351. *Nucleophilic Displacements in Organic Sulphites. Part V.* The Acid-catalysed Hydrolysis of Diethyl Sulphite and of Dimethyl Sulphite.*

By C. A. Bunton, P. B. D. de la Mare, and J. G. Tillett.

The hydrolyses of diethyl sulphite and dimethyl sulphite have been studied in aqueous solutions of mineral acids. They are considered to be of the concentration-dependent type of acid-catalysed reaction, with a superposed salt effect. Nucleophilic anions catalyse the reaction. The rates of the chloride-ion-catalysed reaction follow more closely Hammett's acidity function than the stoicheiometric acid concentration. By the use of oxygen-18, sulphur–oxygen bond-fission was found for both these compounds. The results are compared with those obtained earlier for the cyclic sulphites. The general applicability of the Zucker–Hammett hypothesis is discussed.

In Part II [1] it was shown that the hydrolyses of cyclic sulphites are catalysed by mineral acids. The variation of the rate with concentration of acid and the dependence of the rate on added salts were examined. The present paper provides similar data for two dialkyl sulphites, thus enabling a comparison to be made between the cyclic and open-chain systems.

Experimental

Dialkyl sulphites were prepared by the standard method.[2] Diethyl sulphite had b. p. 158°/760 mm., n_D^{25} 1·4130; dimethyl sulphite, b. p. 126°/760 mm., n_D^{25} 1·4070. The infrared spectrum of diethyl sulphite, determined by using a Grubb-Parsons double-beam infrared spectrometer in the range 700—3100 cm.$^{-1}$, had absorption bands at 714, 743, 813, 877, 894, 1000, 1010, 1093, 1157, 1208, 1289, 1393, 1451, 1479, 1623, and 3030 cm.$^{-1}$.

Position of Bond-fission.—Hydrolysis in acid solution. Diethyl sulphite (*ca.* 16 g.) was added to water enriched with ^{18}O (100 ml.) and perchloric acid (3·0M) and kept for 12 hr. at room temperature. The resulting solution was neutralised (phenolphthalein) and fractionated through a 20 × 1½ cm. column packed with glass helices. The fraction of b. p. 78—80° was collected and dried ($MgSO_4$). After redistillation the sample of b. p. 75—75·5°, n_D^{25} 1·3630, was used for isotopic analysis. A similar procedure was used for dimethyl sulphite.

Isotope analysis. The alcohol was pyrolysed to carbon monoxide on red-hot carbon at low pressure in a radiofrequency heater. The carbon monoxide was analysed mass-spectrometrically. The following values (atoms % excess of ^{18}O) were obtained. Dimethyl sulphite: water (solvent) 0·325, alcohol 0·008; diethyl sulphite: water (solvent) 0·453, alcohol 0·034.

Absence of ethyl chloride from the hydrochloric acid-catalysed hydrolysis of diethyl sulphite. Diethyl sulphite (0·88M) was hydrolysed in 100 ml. of aqueous hydrochloric acid (3M). When reaction was complete, nitrogen was bubbled through the solution to displace any ethyl chloride (which would not have been hydrolysed under the mild conditions needed for decomposition of the sulphite). Chloride ion was then determined. A blank solution, from which sulphite had been omitted, was treated similarly. No significant difference in concentration of chloride ion was observed, so no significant quantity of ethyl chloride had been produced.

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 perchlorate were dried at 120°; the latter was free from halide. Sodium toluene-*p*-sulphonate was a commercial recrystallised specimen.

The rates of hydrolysis at 35° and above were determined by a conventional sealed-tube method. The conversion of organic sulphite into sulphur dioxide was determined at intervals by breaking samples under excess of standard iodine solution, which was then back-titrated with sodium thiosulphate. The runs at 0° and 25° were carried out in stoppered flasks. Aliquot portions (usually 5·0 ml.) were withdrawn at intervals and quenched in a large excess (200 ml.) of ice-cold water containing excess of iodine which was then back-titrated as above.

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* Parts I—IV, *J.*, 1958, 4751, 4754, 4761, 4766.

[1] Bunton, de la Mare, and Tillett, *J.*, 1958, 4754.

[2] Voss and Blanke, *Annalen*, 1931, **485**, 273.

The following exemplifies a typical kinetic run for 0·033M-diethyl sulphite in 0·270M-perchloric acid at 35·0°.

