitrobenzenesulphonate hydrolysed in a given time are 46 and 4% respectively. An analogous phenomenon is observed when a third nitro-group is introduced into the phenol or into the benzenesulphonic acid. *o*-Nitrophenyl 2,4-dinitrobenzenesulphonate also is not hydrolysed by water, whereas 2,4-dinitrophenyl *o*-nitrobenzenesulphonate is hydrolysed rapidly.

The rate of aqueous hydrolysis of aryl sulphonates is considerably lower than that of the corresponding ethyl sulphonates [$k_{50} = 3.14 \times 10^{-3}$ min^{-1} for m-$NO_2C_6H_4SO_2OC_2H_5$, while $k_{70} = 0.54 \times 10^{-4}$ min^{-1} for $C_6H_5SO_2OC_6H_3(NO_2)_2$-2,4].

Among the dinitrated aryl sulphonates the 3,4-dinitrophenyl esters show the lowest rate of hydrolysis. Chloronitro-derivatives other than the 4-chloro-2-nitrophenyl ester are not hydrolysed by water. Dinitro-substituted esters containing methyl groups in the benzenesulphonic acid are hydrolysed more rapidly than the corresponding non-methylated esters, whereas the opposite order is observed in alkaline hydrolysis. Investigation of the neutral hydrolysis of 2,4-dinitrophenyl mesitylenesulphonate in the presence of $H_2{}^{18}O$ points to an acyl–oxygen mechanism alone[48]. The phenols isolated after hydrolysis contain no heavy oxygen isotope. Unchanged 2,4-dinitrophenyl toluenesulphonate recovered after neutral hydrolysis in the presence of $H_2{}^{18}O$ contained no ^{18}O. This suggests that the intermediate complex



is formed reversibly during the hydrolysis or not at all. The proton has insufficient time to move from one oxygen atom to another before the complex decomposes, and thus the oxygen atoms do not lose their identity. The reaction has a synchronous bimolecular mechanism. On the basis of an acyl–oxygen mechanism of neutral hydrolysis and its occurrence only with mono- and di-nitrophenyl esters, and also in view of the absence of steric effects in the presence of two *o*-methyl groups, the main factor influencing the neutral hydrolysis of aryl sulphonates can be assumed to be the polarity of the S–O bond.

Examination of the kinetics of the neutral hydrolysis of dinitrophenyl benzenesulphonates containing nucleophilic substituents enables an approach to be made to an interpretation of the mechanism of neutral hydrolysis[115] (see Table 17).

In this case an increase in polarity of the medium — the change from a 70 to a 50% dioxan–water solution — does not diminish the rate of hydrolysis of dinitrophenyl benzenesulphonates, but increases it by a factor of 3.1. The opposite influence of solvent polarity on the rates of alkaline and of neutral hydrolysis of aryl sulphonates is evidence of different reaction mechanisms. In the former case the S_N2 mechanism predominates, whereas in the latter an S_N1 mechanism may develop.

The activation energy for neutral hydrolysis is high, 21 200 as compared with 11 900 for alkaline hydrolysis, and approximates to that for the hydrolysis of alkyl sulphonates (19 100). In this case increase in solvent polarity produces an increase in activation energy and in the preexponential factor for H, 4-CH_3, and 2,4-$(CH_3)_2$. With 2,4,6-$(CH_3)_3$ there is a fall in activation energy accompanied by an increase in the preexponential factor.

The rate of neutral hydrolysis gives the following sequence for methylated aryl sulphonates:

$$2,4,6\text{-}(CH_3)_3 > H > 4\text{-}CH_3 > 2,4\text{-}(CH_3)_2 .$$

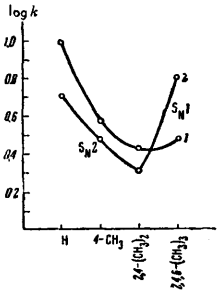


Fig. 7. Rate of alkaline hydrolysis of aryl sulphonates in 70% solution: 1) alkaline, log ($10^3 k_{15}$); 2) neutral, log ($10^5 k_{70}$).

