960. *Nucleophilic Displacements in Organic Sulphites. Part III.* Comparison of Alkaline and Acidic Hydrolyses of Trimethylene Sulphite and Related Compounds.*

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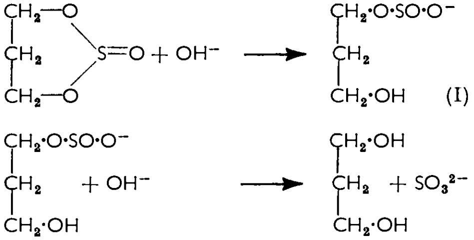
Trimethylene and 1 : 3-butylene sulphites are hydrolysed in alkaline solution at rates which can be followed by conventional techniques at 0°. The reactions are of the second kinetic order, and have the same rates whether measured by the uptake of alkali or the liberation of sulphur dioxide. The possible intermediate (*e.g.*, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}SO_2H$ or its anion) does not build up to high concentration during reaction. Alkyl substitution in the carbon chain seems to have little effect on the rate of alkaline hydrolysis, but 1 : 2-sulphites are in this process very much more rapidly hydrolysed. These results, in conjunction with studies of bond-fission (Part I) allow comparison with the corresponding data for acid-catalysed hydrolysis (Part II). In the latter reaction also, the possible intermediate does not build up in concentration; and alkyl substitution in the carbon chain has little influence on the rate, which now is little changed when the ring-size is altered.

The detailed courses of hydrolyses of cyclic sulphites, and the kinetic effects of structural changes, are considered. In contrast to the acid-catalysed hydrolyses of cyclic sulphites discussed in Part II, those in alkaline solution are very rapid. Possible stages in the reaction (*e.g.*, of trimethylene sulphite) are as follows:



. . . . (*a*)

. . . . (*b*)

Stages (*a*) and (*b*) have been shown both to involve sulphur–oxygen bond fission. In principle, either may be reversible, and either may be rate-determining.

The intermediate at the stage of half-hydrolysis would, if it were to accumulate during the reaction because the rate of stage (*b*) were similar to that of stage (*a*), be converted into its most stable prototropic form, (I), by rapid proton-transfer to and from oxygen. It is the anion of an acid of the type $RO{\cdot}SO_2H$, which would be expected to be similar in strength to sulphurous acid in its first dissociation ($K_a = 1{\cdot}7 \times 10^{-2}$). Sulphurous acid, produced in the second stage, is moderately strong in its first dissociation but weak in its second ($K_a = 1{\cdot}0 \times 10^{-7}$), so any build-up of the intermediate (I) could be measured by following the consumption of alkali with two indicators, to one of which sulphurous acid behaves as a monobasic acid (*e.g.*, Methyl Red) and to the other as a dibasic acid (*e.g.*, phenolphthalein).

Experimental

The materials have been described in the preceding papers.

Alkaline Hydrolyses.—Since trimethylene and 1 : 3-butylene sulphites still contained up to 5% of rapidly hydrolysed material derived from a 1 : 2-diol, the rates were measured with use of the first experimental point as the zero of time. The following are examples of typical kinetic runs.

Rate of liberation of sulphur dioxide. To 0·0328N-sodium hydroxide at 0° (100 ml.) was

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* Parts I and II, preceding papers.

added trimethylene sulphite (1·0 ml., 0·2573M). Nitrogen was bubbled through the alkaline solution for 30 min. before the start, and was continued throughout to displace carbon dioxide. The solution was well shaken and at intervals samples (10 ml.) were pipetted into a mixture of 0·1N-hydrochloric acid (2 ml.) and 0·0100N-iodine in potassium iodide (25 ml.). The excess of iodine was then back-titrated with 0·01103N-sodium thiosulphate. The results are given in Table 1.

TABLE 1.

Time (min.)	0	0·75	1·38	2·38	3·34	4·38	6·32	infinity
Titre (ml.)	8·36	7·92	7·62	7·18	6·86	6·50	6·04	4·46
10^4x (M)	0	2·37	4·03	6·45	8·22	10·20	12·74	21·46
10^3[Sulphite] = $10^3(a - x)$ (M)...	2·15	1·91	1·74	1·50	1·32	1·13	0·87	0·00
10^3[NaOH] = $10^3(b - 2x)$ (M)...	31·70	31·21	30·88	30·40	30·04	29·65	29·14	27·40
k_2 (l. mole^{-1} min.$^{-1}$)	—	4·9	4·8	4·8	4·7	4·8	4·7	—

Second-order rate-coefficients are calculated from $k_2 = 2{\cdot}303\{\log_{10}[a(b - 2x)/b(a - x]\}/t(b - 2a)$ where a and b are the initial molarities of sulphite and alkali respectively, and x is the molarity of sulphite used up at time t, one mole of sulphite being assumed to liberate one mole of sulphur dioxide.