Time (min.)	0	5	10	15	20	25	
Titre (ml. of 0·0100N-iodine)	6·48	8·35	10·27	12·25	13·98	14·95	
10^4k_1 (min.$^{-1}$)	—	1·75	1·68	1·79	1·78	1·70	
Time (min.)	30	40	50	60	90	120	∞
Titre (ml. of 0·0100N-iodine)	16·15	18·66	20·26	22·29	25·17	27·91	30·99
10^4k_1 (min.$^{-1}$)	1·67	1·72	1·65	1·73	1·60	1·73	—

The finite titre for time (t) = 0 represents reaction during the time allowed for warming the samples to the temperature of the thermostat. Values of k_1 have been calculated by the use of the formula $k_1 = 2{\cdot}303 \log_{10}\{a/(a - x)\}/t$, 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 use of the above formula are substantially constant over considerably more than 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 Tables. Values of H_0 are included for reference, and mostly are taken from Long and Paul's review.[3]

TABLE 1. *First-order rate-coefficients and related data for the hydrolysis of diethyl sulphite in water.*

(*a*) *At* 0·0°.

[HClO$_4$] (M)	0·50	1·03 *	2·06	3·09	3·61	4·12
10^3k_1 (min.$^{-1}$)	0·50	1·22	2·76	5·14	8·92	13·4
10^3k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	1·00	1·19	1·34	1·66	2·47	3·26
H_0	0·31	−0·25	−0·80	−1·28	−1·53	−1·78
[HClO$_4$] (M)	4·64	5·15	5·67	6·18	6·70	7·21
10^3k_1 (min.$^{-1}$)	20·7	27·7	51·1	69·6	135	265
10^3k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	4·47	5·38	9·02	11·2	20·1	37·8
H_0	−2·05	−2·32	−2·65	−2·98	−3·36	−3·76

(*b*) *At* 0·0°, *with added sodium perchlorate.*

[HClO$_4$] (M)	0·000	1·000 *	2·000	3·000	4·000	5·000
[NaClO$_4$] (M)	6·000	5·000	4·000	3·000	2·000	1·000
10^3k_1 (min.$^{-1}$)	0·00	3·29	8·05	14·8	24·9	41·9
10^3k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	—	3·29	4·03	4·93	6·23	8·38
H_0	—	−1·46	−1·84	−2·13	−2·47	−2·77
[HClO$_4$] (M)	6·000	0·000	1·000 *	2·000	3·000	4·000
[NaClO$_4$] (M)	0·000	4·000	3·000	2·000	1·000	0·000
10^3k_1 (min.$^{-1}$)	60·0	0·00	1·99	4·24	7·97	13·4
10^3k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	10·0	—	1·99	2·12	2·66	3·35
H_0	−3·05					

(*c*) *At* 0·0°, *with hydrochloric acid.*

[HCl] (M)	1·000	1·500	2·000	3·000	4·000
10^3k_1 (min.$^{-1}$)	3·95	9·99	21·6	76·2	246
10^3k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	3·95	6·66	10·8	25·4	61·5
H_0	−0·20	−0·47	−0·69	−1·05	−1·40

(*d*) *At* 0·0°, *with* 0·25M-*sodium chloride and added sodium perchlorate.*

[HClO$_4$] (M)	1·03	2·06	3·09	4·12	5·15	5·67
[NaClO$_4$] (M)	0·000	0·000	0·000	0·000	0·000	0·000
10^3k_1 (min.$^{-1}$)	1·92	6·04	16·9	51·0	185	328
H_0 †	−0·25	−0·80	−1·28	−1·78	−2·32	−2·65
$4 + \log_{10} \Delta k_1$ ‡	0·898	1·516	2·072	2·575	3·196	3·443
[HClO$_4$] (M)	6·18	1·000	2·000	3·000		
[NaClO$_4$] (M)	0·000	5·000	4·000	3·000		
10^3k_1 (min.$^{-1}$)	566	14·9	41·8	83·8		
H_0 †	−2·98	−1·46	−1·84	−2·13		
$4 + \log_{10} \Delta k_1$ ‡	3·696	2·065	2·529	2·839		

(*e*) *At* 0·0°, *with hydrochloric acid and added sodium chloride.*

[HCl] (M)	1·000	2·000	3·000	4·000
[NaCl] (M)	3·000	2·000	1·000	0·000
10^3k_1 (min.$^{-1}$)	35·4	84·6	164	246
10^3k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	35·4	42·3	54·6	61·5

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

TABLE 1. (*Continued.*)

(*f*) *At* 0·0°, *with added sodium chloride.*

[HClO$_4$] (M)	1·03	1·03	2·06	2·06	3·09	3·09	4·12	5·15	5·15
[NaCl] (M)	0·500	1·000	0·500	1·000	0·500	1·000	0·500	0·100	0·200
10^3k_1 (min.$^{-1}$)	3·34	5·84	10·6	20·9	32·2	61·2	90·9	92·0	142

(*g*) *At* 35·0°.

