991. *Nucleophilic Displacements in Organic Sulphites. Part VII.*[1] *The Acid-catalysed Hydrolyses of Cyclic and Open-chain Sulphites in Aqueous Dioxan.*

By J. G. Tillett.

The hydrolysis of catechol sulphite in 60% dioxan–water is dominated by its exceptionally high rate in neutral solution. The acid-catalysed rate passes through a maximum with both perchloric and toluene-*p*-sulphonic acids. The results are interpreted in terms of a large negative salt effect for reaction in neutral solution, combined with a smaller positive acid-catalysis. Nucleophilic anions catalyse the reaction. The rates of the reaction catalysed by halide-ion follow stoicheiometric acidity more closely than they follow h_0.

The effect of perchloric acid on the hydrolysis of ethylene sulphite and of diethyl sulphite has been studied in 60% dioxan. These reactions are considered to proceed by the $A2$ mechanism with a superposed salt effect. The rates of the halide-catalysed reaction follow Hammett's acidity function more closely than they follow the stoicheiometric acid concentration. The results are therefore qualitatively similar to those obtained earlier in aqueous solution and indicate that the mechanism of hydrolysis in the two solvents is similar.

Recent criticisms of the Zucker–Hammett hypothesis are discussed.

Earlier work on nucleophilic displacements in organic sulphites has been confined to reactions in aqueous solution of saturated cyclic and open-chain sulphites. The present investigation extends these studies to aromatic systems. Catechol sulphite may be regarded as the simplest aromatic cyclic sulphite. Because of its limited solubility in water, its hydrolysis has been studied in 60% dioxan.

60% Dioxan is very suitable for studies of acid-catalysis because an acidity scale has recently been established for it.[2] Also, it has a relatively high dielectric constant and therefore drastic changes in mechanism would not be expected on changing to it from water as solvent.

The rates of acid-hydrolysis of ethylene and of diethyl sulphite have also been studied in 60% dioxan, and compared with those for aqueous solution.

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[1] Part VI, Tillett, *J.*, 1960, 37.

[2] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

EXPERIMENTAL

The sulphites were prepared by the standard method.[3] Diethyl sulphite had b. p. 156°/750 mm., n_D^{25} 1·4130; ethylene sulphite had b. p. 73°/27 mm., n_D^{25} 1·4450. Catechol sulphite, prepared by Anschutz and Posth's method [4] in 66% yield, had b. p. 76°/7 mm., 203°/760 mm., n_D^{25} 1·5408 (Found: C, 46·5; H, 2·6; S, 20·3. Calc. for $C_6H_4O_3S$: C, 46·2; H, 2·3; S, 20·5%).

Acid-catalysed Hydrolyses.—The acids were of Analytical Reagent quality. Their concentrations were determined by titration with standard alkali. Sodium chloride, sodium bromide, and sodium hydrogen sulphate were dried at 120°. Lithium perchlorate was a recrystallised commercial specimen. It was dehydrated at *ca.* 150° and kept in a vacuum at this temperature for 24 hr. with a diffusion pump.[5] Anhydrous lithium chloride and lithium bromide were prepared in a similar manner. Toluene-*p*-sulphonic acid was a recrystallised commercial sample.

The rates of hydrolysis at 25° and above were determined by a conventional sealed-tube method. The conversion of organic sulphite into sulphur dioxide was determined at intervals by breaking sample-tubes under an excess of standard iodine solution, which was then back-titrated with sodium thiosulphate. The runs at 0° were carried out in stoppered flasks. Aliquot portions were withdrawn at intervals and quenched in a large excess (*ca.* 400 ml.) of ice-cold water containing an excess of iodine, which was then back-titrated as above.

The following records a typical kinetic run for 0·030M-catechol sulphite in 0·750M-perchloric acid with added lithium perchlorate (0·750M) at 0°:

Time (min.)	0	29·76	66·10	122·1	179·0	237·9	299·3	363·5	417·6	∞
Titre (ml. of 0·0100N-iodine) ...	0·77	1·71	2·71	4·33	5·65	7·16	8·48	9·89	10·76	24·95
10^3k_1 (min.$^{-1}$)	—	1·33	1·26	1·30	1·26	1·29	1·29	1·30	1·28	—

The finite titre for time $t = 0$ represents reaction during the time allowed for the reaction solution to acquire the temperature of the thermostat. Values of k_1 have been calculated by use of the formula $k_1 = (2{\cdot}303/t) \log_{10} a/(a - x)$, where a is the molarity of organic sulphite at time $t = 0$ and x is the molarity of sulphur dioxide liberated at time t. The fact that the first-order rate-coefficients calculated by the above equation are substantially constant over at least 50% of reaction implies that one mole of material titrating as sulphur dioxide is liberated for each mole of organic sulphite decomposed. The results are summarised in the following Tables.

TABLE 1. *First-order rate-coefficients for the hydrolysis of catechol sulphite in* 60% *dioxan.*

(*a*) At 0·0°.

$[HClO_4]$ (M)	—	—	0·100	0·250	0·400	0·600	0·750
10^3k_1 (min.$^{-1}$)	2·17	0·364 *	2·35	2·50	2·56	2·48	2·30
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$) ...	—	—	23·5	10·0	6·40	4·13	3·07
$[HClO_4]$ (M)	1·00	1·25	1·50	2·00	3·00	4·00	5·00
10^3k_1 (min.$^{-1}$)	2·07	1·86	1·70	1·29	0·945	0·729	0·620
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$) ...	2·07	1·49	1·11	0·645	0·315	0·182	0·124

* In 99·8% D_2O.