Rate of disappearance of alkali. The sulphite (1·0 ml., 0·2547N) was added to 0·0101N-sodium hydroxide (100 ml.), as described above, at 0°. At intervals samples (10 ml.) were withdrawn and quenched rapidly in excess of 0·00478N-hydrochloric acid (25 ml.) in stoppered flasks which had been bubbled out with nitrogen. The excess of acid was then back-titrated against 0·00470N-sodium hydroxide with a mixture of phenolphthalein and α-naphtholphthalein (referred to below as " phenolphthalein ") as indicator, titrations being carried out with a slow stream of nitrogen passing over the solution. Results are in Table 2.

TABLE 2.

Time (min.)	0	1·98	6·32	10·27	18·9	28·5	58·2	infinity
Titre (ml.)	6·06	6·86	8·00	8·80	10·62	11·69	13·27	15·28
10^4x (M)	0·00	1·85	4·55	6·40	10·70	13·20	16·95	21·50
10^3[NaOH] = $10^3(b - 2x)$ (M)...	9·29	8·92	8·38	8·01	7·15	6·65	5·90	4·99
10^3[Sulphite] = $10^3(a - x)$ (M)	2·15	1·97	1·70	1·51	1·08	0·83	0·46	0·00
k_2 (l. mole^{-1} min.$^{-1}$)	—	5·0	4·3	5·0	4·5	4·3	4·8	—

Measurements were also made in which a mixture of Methyl Red and Bromocresol Green (referred to later as " Methyl Red ") was used as indicator.

The formula used in both cases to calculate the rate-coefficients in Table 3 was $k_2 = 2{\cdot}303\{\log_{10}[a(b - 2x)/b(a - x)]\}/t(b - 2a)$. Iodometry was used unless otherwise specified.

TABLE 3.

10^3[Trimethylene sulphite] (M)	2·34	2·14	2·09	2·36	2·15 [a]	1·76 [b]	2·15		
10^3[Sodium hydroxide] (M)	19·4	9·55	40·4	10·1	9·29	10·2	31·7		
k_2 (l. mole^{-1} min.$^{-1}$)	5·0	4·7	4·9	4·6	4·7	4·7	4·8		
10^3[1 : 3-Butylene sulphite] (M)	2·27	2·20	2·24	2·22	2·26	1·91	1·99	2·11	2·05
10^3[Sodium hydroxide] (M)	10·02	20·02	10·01	9·98	10·04	36·2	63·4	77·2	98·2
k_2 (l. mole^{-1} min.$^{-1}$)	1·37	1·23	1·25	1·17	1·30	1·38	1·25	1·30	1·34

[a] Followed by acid-base titration with " phenolphthalein." [b] Followed by acid-base titration with " Methyl Red."

Acid Hydrolyses.—Experiments were made to compare the rates of hydrolysis of the various cyclic sulphites. The methods used are described in Part II. The following are results for catalysis by dilute sulphuric acid (<0·1M) at 100°:

Sulphite:	Ethylene	Propylene	3-Chloropropylene	1 : 3-Butylene
k_1/[H$^+$] (l. mole^{-1} min.$^{-1}$)	0·72	0·70	0·22	1·70

The following are values of $10^2k_1/[\mathrm{H}^+]$(l. mole^{-1} min.$^{-1}$) for hydrolyses catalysed by higher concentrations of perchloric acid at 35° (the value marked * is interpolated):

HClO$_4$ (M)	1	2	3	4	5	6
(−)2 : 3-Butylene sulphite	0·17	0·19	0·30	0·42	—	0·89
meso-2 : 3-Butylene sulphite	0·25	0·27	0·27	0·38	0·51	0·73
Tetramethylethylene sulphite	0·15 *	0·17	0·20	0·26	0·38	—

These results for catalysis by perchloric acid show the increase of the second-order rate constant ($k_1/[H^+]$) with increasing acid concentration. This is similar to the kinetic form for the acid hydrolyses of ethylene and trimethylene sulphites (Part II). A few experiments were done with tetramethylethylene sulphite at 35° at an ionic strength kept constant ($\mu = 4$) by addition of sodium perchlorate to the perchloric acid. A linear relationship between k_1 and $[HClO_4]$ was observed (cf. Part II) (see Table 4).

TABLE 4.