[HClO$_4$] (M)	0·000	0·103	0·270	0·412	0·540	1·08	1·500	2·060
10^3k_1 (min.$^{-1}$)	0·000	6·7	17·1	27·5	38·5	104	111	176
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	—	65·2	63·2	66·7	71·2	96·5	74·0	85·5

(*h*) *At* 35·0° *with* 0·270M-*perchloric acid.*

[NaClO$_4$] (M)	0·000	1·000	2·000	3·000
10^3k_1 (min.$^{-1}$)	17·1	21·8	27·6	34·9
[NaCl] (M)	0·000	0·100	0·200	0·300
10^3k_1 (min.$^{-1}$)	17·1	23·0	29·8	34·9
[NaBr] (M)	0·000	0·030	0·100	0·200
10^3k_1 (min.$^{-1}$)	17·1	19·7	30·0	38·7
[$C_7H_7\cdot SO_3Na$] (M)	0·000	0·500	1·000	1·500
10^3k_1 (min.$^{-1}$)	17·1	20·0	20·5	21·5

(*i*) *At* 24·9°.

[HClO$_4$] (M)	1·03	2·06	3·09	4·12
10^3k_1 (min.$^{-1}$)	20·8	55·9	123	250
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	20·2	27·2	39·8	60·8
H_0	−0·25	−0·80	−1·28	−1·78

For 0·27M-HClO$_4$ at 50°, $10^3k_1 = 85{\cdot}0$; for 0·03M-HClO$_4$ at 73·0°, $10^3k_1 = 78{\cdot}4$.

* See text.
† In absence of added chloride ions.
‡ $\Delta k_1 = k_1$ in presence of chloride $-k_1$ in absence of chloride, under otherwise identical conditions.

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

(*a*) *At* 0·0°.

[HClO$_4$] (M)	2·06	3·09	4·12	5·15	6·18	7·21
10^3k_1 (min.$^{-1}$)	1·22	2·29	7·78	13·5	30·0	73·5
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	0·59	0·74	1·89	2·61	4·85	10·2
H_0	−0·80	−1·28	−1·78	−2·32	−2·98	−3·76

(*b*) *At* 0·0° *with added sodium perchlorate.*

[HClO$_4$] (M)	1·000	3·000	4·000	5·000	6·000
[NaClO$_4$] (M)	5·000	3·000	2·000	1·000	0·000
10^3k_1 (min.$^{-1}$)	1·62	8·33	12·6	16·5	27·5
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	1·62	2·78	3·15	3·30	4·50
H_0	−1·46	−2·13	−2·47	−2·77	−3·05

(*c*) *At* 0·0°, *with hydrochloric acid.*

[HCl] (M)	2·000	3·000	4·000
10^3k_1 (min.$^{-1}$)	8·08	21·9	82·6
$10^3k_1/[H^+]$ (l. mole^{-1} min.$^{-1}$)	4·04	7·30	20·65
H_0	−0·69	−1·05	−1·40

Influence of temperature. The entropy (ΔS^*) and the energy of activation (ΔE), calculated by using the formula $k = (\mathbf{e}\mathbf{k}T/\mathbf{h}) \exp(\Delta S^*/\mathbf{R}) \exp(-\Delta E/\mathbf{R}T)$ for diethyl sulphite in 1M-perchloric acid are $\Delta S^* = -8{\cdot}2$ e.u. and $\Delta E = 20{\cdot}3$ kcal. mole^{-1}. The entropies of activation found for ethylene and trimethylene sulphites [1] were respectively −15·8 e.u. and −13·0 e.u., so the value now found for diethyl sulphite is significantly less negative; the activation energy is correspondingly slightly higher.

Long, Pritchard, and Stafford [4] have recently elaborated Taft's earlier suggestion [5] that Hammett-dependent and concentration-dependent reactions within the same class of compound should differ in entropy of activation (ΔS^*) by some 20—30 e.u. Typical values for unimolecular ($A1$) and bimolecular ($A2$) acid-catalysed hydrolyses of carboxylic esters are

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[4] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.
[5] Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372.