(*b*) At 0·0° with hydrochloric acid.

[HCl] (M)	0·250	0·500	0·750	1·00	1·25	1·50	2·00
10^3k_1 (min.$^{-1}$)	4·65	9·02	15·9	26·5	40·7	60·4	154
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$) ...	18·6	18·0	21·2	26·5	32·6	40·3	77·0

(*c*) At 0·0° with sulphuric acid.

$[H_2SO_4]$ (M)	0·250	0·500	1·00	2·00	3·00	4·00
10^3k_1 (min.$^{-1}$)	2·89	3·36	4·22	4·71	6·01	5·36
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$) ...	11·6	6·72	4·22	2·36	1·67	1·09

(*d*) At 0·0° with toluene-*p*-sulphonic acid.

$[C_7H_7{\cdot}SO_3H]$ (M)	0·100	0·250	0·500	0·750	1·00	1·25	1·50	2·00	2·50	3·00
10^3k_1 (min.$^{-1}$)	2·43	2·66	2·83	2·88	2·86	2·80	2·67	2·45	2·22	2·03
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$) ...	24·3	10·6	5·66	3·84	2·86	2·24	1·78	1·23	0 889	0·68

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[3] Voss and Blanke, *Annalen*, 1931, **485**, 273.
[4] Anschutz and Posth, *Ber.*, 1894, **27**, 2752.
[5] Pullen and Peacock, *Trans. Faraday Soc.*, 1958, **54**, 11.

TABLE 1. (*Continued.*)

(*e*) At 0·0° with added salts.

[LiCl] (M)	—	0·250	0·500	0·750
10^3k_1 (min.$^{-1}$)	2·17	1·87	1·57	1·31
[LiBr] (M)	0·250	0·500	0·750	
10^3k_1 (min.$^{-1}$)	2·06	1·94	1·83	
[$LiClO_4$] (M)	0·500	1·00	1·50	
10^3k_1 (min.$^{-1}$)	1·70	1·25	0·78	

(*f*) At 0·0° with hydrochloric acid and added lithium chloride.

[HCl] (M)	0	0·500	0·750	1·00
[LiCl] (M)	—	0·500	0·250	—
10^3k_1 (min.$^{-1}$)	1·02 *	13·1	18·2	26·5
10^3k_1/[H^+] (l. mole^{-1} min.$^{-1}$)	—	26·2	24·3	26·5

* Extrapolated value.

(*g*) At 0·0° with perchloric acid and 0·250M-lithium chloride.

[$HClO_4$] (M)	1·00	2·00	2·50	3·00	3·50	4·00
10^3k_1 (min.$^{-1}$)	5·43	10·4	14·1	22·3	36·5	53·5
$10^3\Delta k_1$ * (min.$^{-1}$)	3·24	9·11	13·0	21·4	35·7	52·8
H_0 †	+0·75	−0·26	−0·70	−1·10	−1·48	−1·84

* $\Delta k = k_1$ (in presence of added salt) − k_1 (in absence of added salt).

† Values of H_0 are those for solutions of perchloric acid in 60% dioxan, *i.e.*, in the absence of added salts.

(*h*) At 0·0° with perchloric acid and added lithium chloride.

[$HClO_4$] (M)	1·00	1·00	1·00	2·00	2·00	2·00	3·00	3·00	3·00	4·00	4·00	4·00
[LiCl] (M)	0·100	0·400	0·250	0·100	0·200	0·250	0·100	0·200	0·250	0·100	0·200	0·250
10^3k_1 (min.$^{-1}$)	3·39	8·04	5·43	4·52	7·95	10·4	9·09	17·2	22·3	21·7	42·6	72·2

(*i*) At 0·0° with perchloric acid and 0·100M-lithium bromide.

[$HClO_4$] (M)	1·00	2·00	3·00	3·50	4·00
10^3k_1 (min.$^{-1}$)	4·80	9·14	22·4	41·0	65·6
k_1 (min.$^{-1}$)	2·61	7·85	21·5	40·1	64·9

(*j*) At 0·0° with 2·00M-perchloric acid and added lithium bromide.

[LiBr] (M)	—	0·200	0·300
10^3k_1 (min.$^{-1}$)	1·29	18·3	29·0

(*k*) At 0·0° with perchloric acid and added lithium perchlorate.

[$HClO_4$] (M)	—	0·250	0·500	0·750	1·00	1·25	1·50
[$LiClO_4$] (M)	1·50	1·25	1·00	0·750	0·500	0·250	—
10^3k_1 (min.$^{-1}$)	0·78	0·45	1·11	1·29	1·45	1·61	1·70
$10^3\Delta k_1$ (min.$^{-1}$) *	—	0·17	0·33	0·51	0·67	0·83	0·92
$10^3\Delta k_1$/[H^+] (l. mole^{-1} min.$^{-1}$)	—	0·68	0·66	0·68	0·67	0·66	0·61

* $\Delta k_1 = k_1$ (obs.) − k_1 (neutral rate + 1·50M-$LiClO_4$).

(*l*) At 25·0°.