TABLE 17. Neutral hydrolysis of dinitrophenyl benzenesulphonates $XC_6H_4SO_2OC_6H_3(NO_2)_2$-2,4 in 70 and 50% dioxan–water medium.

Substituent X	70%			50%		
	$10^4 k_{70}$	log P_z	E	$10^4 k_{70}$	log P_z	E
H	0.53	9.22	21 200	1.64	9.86	21 500
4-CH_3	0.304	9.25	21 600	1.19	9.90	21 800
2,4-$(CH_3)_2$	0.206	9.36	22 050	1.06	10.42	22 100
2,4,6-$(CH_3)_3$	0.64	8.88	20 500	2.20	9.20	20 200

The fact that in this case the activation energy and the pre-exponential factor are changed in opposite senses may indicate a different mechanism of hydrolysis for the trimethylbenzenesulphonate compared with the other arenesulphonates. Replacement of H by 4-CH_3 and by 2,4-$(CH_3)_2$ produces a successive decrease in rate of hydrolysis; introduction of three methyl groups is accompanied by an increase in rate of hydrolysis ($k_{70} = 1.64 \times 10^{-4}$ for 2,4-dinitrophenyl benzenesulphonate, $k_{70} = 2.2 \times 10^{-4}$ for the corresponding methylated compound), which may be explained by a change in mechanism from S_N2 to S_N1 resulting from the accumulation of methyl groups causing steric hindrance to nucleophilic attack at the site of reaction (Fig. 7).

The effect of all the above factors on the rate of the aqueous hydrolysis of aryl sulphonates suggests that 2,4-dinitrophenyl benzenesulphonates can react in the more polar solvents by an S_N1 mechanism. This can be regarded as proved in the case of the trimethylated ester.

The fact that aqueous hydrolysis occurs only when two nitro-groups are present in the phenol, and not when they are present in the benzenesulphonic acid, can be interpreted on the basis of two mechanisms S_N2 and S_N1 being present. Whereas the activation energy of alkaline hydrolysis is determined by the electrophilic character of the sulphur, and is employed mainly in overcoming the repulsion of the approaching reagent, in aqueous hydrolysis the activation energy is determined by the ease of rupture of the S–O bond, and therefore aqueous hydrolysis takes place only with aryl sulphonates containing electronegative substituents in the phenolic part of the ester.

8. CORRELATION OF RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ARENESULPHONIC ESTERS WITH THEIR STRUCTURE [134]

Rate constants have been cited earlier for alkaline hydrolysis in the reaction series [50,68,71,72,74,83,103]: (1) $C_6H_5SO_2OAr$, (2) $ArSO_2OC_6H_5$, (3) $ArSO_2OAr'$, and (4) $ArSO_2OC_2H_5$. The symbols Ar and Ar′ denote mono- or poly-substituted phenyl groups. The experimental results can be evaluated quantitatively by means of the rule of linear relations between the free energy changes of activation for the standard substance and for substances containing different substituents within a given reaction series. The change in free energy can be measured by the expression $\log k_i/k_0$, *i.e.* the logarithm of the ratio of the rate constant for a substance containing a substituent i to that for the standard substance. The total change in free energy is the sum of the separate elementary changes due to the various structural factors affecting reactivity.

In general, the dependence on the nature of Ar of the reactivity of compounds of the type Ar–Y, where Y represents the reactive centre, can be expressed [67]:

$$\log k = \log k_0 + \rho_0\sigma^\circ + \psi + S, \qquad (1)$$

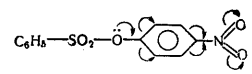
where k_0 is the rate constant for C_6H_5–Y, σ° the inductive constant of the substituent Ar with C_6H_5 as standard (for which $\sigma^\circ = 0$), ρ_0 is a constant representing the sensitivity of the given reaction to the inductive effect of the substituent Ar, ψ a term representing the quantitative effect of direct polar conjugation between the reactive centre and the substituent X in $X\text{-}C_6H_4 = Ar$, and S a measure of the steric factor in the case of *ortho*-substituents in Ar.