+5 and −20 e.u. respectively; but there is no certainty that other classes of ester would have these typical values.*

On this criterion, the hydrolyses of cyclic and non-cyclic sulphites do not differ greatly, but both lie intermediate between values characteristic of typical reactions of the two classes of carboxylic ester. A definite answer concerning the presence or absence of a water molecule in the rate-determining stage is therefore not yet given by the data on entropies of activation for hydrolysis of organic sulphites, but it is considered that the negative values obtained are not inconsistent with the bimolecular mechanism proposed for the cyclic sulphites.

Position of bond-fission. Hydrolysis of dimethyl or diethyl sulphite in water enriched in ^{18}O gives essentially normal alcohol. The slight enrichment recorded for the hydrolysis of diethyl sulphite is probably caused by incomplete drying of the sample, and we consider that entire sulphur–oxygen bond-fission has occurred.

DISCUSSION

Kinetic Form.—The kinetic forms observed for diethyl and dimethyl sulphite are very similar. A more extensive examination has, however, been made of diethyl sulphite, and the illustrations for the discussions will be taken from data on this compound.

Many acid-catalysed reactions fall into one of two classes, according to whether the logarithm of the first-order rate-coefficient increases linearly with the logarithm of the stoicheiometric acidity or with Hammett's acidity function, H_0. This criterion has been used widely in the study of acid-catalysed reactions, and evidence obtained by its use has, in general, been in accord with expectations derived from other data. The terms concentration-dependent and Hammett-dependent will be used to describe the two types of mechanism.

Ethylene and trimethylene sulphites undergo acid-catalysed hydrolysis; the reactions behave kinetically in a way which at first sight is intermediate between the above classes. From consideration of the detailed effects of nucleophilic anions as catalysts, in conjunction with studies of the position of bond-fission, it was concluded that the hydrolyses of these sulphites fall into the concentration-dependent class, with a superposed increase in the rate of reaction when the concentration of electrolyte in the medium is increased, as it is by increase in concentration of acid.

The behaviour of the open-chain sulphites is generally very similar, but there are significant differences which require special comment.

Correlation of rate with acidity. In Fig. 1 are plotted the logarithms of the rate of hydrolysis of diethyl sulphite against values[3] of Hammett's acidity function. The reaction had been followed well into the region of acidity in which h_0 and $[HClO_4]$ are markedly different.

Considering first only the effects of variation in the concentration of perchloric acid, the values lie near to a straight line of slope 0·69. In contrast with the results obtained previously for ethylene sulphite, there is no curvature at the highest acidities. A Hammett-dependent reaction would give a straight line of unit slope, although appreciable deviations from such ideal behaviour have been observed for reactions which are accepted as falling into this class.[3]

A low Hammett slope for an acid-catalysed reaction might arise from a bimolecular reaction which has a high positive salt effect (cf. the hydrolysis of ethylidene diacetate[6]), or from a unimolecular reaction which has a negative salt effect, *i.e.*, from a unimolecular reaction in which conditions are such that the activity-coefficient equality, $f_S/f_{X^+} = f_B/f_{BH^+}$, which is one of the main conditions for a unit slope, does not hold.

It seems necessary, therefore, to use some further criterion to decide whether or not the reaction is Hammett-dependent. The addition of sodium perchlorate to solutions of

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* Thus the characteristic value for the unimolecular acid-catalysed ring opening of epoxides[4] is −5 e.u.

[6] Bell and Lukianenko, *J.*, 1957, 1687.

perchloric acid increases the acidity of the solution as measured by H_0.[3] As for the cyclic sulphites, however, the rates of the acid-catalysed hydrolysis of diethyl sulphite are not increased to the same extent. This is shown in Fig. 1; the triangles refer to experiments in which sodium perchlorate has been added to perchloric acid to make the total concentration of perchlorate ion 6·0M.

The above results, considered as a whole, suggest that the reaction is not Hammett-dependent. Neither, however, is the rate directly proportional to the stoicheiometric concentration of acid. This is illustrated by the values given in Tables 1(*a*), 1(*b*), 1(*g*), 1(*h*), 1(*i*), 2(*a*), and 2(*b*). The values of $k_1/[H^+]$ rise quite considerably, and vary twenty-fold over a range of concentration of perchloric acid 0·5—6·7M.