[$HClO_4$] (M)	—	0·250	0·500	0·750	1·00	1·25	2·00
10^3k_1 (min.$^{-1}$)	15·7	18·3	19·8	20·8	19·1	18·0	14·5
10^3k_1/[H^+] (l. mole^{-1} min.$^{-1}$)	—	73·2	39·6	27·7	19·1	14·4	7·25

The values of H_0 are taken from the work of Bunton and his co-workers [2] and from Long and Paul's review.[6]

Influence of Temperature.—The entropies (ΔS^*) and the energies of activation (ΔE) calculated by using the formula $k = (e\boldsymbol{k}T/\boldsymbol{h}) \exp (\Delta S^*/\boldsymbol{R}) \exp (-\Delta E/\boldsymbol{R}T)$ are given in Table 5.

Dioxan Solutions.—Dioxan was purified by the standard method.[7] The 60% dioxan was prepared as follows: dioxan (60 vol.) and water (40 vol.) were mixed together. The required volume of 72% "AnalaR" perchloric acid was added. The amount of water in this volume of acid was calculated from the concentration of the acid, and a further volume of dioxan was added to bring the final solvent composition up to 60% dioxan. A similar procedure was adopted for hydrochloric and sulphuric acid. Toluene-*p*-sulphonic acid was weighed as the anhydrous compound.

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[6] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.

[7] Eigenberger, *J. prakt. Chem.*, 1931, **130**, 75; Hess and Frahm, *Ber.*, 1938, **71**, 2627.

TABLE 2. *First-order rate-coefficients for the hydrolysis of diethyl sulphite in water.*

(*a*) At 0·0°.

$[HClO_4]$ (M)	1·00	1·50	2·00	2·00 *	2·50	3·00	3·50	4·00
10^3k_1 (min.$^{-1}$)	1·08	1·81	3·06	4·76	4·13	6·32	8·81	13·9
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	1·08	1·21	1·53	—	1·65	2·11	2·52	3·47
H_0	−0·22	−0·53	−0·78	—	−1·01	−1·23	−1·47	−1·72

* In 90·9% D_2O.

(*b*) At 0·0° with perchloric acid and 0·250M-sodium chloride.

$[HClO_4]$ (M)	1·00	2·00	2·00 *	3·00	4·00
10^3k_1 (min.$^{-1}$)	2·10	6·80	10·0	18·1	49·8
$10^3\Delta k_1$ (min.$^{-1}$)	1·02	3·74	—	11·8	35·9

* In 90·9% D_2O.

(*c*) At 0·0° with perchloric acid and 0·100M-sodium bromide.

$[HClO_4]$ (M)	1·00	2·00	2·00 *	3·00	4·00
10^3k (min.$^{-1}$)	2·73	9·18	17·1	26·5	82·8
$10^3\Delta k_1$ (min.$^{-1}$)	1·65	6·12	—	20·2	68·9

* In 90·9% D_2O.

(*d*) At 25·0°.

$[HClO_4]$ (M)	1·00	1·50	1·00 *	1·00 †
10^3k_1 (min.$^{-1}$)	23·6	36·7	54·0	42·5

* With 0·100M-sodium bromide. † With 0·250M-sodium chloride.

TABLE 3. *First-order rate-coefficients for the hydrolysis of diethyl sulphite in* 60% *dioxan.*

(*a*) At 0·0°.

$[HClO_4]$ (M)	1·00	1·50	2·00	2·00 *	2·50	3·00	3·50	4·00
10^3k_1 (min.$^{-1}$)	0·470	1·13	2·23	2·96	4·47	8·61	17·5	33·5
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	0·470	0·753	1·12	—	1·79	2·87	5·00	8·37
H_0	+0·75	+0·22	−0·26	—	−0·70	−1·10	−1·48	−1·84

* In 90·9% D_2O.

(*b*) At 0·0° with perchloric acid and 0·100M-lithium chloride.

$[HClO_4]$ (M)	1·00	1·50	2·00	2·50	3·00	3·50	4·00
10^3k_1 (min.$^{-1}$)	0·62	1·43	2·95	6·44	13·0	29·5	64·9
$10^3\Delta k_1$ (min.$^{-1}$)	0·15	0·30	0·72	1·97	4·40	12·0	31·4

(*c*) At 0·0° with perchloric acid and 0·0040M-lithium bromide.

$[HClO_4]$ (M)	1·00	1·50	2·00	2·50	3·00	3·50	4·00
10^3k_1 (min.$^{-1}$)	0·590	1·37	2·97	6·30	13·9	31·2	68·3
$10^3\Delta k_1$ (min.$^{-1}$)	0·120	0·240	0·740	1·83	5·30	13·7	34·8

For 1·00M- and 1·500M-$HClO_4$ at 25·0° the values of 10^3k_1 are 10·1 and 22·9 min.$^{-1}$, respectively.

TABLE 4. *First-order rate-coefficients for the hydrolysis of ethylene sulphite in aqueous dioxan.*

(*a*) At 44·6° in 40% dioxan.

$[HClO_4]$ (M)	0·495	0·980	1·92	2·82	3·69
10^3k_1 (min.$^{-1}$)	1·69	4·09	10·8	21·4	44·8
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	3·62	4·17	5·62	7·59	12·1
H_0	+1·00	+0·42	−0·24	−0·87	−1·46

(*b*) At 44·6° in 60% dioxan.