For all *meta*-substituents and those *para*-substituents which cannot undergo direct conjugation with the reactive centre, Eqn. (1) reduces to the Hammett equation [41,135] with σ replaced by σ°

$$\log k = \log k_0 + \rho_0\sigma^\circ. \qquad (2)$$

Fig. 8 illustrates the relations between log k and σ° for the reaction series (1)–(3). The straight lines are drawn through points corresponding to substituents for which ψ and S are put equal to zero.

(1) Alkaline hydrolysis of substituted phenyl benzenesulphonates in 70% aqueous dioxan (Table 8). In this case there are no deviations from a linear relation between log k and σ°, indicating practically complete absence of possible conjugation between *para*-substituents of type S† and the reactive centre:



Consequently the influence of substituents in the phenol ring on the reactive centre is transmitted only as an inductive effect. The electronegative group $>SO_2$ probably suppresses conjugation of the p-electrons of the oxygen with the benzene ring.

At 50° $\rho_0 = 2.747 \pm 0.041$, $\log k_{calc} = -3.36$, and $r = 0.9996$. The reaction constant for the hydrolysis of substituted phenyl benzenesulphonates is quite high, which indicates the great sensitivity of the hydrolysis rate constant to structural changes in the ester molecule. This

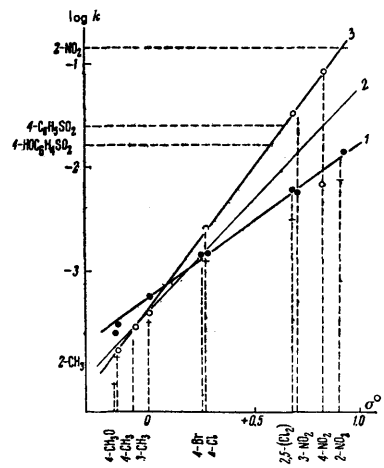


Fig. 8. Dependence of log k on inductive constants σ° of aromatic substituents in the hydrolysis of: 1) $ArSO_2OC_2H_5$; 2) $ArSO_2OC_6H_5$; 3) $C_6H_5SO_2OAr$.

† Substituents of type +S possess an unshared pair of electrons and are electron-donors; substituents of type -S are electron-acceptors by a mechanism of polar conjugation [67].

reaction series is extremely convenient for calculating new values of σ° by means of the formula $\sigma^\circ = (\log k + 3.36)/2.747$, the following having been obtained. 2-CH_3 -0.19, 2-NO_2 +0.91, 4-*p*-$HOC_6H_4SO_2$ +0.56, and 4-$C_6H_5SO_2$ +0.66. The value of σ° for *o*-NO_2 is somewhat greater than published values of σ-*ortho* for this substituent (+0.80 [117] and +0.65). This clearly indicates that in this case $S = 0$. This conclusion is not unexpected, since the sulphur atom undergoing attack by the OH^- ion is quite remote from the substituted benzene ring.

At 0° $\rho_0 = +3.09 \pm 0.059$, $\log k_{calc} = -5.63$, and $r = 0.999$. The temperature-dependence of ρ_0 is represented by the equation

$$\rho_0 = +0.20 + 3660/2.3\,RT.$$

(2) Alkaline hydrolysis of phenyl esters of substituted benzenesulphonic acids in 70% aqueous dioxan (Table 1). In this case *para*- and *ortho*-substituents of +S type can be directly conjugated with the reactive centre. Values of ρ_0' and ρ_C in the equation

$$\log k = \log k_0 + \rho_0\sigma^\circ + \rho_C\sigma_C^\circ$$

calculated by the method of least squares from experimental data for the substituents 4-CH_3O, 4-CH_3, H, 4-Cl, 4-Br, 3-NO_2, and 4-NO_2 at 50° are $\rho_0' = +2.24$, $\rho_C = +0.54$, and $\log k_0 = -3.43$. The reaction constant for the hydrolysis of aryl sulphonates, +2.24, is close to the value of +2.6 calculated by Hammett [41] for the hydrolysis of ethyl benzoates.