When the reaction is carried out with the perchlorate-ion concentration kept constant by addition of sodium perchlorate, the rate is proportional to the concentration of perchloric acid only below about 2·0M; above this concentration, considerable deviations occur, and the plot takes the form of an upward curve; in this, the behaviour differs from that of ethylene sulphite.

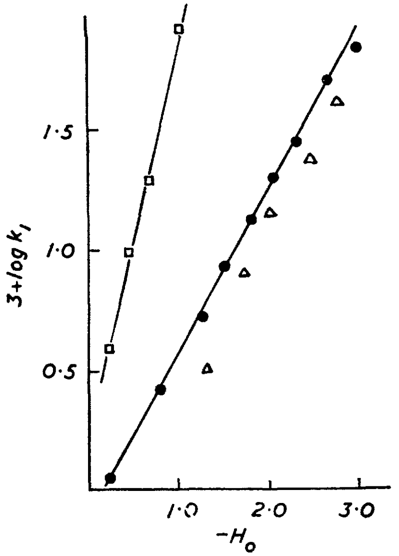


FIG. 1. *Hammett plot for the acid hydrolysis of diethyl sulphite at 0°.*

● $HClO_4$
△ $HClO_4 + NaClO_4$
□ HCl

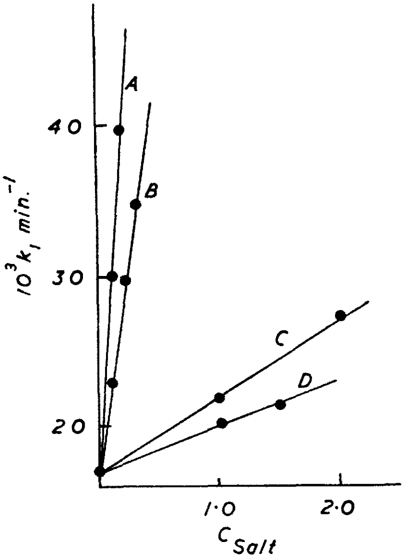


FIG. 2. *Effect of added salts on the acid hydrolysis* (35·0°, 0·27M-$HClO_4$).

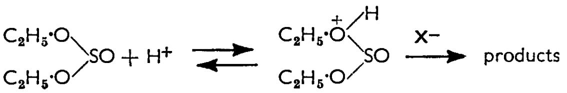
A, NaBr.
B, NaCl.
C, $NaClO_4$.
D, $C_7H_7\cdot SO_3Na$.

Effects of nucleophilic anions and other added salts on the rate of hydrolysis. In Fig. 1 are shown also points corresponding to the use of hydrochloric acid. These fall on a straight line which lies well above the curve obtained for perchloric acid. The difference in rates can be judged from the values shown in Table 1(*c*).

In Fig. 2 are shown the points corresponding to the effects of added salts on the reaction at low acidity. As for hydrolysis of ethylene sulphite, the salts fall into two well-defined classes. The first includes sodium perchlorate and sodium toluene-*p*-sulphonate, for which the overall effect is small. The second includes sodium chloride and sodium bromide. These have a very marked catalytic effect, and the rate is proportional to the concentration of salt.

This enhanced catalytic power, shown by salts in the latter class, seems to be associated with the anion, and we believe that this is another example of specific catalysis by anions. The effects of the negative ions concerned are in order of their nucleophilic power, *i.e.*, $Br^- > Cl^-$. It seems reasonable, therefore, to attribute this type of catalysis to nucleophilic attack by the negative ion on the sulphur atom of the conjugate acid, as was found also for the cyclic sulphites.

Mechanism.—The acid-catalysed aqueous hydrolysis of esters usually involves a pre-equilibrium non-rate-determining proton-transfer to form the conjugate acid, as in the first step of sequence (1). The proton might be associated with either of the two different types of oxygen atoms.