$[HClO_4]$ (M)	0·500	1·00	1·83	3·00	3·36	3·50	4·00
10^3k_1 (min.$^{-1}$)	1·30	3·38	10·2	33·3	45·7	53·9	88·8
$10^3k_1[H^+]$ (l. mole^{-1} min.$^{-1}$)	2·60	3·38	5·56	11·1	13·7	15·4	22·2
H_0	+1·40	+0·75	−0·10	−1·10	−1·40	−1·48	−1·84

TABLE 5. *Entropies and energies of activation.*

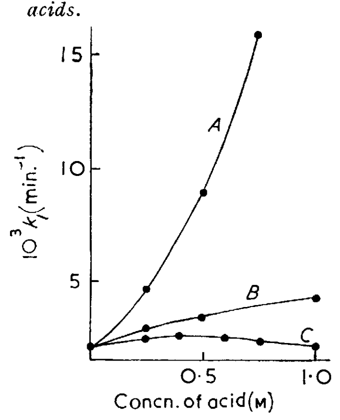
Sulphite	Solvent	$[HClO_4]$ (M)	Salt	[Salt] (M)	ΔE (kcal. mole^{-1})	ΔS^* (e.u.)
Diethyl	H_2O	1·00	—	—	19·95	−9·14
Diethyl	H_2O	1·00	NaCl	0·250	18·90	−13·10
Diethyl	H_2O	1·00	NaBr	0·100	18·90	−12·16
Diethyl	60% Dioxan	1·50	—	—	16·40	−22·00
Catechol	60% Dioxan	—	—	—	12·80	−34·10

DISCUSSION

Hydrolysis of Catechol Sulphite.—Kinetic form. In Fig. 1 are plotted the rates of hydrolysis of catechol sulphite against stoicheiometric acid concentration for perchloric, sulphuric, and hydrochloric acid. The region of lower acidity is shown in more detail for perchloric acid and toluene-*p*-sulphonic acid in Fig. 2. The rate passes through a maximum with concentration of either acid and then falls below the value ascribed to the rate of neutral hydrolysis. The values for sulphuric and hydrochloric acid, given in Tables 1(*b*) and 1(*c*), show that the values of $k_1/[H^+]$ for sulphuric acid decrease with increasing acid concentration. The corresponding values for hydrochloric acid, however, increase steadily, leading to the upward curve obtained for hydrochloric acid in Fig. 1.

The acids used seem to fall into two classes. The first, in which the rate passes through a definite maximum, includes perchloric and toluene-*p*-sulphonic acids. The second class includes hydrochloric acid. This has a very marked effect on the rate. The behaviour of sulphuric acid seems to be intermediate but more nearly similar to that of acids of the second than of the first class.

FIG. 1. *Acid-catalysed hydrolysis of catechol sulphite with mineral acids.*



(*A*) HCl. (*B*) H_2SO_4. (*C*) $HClO_4$.

FIG. 2. *Acid-catalysed hydrolysis of catechol sulphite by* (*A*) *toluene-*p*-sulphonic and* (*B*) *perchloric acid.*

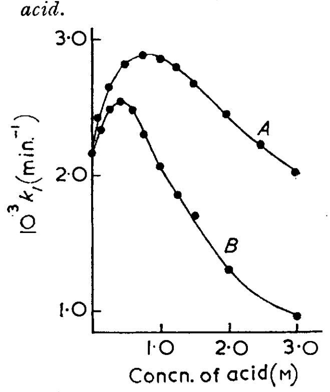
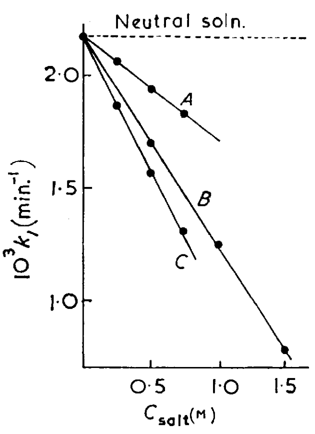


FIG. 3. *Effect of added salts on the neutral rate of hydrolysis of catechol sulphite.*



(*A*) LiBr. (*B*) $LiClO_4$. (*C*) LiCl.

The effect of the acids falls in the order $HCl \gg H_2SO_4 > C_7H_7{\cdot}SO_3H \sim HClO_4$. This is the order of decreasing nucleophilic power of the anions of the acids. It seems reasonable to attribute this type of catalysis to nucleophilic attack by the negative ion on the sulphur atom of the protonated sulphite, as was found for other organic sulphites. However, because of the peculiar kinetic form observed, there must be other factors contributing to the overall rate.

The rate in neutral solution. The hydrolysis of catechol sulphite is dominated by its exceptionally high rate in neutral solution ($10^3k_1 = 2{\cdot}17$ min.$^{-1}$) which is comparable to that for the hydrolysis of diethyl sulphite in 1·00M-perchloric acid. The only rate of neutral hydrolysis of an organic sulphite previously measured has been that of ethylene sulphite[8] at 44·6° ($10^3k_1 = 0{\cdot}0065$ min.$^{-1}$). The rates for neutral hydrolysis of other organic sulphites previously investigated were negligible.