$[NaClO_4]$ (M)	3·0	2·0	1·0	0·0
$[HClO_4]$ (M)	1·0	2·0	3·0	4·0
10^2k_1 (min.$^{-1}$)	0·25	0·47	0·72	1·05
$10^2k_1/[H]^+$ (l. mole^{-1} min.$^{-1}$)	0·25	0·24	0·24	0·26

The entropy and energy of activation for the acid-catalysed hydrolysis of tetramethylethylene sulphite were calculated from the rates in 1M-perchloric acid at 73·0° ($10^2k_1 =$ 5·12 l. mole^{-1} min.$^{-1}$) and at 35·0°: $\Delta S^* = -17{\cdot}8$ e.u., $E = 19{\cdot}7$ kcal. mole^{-1}. These values are very similar to those observed for the acid-catalysed hydrolyses of ethylene and trimethylene sulphites (Part II), and are in the range usually found for bimolecular acid-catalysed hydrolyses.[1]

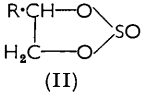
DISCUSSION

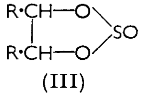
Alkaline Hydrolyses.—Alkaline hydrolyses of the 1 : 2-sulphites were too rapid for convenient kinetic measurement, but it is presumed that the same considerations apply to these as to the 1 : 3-sulphites. The latter are hydrolysed according to the kinetic form: $d[SO_2]/dt = k_2[\text{Sulphite}][OH^-]$, the assumption being made that for every mole of titratable sulphite formed, two moles of hydroxide ion were used up. The decrease in concentration of hydroxide ion, whether followed by titration of the remaining alkali to " Methyl Red " or to " phenolphthalein," obeyed the same law, and proceeded at the same rate, within experimental error, as the increase in concentration of sulphur dioxide followed by titration with iodine.

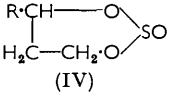
The significance of these results is as follows. The hydrolysis under alkaline conditions follows the sequence given earlier [reactions (*a*) and (*b*)].

If stage (*a*) were more rapid than stage (*b*), and were irreversible, the intermediate alkylsulphonate ion (I) would build up in concentration during reaction. If this intermediate did not react with iodine as sulphur dioxide does, then the rate of consumption of alkali could not equal the rate of liberation of material titratable with iodine. If, alternatively, the intermediate reacted with iodine as sulphur dioxide does, then different rates of disappearance of alkali would be observed, depending on which indicator was chosen for the titration. In fact, the liberation of material titratable with iodine, and the disappearance of alkali based on titration with either indicator, have the same rates. Hence the second stage of the reaction must be much more rapid than the first, and the intermediate (I) does not build up in concentration during the reaction.

Another formally possible reaction scheme is that the intermediate (I) is in equilibrium with the reactants. This would give a rapid equilibration between the oxygen atoms of the SO_2 group, which in the ion are structurally equivalent. There is no such equilibration, as was shown in Part I. Hence the second stage (*b*) must be faster than the possible reverse step of stage (*a*), and the intermediate (I) decomposes as soon as it is formed.


(II)


(III)


(IV)

1 : 3-Butylene sulphite reacts with alkali about a quarter as fast as does trimethylene sulphite. That the effect of such a structural change should be small is not surprising, since in all the examples studied, which include the structural types (II), (III), and (IV),

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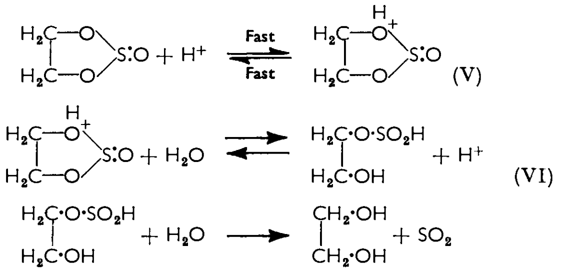
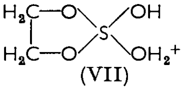
[1] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.

the diol recovered from the hydrolysis in enriched water was found to be isotopically normal, within experimental error. This implies that sulphur–oxygen bond-fission prevails in these cases to the extent of 95% or more, and this conclusion applies to both stages of the hydrolysis. Thus, the reaction-centre is far removed from the point of structural change.

Acid-catalysed Hydrolysis.—This also is a multi-stage reaction. The first step is a pre-equilibrium proton-transfer (Part II), and is followed by a slow displacement of sulphur dioxide. This step is bimolecular, and, as for the alkaline hydrolysis, must take place in stages; it could in principle involve the accumulation of an intermediate (VI), the conjugate acid of (I). The following is a representation of the process for the case of ethylene sulphite; there is no evidence as to the position of the proton in the intermediate (V), and this has been assigned arbitrarily.