. . . . . . (1)

Both for the cyclic sulphites and for the non-cyclic sulphites, hydrolysis could in principle proceed either by the bimolecular ($A2$) mechanism (sequence 1) in which a water molecule participates covalently in the rate-determining attack on sulphur, or by the $A1$ mechanism, in which the second stage is unimolecular, followed by a non-rate-determining process. The present hydrolysis gives behaviour intermediate between these two as judged by (*a*) by the Zucker–Hammett criterion, (*b*) the effects of added salts, (*c*) the entropy of activation. Three interpretations are possible, *viz.*: (i) that the reaction falls into one or other of the two classes, and therefore that the criteria are not satisfactory for mechanistic diagnosis in this case; (ii) that the two mechanisms proceed concurrently, making similar contributions to the rate; and (iii) that the reaction in some ill-defined way can be regarded as of intermediate mechanism. Interpretation (ii) would imply that the contributions from the two mechanisms would change with structure and with conditions, as in the hydrolysis of diphenylmethyl trifluoroacetate[7] in aqueous dioxan, where the contributions of mechanism $A_{\mathrm{Ac}}2$ and $A_{\mathrm{Al}}1$ can be changed by change in acidity or temperature. No indication of such a change has been found in the present results. It has been pointed out that, when a single molecular encounter leading to reaction is considered, interpretation (iii) involves difficulties[8] which seem to us to be associated with the problem of differentiating between covalent and electrostatic interactions in the transition state. In the present discussion, therefore, interpretation (i) has been adopted; so, by analogy with the halide-catalysed reaction, discussed below, and in accordance with our treatment of the cyclic sulphites, the bimolecular mechanism is considered to be the most probable. This is the basis of the following discussion (cf. ref. 9).

Environmental Effects.—For a concentration-dependent hydrolysis of the type shown in equation (1), the Brönsted equation takes the form:[3]

$$\text{Rate} = k[\mathrm{S}][\mathrm{H}^+] \cdot f_{\mathrm{S}}a_{\mathrm{w}} \cdot f_{\mathrm{H}^+}/f^{\ddagger} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

Here $f^{\ddagger}$ is the activity coefficient of the transition state, which contains the substrate (S), water, and a proton; a_{w} is the activity of water; the other symbols have their customary meaning.

In some examples of reactions considered to follow this path, the activity coefficient ratio $f_{\mathrm{S}}a_{\mathrm{w}}f_{\mathrm{H}^+}/f^{\ddagger}$, is near to unity in the critical experimental region, and hence the rate of reaction is a linear function of the stoicheiometric concentration of acid, as is required by the Zucker–Hammett hypothesis. Such a limiting situation is not achieved in the present case, and many other examples of such deviations from ideal behaviour have been found. Thus, the rate of hydrolysis of ethylidene diacetate[6] is not accurately proportional to the acid concentration, the deviation increasing with increasing acid-strength. Similarly, the rates of hydrolysis of methyl formate and ethyl acetate,[10] of methyl

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[7] Bunton and Hadwick, unpublished result.

[8] Gold, *J.*, 1956, 4633.

[9] Bunton, de la Mare, Lennard, Llewellyn, Pearson, Pritchard, and Tillett, *J.*, 1958, 4761.

[10] Bell, Dowding, and Noble, *J.*, 1955, 3106.

benzoate,[11] and of methyl phosphate [12] show this positive salt-effect with increasing ionic strength.

In the present experiments, it is found that the rate of hydrolysis increases much more rapidly than would be expected if the rate was linearly dependent on acid concentration. If sodium perchlorate is added to keep the total concentration of electrolyte constant at 6M, the rate of hydrolysis still increases with acidity more rapidly than required for a linear relation when the concentration of perchloric acid is greater than about 2M. Hence, even in these mixtures the above activity-coefficient term is still not constant.

Since the salt-effects observed for diethyl and dimethyl sulphites are very similar, the size of the ester molecule does not seem to be critically important in determining the magnitude of the observed changes.

The following values are for the reaction catalysed by perchloric acid at constant concentration (1·03 ≏ 1·0M) in the presence of various amounts of added sodium perchlorate; they are taken from Tables 1(*a*) and 1(*b*), marked (*):

$[NaClO_4]$ (M) (and μ)	0 (1·0)	3·000 (4·0)	5·000 (6·0)
$3 + \log_{10} k_2$	0·079	0·299	0·517

There is an approximately linear relationship between $\log_{10} k_2$ and μ, the ionic strength. Bell [13] has pointed out that such a " linear salt-effect," varying with the nature of the electrolyte, can be justified in terms of the extension of the Debye–Hückel theory in which a term proportional to the ionic strength is included in the expression for the logarithm of the activity coefficient of an electrolyte; this term involves an empirical parameter characteristic of the ions present in the solution. In the present investigation, the catalytic powers of the three electrolytes, sodium perchlorate, sodium toluene-*p*-sulphonate, and perchloric acid are rather similar, but if a wider range of electrolytes were examined it is probable that this would not be found to be general. For the hydrolysis of ethylene sulphite, tetraethylammonium perchlorate had very little catalytic power.