The effect of added salts on the rate of neutral hydrolysis of catechol sulphite is shown in Fig. 3. The salts studied all retard the reaction. It seems that the activity coefficient ratio $f_S \, . \, a_W/f^{\ddagger}$, in the Brönsted equation for the neutral reaction, is modified by the

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[8] Bunton, de la Mare, and Tillett, *J.*, 1958, 4654.

presence of added salts, by an amount which is approximately proportional to the concentration of the salt, but has a specific value for each particular salt. The marked specificity of salts in their action is well known.[9]

The activity of water decreases with increasing salt concentration but to an extent insufficient, it is considered, to cause the changes observed. The negative salt effects may arise from changes in f_S, in $f^\ddagger$, or in both terms. The effects of added salts on the rates of acid hydrolysis of ethylene sulphite[8] do not correlate with their effects on the activity coefficients, f_S, of the organic substrate as indicated by solubility measurements in solutions of electrolytes.[10] Sodium perchlorate and sodium toluene-*p*-sulphonate have a " salting in " effect, whereas sodium chloride and sodium bromide " salt out." All the salts studied, however, increase the rate of acid-hydrolysis. Thus, in the present example, although all the salts used decelerate the neutral hydrolysis, the way in which they produce this effect may be different.

The neutral hydrolysis of catechol sulphite is subject to an inverse deuterium effect. This rate in 60% dioxan–water is 5·95 times greater than that in 60% dioxan–deuterium oxide. Similar large inverse deuterium effects have recently been observed by Butler and Gold[11] for the spontaneous hydrolysis of acetic anhydride in water, and by Pocker[12] for the formation and decomposition of acetaldehyde hydrate in water. It is noteworthy that the hydrolysis of acetic anhydride described above is also exceptionally fast in neutral solution.

Overall rate-coefficient. There are thus three reactions contributing to the overall rate, and at low acidity the observed rate constant ($k_{\text{obs.}}$) may be written in the form:

$$k_{\text{obs.}} = k_{\text{W}} + k_{\text{H}^+}[\text{H}^+] + k_{\text{X}^-}[\text{H}^+][\text{X}^-]$$

where k_{W}, k_{H^+}, and k_{X^-} are the rate-coefficients corresponding to the neutral, acid-catalysed, and halide-ion-catalysed reactions respectively. Each term may be subject to ionic-strength effects. For perchloric acid and toluene-*p*-sulphonic acid the last term is zero or negligible.

The existence of acid-catalysis may be shown by carrying out the reaction in solutions of perchloric acid and lithium perchlorate, the perchlorate-ion concentration being kept constant (at 1·50M). Thus in all these solutions the neutral rate will have a constant depressed value corresponding to the negative salt effect on it of 1·50M-perchlorate, and any increase above this will be due entirely to acid-catalysis. The results are shown in Table 1(*k*): the values of $k_1/[\text{H}^+]$ stay approximately constant, indicating that the rate is proportional to the concentration of perchloric acid.

Thus the kinetic form observed with both perchloric and toluene-*p*-sulphonic acid is due to a combination of the rates of the acid-catalysed rate and the neutral reaction, the latter being subject to a large negative salt effect. If the values of the observed rate constant for the perchloric acid-catalysed reaction are added algebraically to the values of the observed rate constant (at corresponding perchlorate concentration) for the effect of added lithium perchlorate on the neutral reaction, the resultant should represent the true acid-catalysed rate. This curve rises to a maximum at *ca.* 0·5M-acid and then levels off. This indicates that the acid-catalysed reaction is itself subject to a quite substantial negative salt effect. It is, however, difficult to interpret the levelling off at higher acidities.

The values obtained for acid-catalysis of catechol sulphite by perchloric acid at 25° are shown in Table 1(*l*). As at 0°, the rate passes through a maximum and then falls below the rate in neutral solution. The position of the maximum has, however, shifted from

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[9] Long and McDevitt, *Chem. Rev.*, 1952, **51**, 119.

[10] Davies and Tillett, *J.*, 1958, 4766.

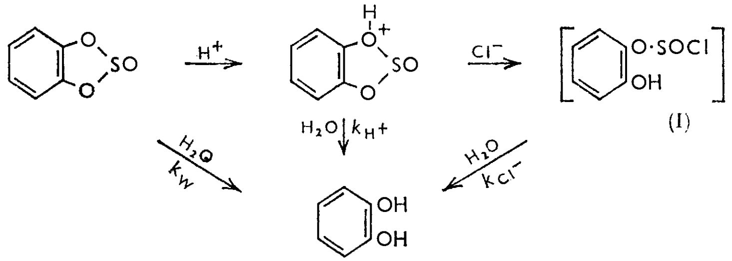
[11] Butler and Gold, *Proc. Chem. Soc.*, 1960, 15.

[12] Pocker, *Proc. Chem. Soc.*, 1960, 17.

ca. 0·4M-acid at 0° to *ca.* 0·7M-acid at 25°. This may indicate a greater contribution to the overall rate by the acid-catalysis at higher temperatures.

It is possible that besides the third term in the equation, there ought to be included a fourth, to allow for the possibility of halide-ion catalysis of the neutral reaction. In Tables 1(*g*) and 1(*h*) is shown the effect of added chloride ions at different acidities. At any given acidity the rate varies linearly with the concentration of added salt. The slopes of these straight lines, when plotted against acid concentration, pass through the zero point within experimental error, indicating that the fourth term is negligible and therefore halide-ion catalysis only occurs with the protonated substrate.

The halide-catalysed reaction. The halide-catalysed hydrolysis of catechol sulphite follows stoicheiometric acid concentration more closely than Hammett's acidity function. The values of the Hammett slopes are 0·45 and 0·50 for added lithium chloride and lithium bromide, respectively. The values of $\Delta k_1/[H^+]$ do not increase with increasing acid concentration as much as the corresponding values for diethyl sulphite in water or in aqueous dioxan. It is assumed, therefore, that this reaction proceeds by the *A*2 mechanism and the halide ions merely compete with water as the nucleophile for the protonated substrate. The most probable reaction pattern is then as in the annexed scheme. The proton might be associated with either the terminal or the ring-oxygen atom. The intermediate chlorosulphinate (I) is a probable intermediate in the formation of catechol sulphite from catechol and thionyl chloride.