Since in this case the hydroxyl attacks a sulphur atom directly linked with a substituted phenyl group, steric hindrance is to be expected with *ortho*-substituents, and $S \neq 0$. The deviations of the experimental values of $\log k$ from the straight line

$$\log k = -3.43 + 2.24\sigma^\circ$$

yield in the case of the *ortho*-substituted phenyl esters values of $S = -0.75$ for 2-NO_2 and of $\psi + S = -0.65$ for 2-Cl.

(3) Alkaline hydrolysis of phenyl benzenesulphonates substituted in both benzene rings (Table 10). This reaction series (3) includes series (1) and (2) as well. In this case methods of "cross-correlation" (the superposition of several independent correlation equations) [138] must be employed to calculate the rate constants. In view of this, the following equation can be written down for this reaction series

$$\log k_{ij} = \log k_{00} + \rho_0\Sigma\sigma_i^\circ + \rho_0'\Sigma\sigma_j^\circ + \rho^*\Sigma\sigma_i^\circ\Sigma\sigma_j^\circ + \rho_C^+\sigma_{C_i}^{\circ+} + S\ldots, \quad (3)$$

where the subscript i refers to nuclear substituents in the benzenesulphonic acid, and j to substituents in the phenyl ring. The value of ρ^* is found from the relation

$$\rho^* = \frac{\rho_{0k} - \rho_0}{\sigma^\circ_k} = \frac{\rho'_{0k} - \rho_0}{\sigma'_k},$$

where ρ_{0k} and ρ'_{0k} relate to the hydrolysis reaction series $X^kC_6H_4SO_2OAr$ and $ArSO_2OC_6H_4X^k$, X^k being some constant substituent. The equality $\rho^* = 0$ means that substitution in one ring has no effect on the interaction between the reactive centre and substituents in the other ring, and conversely. The value of ρ^* calculated by the method of least squares from the values given for ρ_0, ρ_0', and ρ_C and experimental values of $\log k_{ij}$ at 0° is $\rho^* = -0.61 \pm 0.06$. Thus the quantity ρ^* cannot be neglected in the present case. The negative value of ρ^* indicates that the presence of electronegative substituents in one ring diminishes interaction between the reactive centre and electronegative substituents in the other ring, and conversely.

Neglecting the temperature-dependence of ρ_C, ρ^*, and S, we obtain the following equation for calculating rate constants when substituents are present in both aromatic rings

$$\log k_{ij} = 8.35 - 17\,400/2.3\,RT + (-0.20 + 3660/2.3\,RT)\Sigma\sigma_i^\circ + (0.20 + 3660/2.3\,RT)\Sigma\sigma_j^\circ - 0.61\,\Sigma\sigma_i^\circ\Sigma\sigma_j^\circ + 0.54\,\sigma_{C_i}^{\circ+} + S. \quad (4)$$

The precision of the equation is shown by the value $S = 0.185$ for a change in $\log k_{ij}$ by more than six orders of magnitude.

Calculation of the rate constants for 2,4,6-trimethylbenzenesulphonic esters gives satisfactory agreement with experimental results only if the term $0.54\sigma_{C_i}^{\circ+}$ in Eqn. (4) is omitted and it is assumed that $S = 0$. This proves that two *o*-methyl groups, without offering steric hindrance to attack by the hydroxide ion, nevertheless destroy the coplanarity of the system and "cut out" direct conjugation with the reactive centre.

(4) Alkaline hydrolysis of substituted ethyl benzenesulphonates in 70% aqueous dioxan (Table 1). Direct conjugation of +S-type substituents in *para*- and *ortho*-positions with the reactive centre is theoretically possible. However, the deviations from the straight line $\log k = \log k_0 + \rho_0\sigma^\circ$ are small with the 4-CH_3O and 4-CH_3 groups, and are altogether absent with the halogens. In the case of the latter, at least, the quantity ψ can be neglected.

At 50° $\rho_0 = +1.425 \pm 0.091$, $\log k_{calc} = -3.23$, and $r = 0.991$.