The Halide-catalysed Reaction.—This, at low acidities, takes the kinetic form: $-d[\text{sulphite}]/dt = k[\text{sulphite}][H^+][\text{Halide}^-]$. Because of the substantial catalysis, which greatly exceeds that expected for a salt of a non-nucleophilic anion, it is considered that, as for the cyclic sulphites, this reaction involves bimolecular attack by halide ions on the protonated intermediate. Ethyl chloride is not produced in the chloride-catalysed hydrolysis of diethyl sulphite, so the nucleophilic attack is on the sulphur, rather than on the carbon atom.

To investigate the form of the dependence of rate on acidity in this process, the reaction has been studied at relatively high acidity, with chloride ions present in amount (0·25M) sufficient to increase the rate of reaction, but insufficient, it is considered,[cf. 3] to alter differentially the values of H_0 for the solutions. In Table 1(*d*) are values for the reaction catalysed by 0·25M-sodium chloride at different acidities, it being assumed that the added chloride ions do not differentially affect the rate of attack by water on the protonated sulphite. Values of $\log_{10} \Delta k_1$ are shown diagrammatically in Fig. 3. Somewhat surprisingly, points representing behaviour when sodium perchlorate is also added lie closely on the straight line of slope 1·12 which fairly accurately represents the relationship between $\log_{10} \Delta k_1$ and H_0. The corresponding slope for ethylene sulphite was 0·82. Both these values are in the range which would normally be regarded as indicating a Hammett-dependent process.

Comparison of Hammett Slopes for Acid-catalysed Hydrolyses in the Presence and in the Absence of Chloride Ions.—The plot of $\log_{10} k_1$ against H_0 for the hydrolysis of ethylene sulphite has a slope of 0·68; this is increased to 0·82 in the presence of chloride ions. The corresponding values for diethyl sulphite are 0·69 and 1·12. The reasonable correlation of

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[11] Chmiel and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 3326.
[12] Bunton, Llewellyn, Oldham and Vernon, *J.*, 1958, 3574.
[13] Bell, " Acid-Base Catalysis," Oxford, 1941, Chapter II.

$\log_{10} k_1$ with H_0 for the reaction which at low acidities has the kinetic form $-d[\text{sulphite}]/dt = k[\text{sulphite}][H^+][Cl^-]$ carries with it the implication that the ratio $f_Sf_{H^+}f_{Cl^-}/f^{\ddagger}_{(Cl^-)}$ follows the corresponding ratio for protonation of a neutral indicator, $f_Bf_{H^+}/f_{BH^+}$. The overall charge on the transition state for the chloride-catalysed reaction is zero.

It could not have been predicted that the introduction of a chloride ion into the transition state would not change greatly the form of the dependence of rate on acidity from that expected for a unimolecular (*A*1) hydrolysis. It is perhaps not surprising, however, that when it is found that the ratio $f_Sf_{H^+}f_{Cl^-}/f^{\ddagger}_{(Cl^-)}$ accords with that expected for a unimolecular rate-determining reaction, in which the corresponding ratio is $f_Sf_{H^+}/f^{\ddagger}_{(\text{No } Cl^-,\ \text{No } H_2O)}$, it is found also that the ratio for the uncatalysed reaction involving water as the nucleophil is not too different. In the latter case, the corresponding ratio is $f_Sf_Hf_{H_2O}/f^{\ddagger}_{(H_2O)}$. It is interesting that the direction of the change in slope of the plot of rate against acidity, and thence the change in the activity-coefficient ratio, is such that it accords with the most naïve interpretation of the Zucker–Hammett criterion, namely that a bimolecular reaction involving water as the reagent will become more nearly Hammett-dependent if some other nucleophilic agent takes the place of water in the rate-determining nucleophilic attack.

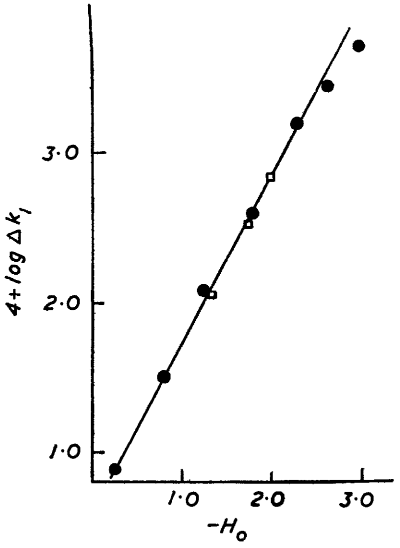

FIG. 3. *Hammett plot for the halide-catalysed acid hydrolysis.*

● $HClO_4$
□ $HClO_4 + NaClO_4$.