It is noteworthy that Bunton and Hendy[13] have recently found similar nucleophilic catalysis by halide ions on a sulphur atom in the acid-catalysed hydrolysis of methyl toluene-*p*-sulphinate in aqueous dioxan.

Comparison of Aromatic and Aliphatic Sulphites.—Previously it was reported[14] that diphenyl and ditolyl sulphite, two of the simplest aromatic " open-chain " sulphites, are unreactive towards water and aqueous alkali. It has now been shown that catechol sulphite, the simplest aromatic cyclic sulphite, is *ca.* 10^4 times more reactive than ethylene sulphite[8] in neutral solution. The rate of hydrolysis of diethyl sulphite under similar conditions is negligible.[15] In this comparison, the value taken for catechol sulphite is that obtained in 60% dioxan, whereas the other sulphites were studied in aqueous solution.

In alkaline solution, ethylene sulphite is *ca.* 10^4 times more reactive than diethyl sulphite.[1] A solution of catechol sulphite in 60% dioxan can be titrated with sodium hydroxide at room temperature, and so its rate of alkaline hydrolysis is at least as high as that of ethylene sulphite.

The order of reactivity in acidic solutions is catechol sulphite > diethyl sulphite > ethylene sulphite, the differences in rate probably being less than a power of ten in each case. Thus, whereas in neutral solution catechol sulphite is very much more reactive than ethylene sulphite, yet in acid solution the two compounds have similar reactivities.

Large differences of reactivity also arise in the phosphate esters. Westheimer has

[13] Bunton and Hendy, *Chem. and Ind.*, 1960, 466.

[14] Richter, *Ber.*, 1916, **49**, 2339.

[15] Bunton, de la Mare, and Tillett, *J.*, 1959, 1766.

suggested[16] that the five-membered cyclic phosphate is exceptionally reactive because of interelectronic repulsions between the lone pairs of electrons on the oxygen atoms of the ring and the adjacent exocyclic oxygen atoms. This strain would be relieved in the puckered trimethylene phosphate. Westheimer and his co-workers have recently demonstrated thermochemically[17] that the energy of the cyclic ester does in fact exceed that of its open-chain analogues by about 7—9 kcal./mole.

It has been suggested[15] that the reactivity sequence in sulphite esters can be explained by the existence of similar repulsions. The abnormally high reactivity of catechol sulphite in neutral solution can be explained on this basis. The sulphite ring attached to a rigid aromatic system is likely to be considerably strained. This strain would be relieved in the protonated species where the positive charge would be expected to reduce the size of the orbitals occupied by the adjacent lone pair of electrons, and might therefore reduce the differential effects of such interelectronic strains.

Hydrolyses of Ethylene and Diethyl Sulphite.—Kinetic form. The kinetic forms observed for ethylene and diethyl sulphite are very similar. Most acid-catalysed reactions fall into one of two classes, according to whether the logarithm of the first-order rate-coefficient increases linearly with stoicheiometric acidity (the $A2$ mechanism) or with Hammett's acidity function H_0 (the $A1$ mechanism). The former correlation is interpreted as meaning that the transition state involves both the conjugate acid of the substrate and a solvent molecule, whereas in the latter case the transition state involves only the conjugate acid.

It has been shown[8] that the acid-catalysed hydrolysis of ethylene sulphite in water proceeds by the $A2$ mechanism with a superimposed positive salt effect. This salt effect causes deviations from linearity in the variation of rate with acid concentration and, furthermore, leads to an apparent dependence on H_0 with a low Hammett slope of *ca.* 0·69.

Bunton and his co-workers recently[2] set up an acidity scale in aqueous dioxan solutions and used the H_0 concept as a mechanistic criterion for this solvent. In Table 4 are shown the rates of hydrolysis of ethylene sulphite in 60% and in 40% dioxan–water. The value of the Hammett slope is 0·69 in both cases and is therefore identical with that obtained in water. The actual rates at corresponding acidities are very similar in the three solvents; 10^3k_1 is 2·59, 1·69, and 1·30 min.$^{-1}$ in water, 40% dioxan, and 60% dioxan respectively.

The $A2$ mechanism for a neutral substrate (S) may be written as

$$S + H_3O^+ \rightleftharpoons SH^+ + H_2O \xrightarrow{k_2} \text{Products} + H^+ \quad . \quad . \quad . \quad . \quad (1)$$

The Brönsted equation then takes the form:

$$k = k_2K_e[H^+]\, f_S \, . \, a_W \, . \, f_{H^+}/f^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k is the experimental first-order rate-coefficient, k_2 is the true rate-coefficient for the rate-determining stage, and K_e is the equilibrium constant for the protonation of the substrate, the other symbols having their customary meaning. The product k_2K_e should be independent of environment, and k will depend on $[H^+]$ alone if the activity ratio term is constant. The results indicate that for ethylene sulphite this is very nearly so.

The results for diethyl sulphite in different solvents are shown in Tables 2 and 3. The Hammett slopes are 0·76 and 0·75 in water and 60% dioxan respectively. The actual values of 10^3k_1 at corresponding acidities are 1·08 min.$^{-1}$ in water and 0·470 min.$^{-1}$ in 60% dioxan.