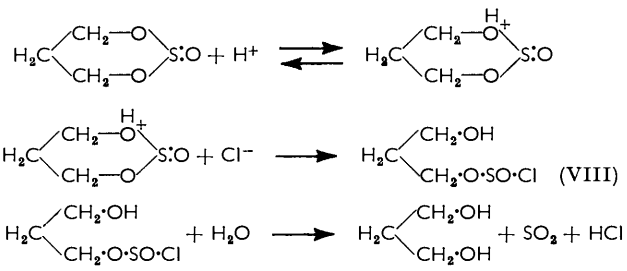


If the formation of an intermediate such as (VI) were reversible to any appreciable extent, the oxygen of the water would equilibrate with that attached to the sulphur atom. It has been shown that this is not so. Hence the intermediate (VI) must decompose to products more rapidly than it reverts to reactants.


(VII)

An alternative formulation of this intermediate is as in the structure (VII), in which water has been added to the S:O-group (cf. ref. 2). We have not distinguished between these possible intermediates, but the same arguments exclude that structure (VII) is in reversible equilibrium with the reactants.

Similar arguments apply to the reactions of kinetic form $d[SO_2]/dt = k[\text{Sulphite}][H^+][Cl^-]$. In these, the halide ion takes the place of a water molecule, and sulphur–oxygen bond-fission is still observed. The most probable reaction-sequence, formulated here for trimethylene sulphite, is as follows:



The intermediate (VIII) is also an intermediate in the reaction between a 1 : 3-diol and thionyl chloride. This reaction gives a mixture of 1 : 3-sulphite [route (*c*)] and chlorohydrin [route (*d*)] in similar proportions. Preparatively, under quite a variety of conditions of reaction, path (*d*) (to chlorohydrin) is always followed to a very considerable extent; it

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[2] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.

is very difficult to increase the yield of 1 : 3-sulphite in this condensation to greater than about 30%.[3] No chlorohydrin is produced *via* intermediate (VIII) [and therefore path (*d*)], in the halide-catalysed hydrolysis of trimethylene sulphite; it is presumed, therefore, that path (*c*) is also not followed, and the intermediate (VIII) is hydrolysed as fast as it is formed.

Structural Effects.—Alkaline hydrolysis. The greater reactivity towards hydroxide ion of the 1 : 2- than of the 1 : 3-cyclic sulphites is qualitatively similar to the behaviour of analogous phosphates;[4] ethylene hydrogen phosphate is hydrolysed by alkalis *ca.* 10^6 times more rapidly than trimethylene or dimethyl hydrogen phosphate. It has been suggested that this very high reactivity of ethylene hydrogen phosphate results from internal repulsions between the lone-pair electrons of the oxygen atoms. A similar explanation could perhaps be applied to cyclic sulphites. Here, as in the phosphate series, the 1 : 3-cyclic compounds have a reactivity towards hydroxide ion which is similar to that of the dialkyl compounds,[5] and both are less reactive than the 1 : 2-compounds, but as the latter in the sulphite series are too reactive for conventional measurement we cannot yet compare the rates.

Acid hydrolysis. The rates and Arrhenius parameters of the acid hydrolyses of the 1 : 2- and 1 : 3-cyclic sulphites vary little with structural changes. The rates (relative to ethylene sulphite) are: propylene,* 1; (—)-2 : 3-butylene, 0·8; *meso*-2 : 3-butylene, 1·2; tetramethylethylene, 0·7; 3-chloropropylene*, 0·3; trimethylene, 4; 1 : 3-butylene,* 2·4. Comparison labelled* were made at 100°, the others at 35°.

The effect of substituents is small, as might be expected, because the substituent groups are well removed from the reaction centre. Changes in ring size have a small effect; in contrast with the situation in alkaline hydrolysis, the six-membered compounds are the more reactive. It is not known whether this arises from a difference in basicity of the two esters, or from a difference in the relative reactivities of their conjugate acids. Changes in ring size have little effect upon the basicities of saturated heterocyclic and carbocyclic nitrogen bases,[6] and from analogy with these we might expect the basicities of the 1 : 2- and 1 : 3-cyclic sulphites to be similar.

There is a considerable difference between the relative reactivities of sulphites and phosphates in acid and alkaline solution. The high reactivity of ethylene hydrogen phosphate (relative to the dialkyl hydrogen phosphates) appears in acid as well as alkaline hydrolysis. This is not so for the sulphites. Preliminary results show that diethyl sulphite hydrolyses faster than either 1 : 2- or 1 : 3-cyclic sulphites in acid solution. These different reactivity-sequences are not due to a different charge-type of reaction, because the relative rates of acid hydrolysis are similar in the presence and absence of halide ions, which specifically catalyse the reaction by attacking the sulphur atom.

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[3] Rovira and Halasz, *Compt. rend.*, 1941, **212**, 644.

[4] Westheimer, Chem. Soc. Spec. Publ., 1958, No. 8, 1.

[5] Voss and Blanke, *Annalen*, 1931, **485**, 258.

[6] Brown, McDaniel, and Häflinger in "Determination of Organic Structure by Physical Methods," Ed. Braude and Nachod, Academic Press, New York, 1955.