The present example so nearly approximates to behaviour characteristic of a Hammett-dependent reaction that it suggests the possibibility that examples may in due course be found in which a bimolecular hydrolysis by water gives the behaviour of a Hammett-dependent reaction.[cf. 14]

Structural Effects: *Comparison of Open-chain and Cyclic Sulphites.*—The mechanisms of hydrolysis of these two groups of sulphites are, under our conditions, very similar. The rates of hydrolysis of the dialkyl sulphites are considerably greater than those of the cyclic sulphites. The relative rates, at 0°, in 1·0M-acid, are: ethylene sulphite,[1] 1; trimethylene sulphite,[1] 4; dimethyl sulphite, 20; diethyl sulphite, 48. This rate-difference is determined essentially by the difference in entropy of activation.

These results can be compared with those for the phosphate esters, which are the only other inorganic esters for which rate-data are available for both the cyclic and open-chain systems. In 1·0M-acid, ethylene phosphate hydrolyses about 10^6 times more rapidly than

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[14] Deno and Perrizolo, *J. Amer. Chem. Soc.*, 1957, **79**, 1345; Taft, Deno, and Skell, *Ann. Rev. Phys. Chem.*, 1958, **9**, 303.

dimethyl phosphate.[25] Similar results are obtained in alkaline solutions. Trimethylene phosphate, however, in 1·0M-alkali hydrolyses only slightly faster than dimethyl phosphate.

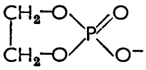
Thus the five-membered ring compound is very reactive in acid and alkaline solutions, but the reactivity of the six-membered phosphate is similar to that of the open-chain esters. This is not the case for the sulphites. Diethyl sulphite hydrolyses faster than either 1 : 2- or 1 : 3-cyclic sulphites in acid solution. The different reactivity sequences are not due simply to a different charge type of reaction, because the relative rates of hydrolysis are similar in the presence and the absence of halide ions, which specifically catalyse the reaction by attacking the sulphur atom of the protonated ester.

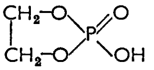
Differences may, however, occur in the basicity of the oxygen atoms. Clearly, under catalysis by acids, greater basicity will favour more protonation and thus increase the rate. The basicity of cyclic sulphoxides increases with ring size,[16] and so the increase in rate on going from ethylene to trimethylene sulphite might conceivably be explained if protonation were on the terminal oxygen atom and the basicities varied in a similar manner.

No data exist for the direct comparison of the basicities of cyclic and open-chain sulphites, but we do not suppose that the basicities would differ greatly, and certainly not sufficiently to cause the observed differences in rate.

Westheimer [15] has suggested that the five-membered cyclic phosphate is very 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, he considers, may be relieved in the less rigid six-membered and acyclic phosphates, so that these compounds are relatively less reactive.

If this explanation is correct, the effect might well be large both in the anion (I) and in the neutral molecule (II). In the protonated species (III), on the other hand, the positive charge would be expected, through its effect on the electronegativity of the oxygen atom, to reduce the size of the orbitals occupied by the adjacent lone-pairs of electrons, and might therefore reduce the differential effects of such interelectronic strains. It is not certain whether hydrolysis of (III) is rapid or not; the above theory fits the results for cyclic sulphites. For these compounds, the structural effects on the hydrolysis of the neutral species (IV) parallel those of the phosphates; ethylene sulphite is more reactive to alkali than is trimethylene sulphite. On the other hand, the conjugate acid (V) of ethylene sulphite shows no abnormal reactivity, as is consistent with the view that the lone-pair repulsions, responsible for the abnormally high reactivities of (I), (II), and (IV), disappear or are greatly reduced in (III) and (V).


(I)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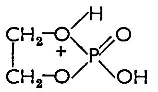
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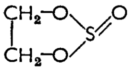
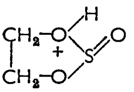

(IV)


(V)

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

[16] Tamres and Searles, Abstracts of Papers, 131st Meeting, Amer. Chem. Soc., 1957, p. 10R.