The rate of acid-hydrolysis of diethyl sulphite is greater in a deuterium oxide–dioxan solvent than in the corresponding aqueous dioxan solvent by a factor of 1·33, confirming that the acid-catalysis is specifically by the hydrogen ion.

The similarity of the present results for ethylene and diethyl sulphite in 60% dioxan and those obtained previously in aqueous solution[8,15] suggests that the same mechanism of hydrolysis operates in both solvents.

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[16] Westheimer, *Chem. Soc. Special Publ.* No. 8, 1957, 1.

[17] Cox, Wall, and Westheimer, *Chem. and Ind.*, 1959, 929.

Comparison of Hammett Slopes for Acid-catalysed Hydrolyses in the Presence and in the Absence of Nucleophiles.—If the Zucker–Hammett hypothesis is considered to be valid, reactions involving a molecule of water in the transition state will correlate with stoicheiometric acidity, whereas reactions which involve only the conjugate acid of the substrate will correlate with h_0. It is of fundamental importance, therefore, to investigate what happens to the form of the dependence of rate on acidity when the molecule of water has to compete with other more reactive nucleophiles.

To examine this, the reaction has been studied in the region of relatively high acidity with and without various nucleophiles. It has been assumed [4,8] that the amount of salt added is insufficient to alter differentially the values of H_0 for the solutions. In Tables 2(*b*) and 2(*c*) are values for the hydrolysis of diethyl sulphite in water catalysed by sodium chloride (0·250M) and sodium bromide (0·100M). In Tables 3(*b*) and 3(*c*) are values for the same reaction in 60% dioxan catalysed by lithium chloride (0·0100M) and lithium bromide (0·0040M). There is a fairly accurately linear relation between $\log_{10} \Delta k_1$ and H_0 in all cases. Values of the Hammett slope are indicated in Table 6. The plot of $\log_{10} k_1$ against H_0 for the hydrolysis of diethyl sulphite in water has a slope of 0·76, which is increased to 1·05 and 1·08 in the presence of chloride and bromide ions respectively. The corresponding values in 60% dioxan are very similar. Those for ethylene sulphite in water are rather lower.

TABLE 6. *Hammett slopes and related data.*

Sulphite	Salt	Solvent	Hammett slope	" Bunnett slope " (*w*)
Diethyl	—	H_2O	0·76	+3·63
Diethyl	NaCl	H_2O	1·05	−0·031
Diethyl	NaBr	H_2O	1·08	−1·00
Ethylene [8]	—	H_2O	0·68	+4·30
Ethylene [8]	NaCl	H_2O	0·82	+1·51
Diethyl	—	60% Dioxan	0·75	—
Diethyl	LiCl	60% Dioxan	1·05	—
Diethyl	LiBr	60% Dioxan	1·05	—

In both solvents the halide-catalysed reaction falls much nearer to the Hammett-dependent category than does the reaction that is not catalysed by halide. The rate equation that should be followed in the former case is

$$\text{Rate} \propto [\text{S}][\text{H}^+][\text{X}^-] \cdot f_\text{S} \cdot f_{\text{H}^+} f_{\text{X}^-} / f^\ddagger \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where X is the halide. For this to be Hammett-dependent, it is required that the ratio $f_\text{S} \cdot f_{\text{H}^+} f_{\text{X}^-} / f^\ddagger$ follow the protonation of a neutral indicator, and this is sometimes only approximately true.[18]

The examples studied indicate how, under suitable conditions, an apparent Hammett-dependence may be obtained for a bimolecular (*A*2) reaction. The more reactive the nucleophile, the more nearly does the rate follow acidity.

Recent Criticisms of the Zucker–Hammett Hypothesis.—The possibility that examples may be found in which a bimolecular reaction shows the behaviour of a Hammett-dependent reaction has been suggested by Taft, Deno, and Skell,[19] who point out also that the Zucker–Hammett hypothesis leads to contradictory conclusions in some cases.

Whalley and his co-workers [20–22] have suggested that the volume of activation of a reaction is a more reliable criterion of its mechanism. Unimolecular (*A*1) reactions will have a volume of activation close to zero, whereas bimolecular (*A*2) reactions will have a relatively large negative volume of activation. They have shown that the volumes of activation for the acid-catalysed hydrolyses of acetals and formals are all either positive

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[18] Long, *Proc. Chem. Soc.*, 1959, 798.

[19] Taft, Deno, and Skell, *Ann. Rev. Phys. Chem.*, 1958, **9**, 303.

[20] Whalley, *Trans. Faraday Soc.*, 1959, **55**, 798.

[21] Whalley and Koskikallio, *Trans. Faraday Soc.*, 1959, **55**, 809.

[22] Koskikallio and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 815.

or close to zero, confirming previous conclusions, based mainly on the use of the acidity function, that the hydrolyses proceed by the *A*1 mechanism.

The use of the Zucker–Hammett hypothesis leads to the conclusion [23] that acid-catalysed hydrolyses of epoxides proceed by the *A*1 mechanism. Evidence from the effect of pressure on the rate, however, indicates that the rate-determining step is bimolecular. Koskikallio and Whalley [22] interpret this as meaning that the Zucker–Hammett hypothesis fails when applied to the hydrolysis of epoxides. Until more studies have been made of the effect of pressure on acid-catalysed reactions, however, it is by no means certain that values of volumes of activation intermediate between those ascribed to *A*1 and *A*2 reactions will not be obtained.