The absence of deviations when a nitro- or a chloro-group is present in the *ortho*-position shows that steric hindrance is absent ($S = 0$). This is because the hydroxide ion is then attacking the ethyl carbon [14]. Differences in the value of ρ for the hydrolysis of aryl and alkyl sulphonates confirm that these reactions have different mechanisms.

The above results show that the rule of the linear relation between changes in free energy and the principle of the independence and additivity of the effects of individual structural factors on reactivity can be successfully applied to these series of reactions.

1. E. W. Timm and C. N. Hinshelwood, J. Chem. Soc., 867 (1938).
2. C. N. Hinshelwood, K. Y. Laidler, and E. W. Timm, J. Chem. Soc., 848 (1938).
3. C. K. Ingold and W. S. Nathan, J. Chem. Soc., 222 (1936).
4. D. P. Evans, J. Y. Gordon, and H. B. Watson, J. Chem. Soc., 1430 (1937).
5. E. Tommila, Ann. Acad. Sci. Fennicae, 57A, 13, 3 (1941).
6. H. S. Levenson and H. A. Smith, J. Amer. Chem. Soc., 62, 2324 (1940).
7. H. Kindler, Ber., 69B, 2792 (1936).
8. N. Fehlandt and H. Adkins, J. Amer. Chem. Soc., 57, 193 (1935).
9. M. Varvoglis, Ber., 71, 2488 (1938).