A similar situation has already been found when using the entropy of activation as a criterion of mechanism. Long, Pritchard, and Stafford [24] suggested that within a given class of compound a rather more positive entropy of activation would be expected for a unimolecular reaction, whereas the corresponding bimolecular reaction will show a relatively large negative entropy. Some idea of the spread of values obtained for organic sulphites is given in Table 5. Whalley [20] has shown, however, that, whereas this criterion may in certain cases give fortuitously correct results, it is not reliable as an unambiguous criterion of mechanism.

Bunnett [25] suggested an alternative empircal criterion of mechanism. Instead of writing the *A*2 mechanism as in equation (1), he used a suggestion by Leisten [26] that for some acid-catalysed reactions the transition state may contain more than one molecule of water and wrote the mechanism as

$$S + H^+,nH_2O \rightleftharpoons SH^+ + nH_2O \xrightarrow{k_2} \text{Products} + H^+,nH_2O \quad . \quad . \quad (4)$$

The Brönsted equation can then be written

$$k = k_2K_eh_0\, a_W{}^n f_S \,.\, f_{BH^+}/f_B f^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and plots of (log $k + H_0$) against log a_W should be linear.

The values (w) of the slopes obtained for organic sulphites are shown in Table 6. The values of a_W used were obtained from the data of Robinson and Baker [27] on isopiestic measurements in perchloric acid, it being assumed that the added salts do not differentially affect the values of the activity of water at different acid concentrations. The values of w vary from +4·30 for the hydrolysis of ethylene sulphite to −1·00 for the bromide-catalysed hydrolysis of diethyl sulphite.

Bunnett distinguishes three classes of reaction by the following criteria: (1) w is zero or has a small negative value, (2) w is *ca.* +2, and (3) w is *ca.* 5—7. These classes represent the *A*1 mechanism, water acting as a nucleophile, and water acting as a proton-transfer agent, respectively. As Bunnett points out, however, the quantities w and n must be related, the difference being a comparison of the degree of hydration of the transition state and the initial state (cf. ref. 28).

The values of w obtained for the hydrolyses of organic sulphites which are considered to proceed by a similar mechanism lie in a range across both of the first two classes. It seems, therefore, that this criterion cannot be used in this case. Further, since with this criterion, just as for the Zucker–Hammett hypothesis, there is an activity coefficient requirement namely that $f_S \,.\, f_{BH^+}/f_B f^{\ddagger}$ must be unity, the same disadvantages are possessed by both functions.

Pritchard and Long [23] have shown that the ratio of the rate-constants in deuterium oxide and in water ($k_1^{D_2O}/k_1^{H_2O}$) for known *A*1 hydrolyses is greater than 2·05, and for

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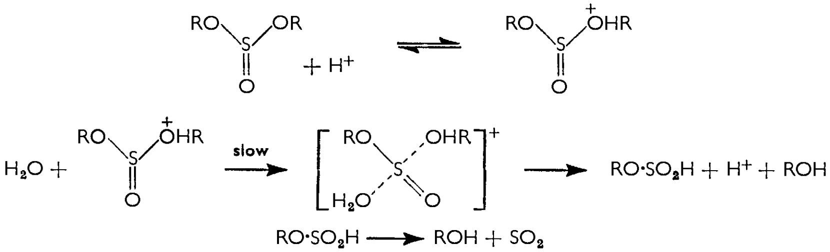
[23] Long and Pritchard, *J. Amer. Chem. Soc.*, 1956, **78**, 2663.
[24] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.
[25] Bunnett, *J. Amer. Chem. Soc.*, 1960, **82**, 499.
[26] Leisten, *Chem. and Ind.*, 1959, 397.
[27] Robinson and Baker, *Trans. Proc. Roy. Soc. New Zealand*, 1946, **76**, 250.
[28] Bascombe and Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

known *A*2 hydrolyses is between 1·37 and 1·7. The values of $(k_1^{D_2O}/k_1^{H_2O})$ are 1·55 and 1·33 for the acid-catalysed hydrolysis of diethyl sulphite in water and 60% dioxan, respectively. The values for the same reaction in water catalysed by bromide and chloride ions are 1·85 and 1·33, respectively. On this basis, all the reactions studied would be classed as *A*2 with the possible exception of the bromide-catalysed reaction which gives an intermediate value.

Whalley and Koskikallio [21] have criticised the above use of the magnitude of the deuterium effect as a criterion of mechanism since it is entirely empirical. The values obtained, however, do indicate that acid-catalysis is specifically by the hydrogen ion.

It being assumed that the mechanism of hydrolysis of both cyclic and " open-chain " sulphites is the same in both water and aqueous dioxan, and since no ethyl chloride or ethylene chlorohydrin is formed in the chloride-ion-catalysed hydrolysis of diethyl sulphite [15] and ethylene sulphite,[8] respectively, the nucleophilic attack must be on the sulphur rather than on the carbon atom. The most probable reaction scheme for the hydrolysis of a dialkyl sulphite with water as the nucleophile is that annexed here, where the proton might be associated with either of the two different types of oxygen atom. The hydrolyses of sulphonates [29] and thiosulphates [30] both involve similar nucleophilic displacements at a sulphur atom.



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[29] Bunton and Welch, *J.*, 1956, 3240.
[30] Pryor, personal communication.