10. M. Gordon, J. Miller, and A. Day, J. Amer. Chem. Soc., 70, 1946 (1948).
11. N. Bets and L. Hammett, J. Amer. Chem. Soc., 59, 1568 (1937).
12. German P. 162 322, Chem. Zentr., II, 726 (1905); B. P. 459 053, Chem. Abs., 31, 4128 (1937); U. S. P. 1 646 785, Chem. Abs., 22, 243 (1928).
13. A. Northey, Chem. Rev., 28, 85 (1940).
14. M. Matas, Chem. prumysl, 5, 505 (1955).
15. M. Neeman and A. Madiano, J. Org. Chem., 21, 667 (1956).
16. F. Drahowzal and D. Klamann, Monatsh., 82, 588 (1951).
17. E. Eliel and H. Gardyn, J. Org. Chem., 19, 1693 (1954).
18. R. V. Vizgert and E. K. Savchuk, Nauch. Zap. L'vov. Politekh. Inst., Ser. X, 3, 63 (1958).
19. N. Moffit, Proc. Roy. Soc., 200A, 409 (1959).
20. H. Zöllinger, Nature, 172, 257 (1953).
21. A. Mangini and C. Zauli, Ricerca sci., 27, 392 (1957).
22. F. Arndt and C. Martius, Annalen, 499, 228 (1932).
23. M. L. Bender, J. Amer. Chem. Soc., 73, 1626 (1951).
24. M. Polanyi and A. L. Szabo, Trans. Faraday Soc., 30, 508 (1934).
25. D. N. Kursanov and R. V. Kudryavtsev, Zhur. Obshch. Khim., 26, 1040 (1956).
26. Y. Roberts and H. Urey, J. Amer. Chem. Soc., 60, 2391 (1938).
27. M. L. Bender, J. Amer. Chem. Soc., 75, 5986 (1953).
28. M. L. Bender and R. S. Deway, J. Amer. Chem. Soc., 78, 317, 319 (1956).
29. R. Dabby and A. Davies, J. Chem. Soc., 3619 (1958).
30. I. Kenyon and M. Balfe, Nature, 148, 196 (1941).
31. S. G. Goen and A. Schneider, J. Amer. Chem. Soc., 63, 3382 (1941).
32. K. G. Mizuch, Zhur. Obshch. Khim., 16, 1971 (1946).
33. K. G. Mizuch and U. M. Gel'fer, Dokl. Akad. Nauk SSSR, 70, 637 (1950).
34. E. Tommilla and O. Heinonen, Suomen Kem., 27B, 27 (1954).
35. J. B. Herbert and E. Blumenthal, Nature, 144, 248 (1939).
36. M. Anbar, I. Dostrowsky, *et al.*, J. Chem. Soc., 3603 (1954).
37. C. A. Bunton and A. Kanasiewicz, J. Chem. Soc., 1354 (1955).
38. P. Bernard, C. Bunton, *et al.*, Chem. and Ind., 27, 760 (1955).
39. M. F. Shostakovskii, Zhur. Obshch. Khim., 18, 1664 (1948).
40. V. Stimson, J. Chem. Soc., 2010, 2673 (1955).
41. L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 280 (1940).
42. S. N. Baranov and R. V. Vizgert, Zhur. Obshch. Khim., 27, 909 (1957).
43. C. K. Ingold, J. Chem. Soc., 756 (1932).
44. J. N. Day and C. K. Ingold, Trans. Faraday Soc., 37, 686 (1941).
45. J. Hawke and V. Stimson, J. Chem. Soc., 4676 (1956).
46. N. Ader, Thesis, London, 1949.
47. C. A. Bunton and C. Frei, J. Chem. Soc., 1872 (1951).
48. R. V. Vizgert, E. K. Savchuk, and M. P. Ponomarchuk, Dokl. Akad. Nauk SSSR, 125, 1257 (1959).
49. E. Tommila and M. Lindholm, Acta Chem. Scand., 4, 491 (1951).
50. R. V. Vizgert, Zhur. Obshch. Khim., 30, 3433 (1960).
51. M. S. Morgan and L. H. Gretcher, J. Amer. Chem. Soc., 70, 375 (1948).
52. R. Robertson and J. Hyne, Canad. J. Chem., 34, 863 (1956).
53. A. Autenrieth and N. Bernheim, Ber., 37, 3803 (1904).
54. D. Shirly and J. Zeitz, J. Org. Chem., 18, 378 (1953).
55. R. V. Vizgert and Ya. P. Berkman, Zhur. Obshch. Khim., 28, 2119 (1958).
56. R. V. Vizgert, Zhur. Obshch. Khim., 30, 3440 (1960).
57. S. C. Datta, J. N. Day, and C. K. Ingold, J. Chem. Soc., 838 (1939).
58. A. Moffat and H. Hunt, J. Amer. Chem. Soc., 81, 2082 (1959)
59. A. C. Rolfe and C. N. Hinshelwood, Trans. Faraday Soc., 30, 935 (1934).
60. R. A. Fairclough and C. N. Hinshelwood, J. Chem. Soc., 593 (1939).
61. E. Tommila and M. Sippola, Suomen Kem., 29, 1364 (1956).
62. K. Ostwald, J. Phys. Chem., 3, 174, 270 (1889).
63. E. Blumenthal and J. B. Herbert, Trans. Faraday Soc., 41, 611 (1945).
64. C. Oliver and C. Berger, Rec. Trav. chim., 46, 515 (1927).
65. J. Gleave, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 236 (1935).
66. R. V. Vizgert and E. K. Savchuk, Zhur. Obshch. Khim., 28, 2114 (1958).
67. V. A. Pal'm, Zhur. Fiz. Khim., 32, 380 (1958).
68. K. Karlsson, Z. anorg. Chem., 145, 1 (1926).
69. S. T. Maironovskii and M. V. Neiman, Dokl. Akad. Nauk SSSR, 79, 185 (1951).
70. H. K. Hall, J. Amer. Chem. Soc., 78, 1450 (1956).
71. R. V. Vizgert, Zhur. Obshch. Khim., 28, 1873 (1958).
72. R. V. Vizgert, Ukrain. Khim. Zhur., 20, 272 (1954).
73. L. Demeny, Rec. Trav. chim., 50, 60 (1931).
74. R. V. Vizgert and E. K. Savchuk, Zhur. Obshch. Khim., 26, 2261 (1956).
75. Ya. K. Syrkin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 238, 389, 401, 600 (1959).
76. Ya. K. Syrkin and I. I. Moiseev, Uspekhi Khim., 27, 717 (1958).
77. O. T. Benfey, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 2494 (1952).
78. E. Tommila, Acta Chem. Scand., 9, 975 (1955).
79. R. E. Robertson, J. Chem. Soc., 31 (1953).
80. A. Muller, Ber., 67, 421 (1934); 68, 1094 (1935).
81. H. Phillips and J. Kenyon, J. Chem. Soc., 399, 2552 (1925).
82. C. A. Bunton and V. Welch, J. Chem. Soc., 3240 (1956).
83. R. V. Vizgert and E. K. Savchuk, Nauch. Zap. L'vov. Politekh. Inst., Ser. Khim. Tekh., 22, 39 (1956).
84. R. V. Vizgert and Ya. P. Berkman, Ukrain. Khim. Zhur., 18, 311 (1952).
85. R. V. Vizgert and Ya. P. Berkman, Ukrain. Khim. Zhur., 18, 179 (1952).
86. K. Kindler, Annalen, 464, 278 (1928).
87. E. Tommila and C. N. Hinshelwood, J. Chem. Soc., 1801 (1938).
88. Ya. P. Berkman and R. V. Vizgert, Ukrain. Khim. Zhur., 20, 264 (1954).
89. F. H. Westheimer and R. P. Metcalf, J. Amer. Chem. Soc., 63, 1339 (1941).
90. E. Tommila and C. Hinshelwood, J. Chem. Soc., 1801 (1938).
91. H. B. Watson, Uspekhi Khim., 8, 918 (1940) [Translated into Russian (Ed. of Translation)].
92. Z. T. Linetskaya and N. V. Sapozhnikova, Dokl. Akad. Nauk SSSR, 86, 763 (1952).
93. R. V. Vizgert and Ya. P. Berkman, Ukrain. Khim. Zhur., 17, 264, 270 (1951).
94. S. N. Baranov, F. A. Zhoglo, and R. V. Vizgert, Zhur. Obshch. Khim., 28, 1274 (1958).
95. S. Popovici and M. Pop, Compt. rend., 245, 846 (1957).
96. H. Brown and G. Ham, J. Amer. Chem. Soc., 78, 2735 (1956).
97. E. Tommila and J. Jutila, Acta Chem. Scand., 6, 975 (1955).
98. C. K. Ingold, J. Chem. Soc., 231 (1936).
99. C. K. Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1959, p. 257.
100. L. C. Bateman, K. A. Cooper, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 925 (1940).
101. Y. Kochi and G. Hammond, J. Amer. Chem. Soc., 75, 3445 (1953).
102. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Inostr. Lit., 1947, p. 205.

103. R. V. Vizgert, E. K. Savchuk, and O. A. Prib, Zhur. Obshch. Khim., 31, 86 (1961).
104. K. Palomaa and N. Salmi, Ber., 72, 790 (1939).
105. K. J. Laidler and P. A. Landkroener, Trans. Faraday Soc., 52, 200 (1956).
106. G. A. Gallagher, I. Miller, and A. Day, J. Amer. Chem. Soc., 79, 4324 (1957).
107. N. Menshutkin, Zhur. Fiz. Khim., 5, 588 (1890).
108. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 244, 252 (1935).
109. K. A. Cooper, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 2043 (1948).
110. I. Meloche and K. J. Laidler, J. Amer. Chem. Soc., 73, 1712 (1951).
111. E. A. Shilov, Dokl. Akad. Nauk SSSR, 18, 643 (1938); 30, 219 (1941); 91, 873 (1953).
112. F. Geiseger and F. Asinger, Chem. Ber., 89, 1100 (1956).
113. E. Tommila and P. Hirsjärvi, Acta Chem. Scand., 4, 659 (1951).
114. E. Tommila and L. Ketonen, Chem. Abs., 52, 6956 (1946).
115. R. V. Vizgert, Zhur. Obshch. Khim., 32, 628, 633 (1962).
116. V. A. Pal'm, Uspekhi Khim., 30, 1069 (1961) [Russ. Chem. Rev., 471 (1961)].
117. R. W. Taft, J. Amer. Chem. Soc., 75, 4231 (1953).
118. E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 70, 846 (1948).
119. H. Shingu, K. Okamoto, and A. Ajisaka, J. Chem. Soc. Japan, Pure Chem. Sect., 78, 547 (1957).
120. E. Tommila, M. Tiilikainen, and L. Vaipon, Ann. Acad. Sci. Fennicae, 11A, 65 (1955).
121. E. Tommila and P. Antikainen, Acta Chem. Scand., 9, 825 (1955).
122. E. Tommila and E. Merrikalio, Suomen Kem., 26, 79 (1953).
123. L. Bateman, A. Cooper, E. Hughes, and C. K. Ingold, J. Chem. Soc., 236 (1935).
124. E. D. Hughes, C. K. Ingold, and C. S. Patel, J. Chem. Soc., 526 (1933).
125. G. E. Branch and A. C. Nixon, J. Amer. Chem. Soc., 58, 2499 (1936).
126. J. F. Norris, E. V. Fasce, and C. Y. Staud, J. Amer. Chem. Soc., 57, 1420 (1935).
127. J. F. Norris and H. H. Young, J. Amer. Chem. Soc., 57, 1415 (1935).
128. D. A. Brown and R. F. Hudson, J. Chem. Soc., 3352 (1953).
129. C. A. Bunton, T. A. Lewis, and D. R. Llewelyn, Chem. and Ind., 1154 (1954).
130. H. L. Goering, T. Rubin, and M. S. Newnan, J. Amer. Chem. Soc., 76, 787 (1954).
131. G. Swain, J. Amer. Chem. Soc., 70, 1119 (1948); 72, 2794, 4578 (1950); 74, 4109 (1952); 75, 141 (1953).
132. J. D. Roberts and C. M. Regan, J. Amer. Chem. Soc., 76, 939 (1954).
133. J. D. Roberts and J. A. Yancey, J. Amer. Chem. Soc., 73, 1011 (1951).
134. V. A. Pal'm and R. V. Vizgert, Dokl. Akad. Nauk SSSR, 142, 5 (1962).
135. H. H. Jaffe, Chem. Rev., 53, 191 (1953).
136. S. I. Miller, J. Amer. Chem. Soc., 81, 101 (1959).

L'vov Polytechnic Institute

THE CHEMISTRY OF SOME 1-SUBSTITUTED ALKA-1,3-DIENES

I. I. Guseinov and G. S. Vasil'ev

CONTENTS

I. Introduction 20

II. 1-Alkoxybuta-1,3-dienes 21
1. Methods of preparation 21
2. Some chemical reactions of 1-alkoxybuta--1,3-dienes 21

III. Sulphur-containing buta-1,3-dienes 22
1. Methods of synthesis 22
2. Some chemical reactions of sulphur-containing buta-1,3-dienes 23

IV. Nitrogen-containing buta-1,3-dienes (methods of synthesis) 23
1. Amino-substituted buta-1,3-dienes 23
2. Nitro-substituted buta-1,3-dienes 24
3. Cyano-substituted buta-1,3-dienes 25
4. Some chemical reactions of nitrogen-containing buta-1,3-dienes 25

V. Hetero-substituted phosphorus-containing buta--1,3-dienes 26
1. Methods of preparation 26
2. Some chemical properties 27

VI. Silicon-containing buta-1,3-dienes 27
1. Methods of preparation 27
2. Some chemical reactions of silicon-containing buta-1,3-dienes 28

I. INTRODUCTION

There are now many publications on the chemistry of the diene hydrocarbons. They are concerned mainly with the order of addition of various nucleophilic and electrophilic reagents, and also with developing ideas on the ability of dienes to form polymers, especially the industrially important buta-1,3-diene and isoprene rubbers.

The most recent views on the properties of dienes, and in particular of butadiene, are inseparably linked with their stereochemistry. Establishment of the *cis*- and *trans*--configurations of dienes is a most important contemporary stage in the evolution of diene chemistry. Conformational analysis makes it possible to obtain a deeper understanding of the various reactions of dienes, and also the structure and properties of the diverse derivatives of these compounds.

The present paper represents an attempt to give a systematic account of the most important investigations associated with various syntheses, leading ultimately to hetero--substituted buta-1,3-dienes.