958. *Nucleophilic Displacements in Organic Sulphites. Part I. The Positions of Bond Fission in the Hydrolyses of Some* 1 : 2- *and* 1 : 3-*Cyclic Sulphites.*

By C. A. BUNTON, P. B. D. DE LA MARE, (MISS) P. M. GREASELEY, D. R. LLEWELLYN, N. H. PRATT, and J. G. TILLETT.

The positions of bond-fission in the hydrolyses of ethylene sulphite, propylene sulphite, *meso*-2 : 3-butylene sulphite, tetramethylethylene sulphite, trimethylene sulphite, and 1 : 3-butylene sulphite have been determined isotopically under acidic and alkaline conditions. Sulphur–oxygen bond-fission occurs in all the examples studied. It has been shown, for ethylene and for trimethylene sulphite, that the organic sulphite, originally isotopically normal, is still normal when recovered after partial hydrolysis in isotopically enriched water under either acidic or alkaline conditions.

GARNER and LUCAS [1] showed that the formation, followed by the acid- or alkali-catalysed hydrolysis, of 2 : 3-butylene sulphite proceeded without change in the optical activity of the butane-2 : 3-diol used as starting material. They concluded that these hydrolyses proceed with sulphur–oxygen bond-fission. Foster, Hancock, and Overend [2] have studied the hydrolyses of the cyclic sulphites of the *cyclo*hexane-1 : 2-diols. The *trans*-isomer gave the *trans*-diol; the *cis*-isomer gave the *cis*-diol in acidic solution, and mainly the *trans*- with some *cis*-diol, in alkaline solution. From this they concluded that some

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[1] Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5496.

[2] Foster, Hancock, and Overend, *Chem. and Ind.*, 1956, 1144.

carbon–oxygen bond-fission occurs under the latter conditions. Other cases are known in which the products of reaction with nucleophilic reagents require the conclusion that carbon–oxygen bond fission has occurred, at least as part of the total reaction. Thus the reactions of ethylene sulphite with aryloxide ions[3] can lead to the formation of products of the type $ArO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and dialkyl sulphites can undergo cleavage with iodide ions in acetone[4] forming, among other products, alkyl iodides.

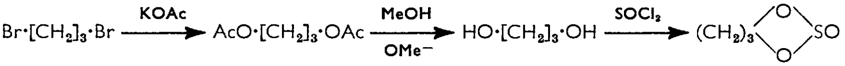
A preliminary account has been given[5] of the establishment, by using ^{18}O as tracer, that sulphur–oxygen bond-fission occurs in the acid- and alkali-catalysed hydrolyses of ethylene sulphite in water. These measurements have now been extended to other sulphites as part of a programme in which we seek to establish the range of conditions over which the various mechanisms available operate.

EXPERIMENTAL

The cyclic sulphites were prepared mostly by standard methods.[cf. 6] Ethylene sulphite had b. p. 88°/52 mm., n_D^{25} 1·4450; propylene sulphite, b. p. 58°/9 mm., n_D^{25} 1·4359. For the preparation of *meso*-2 : 3-butylene sulphite, a commercial specimen of butane-2 : 3-diol, containing much of the *meso*-isomer, was fractionated. The final fractions, b. p. 127°/101 mm., n_D^{25} 1·4370, were converted into the sulphite, which was fractionally distilled in a helix-packed 3 ft column. Initial fractions were still slightly optically active, but the later fractions had no optical activity, and had b. p. 67°/8 mm., n_D^{25} 1·4380. Tetramethylethylene sulphite was prepared by Szmant and Emerson's method.[7] The product, recrystallised first from methanol and finally from light petroleum (b. p. 40—60°), had m. p. 44—45°, *M* (by hydrolysis with excess of alkali), 162 (calc. 164). The infrared spectrum of this and of *meso*-2 : 3-butylene sulphite, determined by using a Grubb-Parsons double-beam infrared spectrophotometer, had absorption bands respectively at 709, 773, 799, 892, 970, 1131, 1167, 1221 cm.$^{-1}$; and at 662, 671, 691, 729, 801, 833, 905, 992, 1017, 1099, 1143, 1167, 1206, 1353, 1393, 1449, 1468 cm.$^{-1}$.

Although trimethylene sulphite, whether prepared from propane-1 : 3-diol which had been fractionally distilled or from a commercial specimen, appeared to be homogeneous from its b. p. and its rate of hydrolysis under acid conditions, it contained impurities which were very difficult to remove. These were shown to be sulphites derived from impurities in propane-1 : 3-diol. This material, even after careful fractional distillation, contained 30%, calculated as propane-1 : 2-diol, of material oxidisable by periodic acid by the method described by Jackson.[8] Some of this may have been propane-1 : 2-diol; some was probably dihydroxyacetone or glyceraldehyde, since the infrared spectrum had a strong maximum at 1727 cm.$^{-1}$, indicating the presence of a C=O group. A similar absorption band appeared in the spectrum of the derived sulphite.

Finally, trimethylene sulphite was prepared by the sequence:



The trimethylene bromide was fractionally distilled and had b. p. 163°/760 mm., n_D^{24} 1·5215. The derived diacetate had b. p. 127°/50 mm., n_D^{25} 1·4171. The derived propane-1 : 3-diol was a colourless liquid, b. p. 113°/15 mm., n_D^{25} 1·4373; its infrared spectrum had no absorption at 1727 cm.$^{-1}$. Reaction with excess of periodic acid showed the presence of 2·1% of 1 : 2-diol. The sulphite prepared from it had b. p. 89°/39 mm., n_D^{25} 1·4509. Since the yields of cyclic sulphite are considerably greater from 1 : 2- than from 1 : 3-diols, it is to be expected that the derived sulphite might contain rather more impurity from the former material, as proved to be so. The diol produced by hydrolysis of our best sample of trimethylene sulphite contained 4·7% of 1 : 2-diol as determined by reaction with excess of periodic acid.

Similar difficulties were experienced in preparing pure 1 : 3-butylene sulphite. Butane-1 : 3-diol (1 : 2-diol, by reaction with periodic acid, 2·3%) gave a sulphite, b. p. 54°/6 mm., n_D^{25} 1·4430, which contained 3·7% of 1 : 2-sulphite.

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[3] Carlson and Cretcher, *J. Amer. Chem. Soc.*, 1947, **69**, 1953.
[4] Foster, Hancock, Overend, and Robb, *J.*, 1956, 2589.
[5] Bunton, de la Mare, Llewellyn, Pearson, and Pritchard, *Chem. and Ind.*, 1956, 490.
[6] de la Mare, Klyne, Millen, Pritchard, and Watson, *J.*, 1956, 1813.
[7] Szmant and Emerson, *J. Amer. Chem. Soc.*, 1956, **78**, 454.
[8] Jackson, *Organic Reactions*, 1944, **2**, 341.

Position of Bond-fission.—Hydrolysis in alkaline solution. A procedure similar to that given below for trimethylene sulphite was followed. The sulphite (*ca.* 20 g.) was added slowly to enriched water (100 ml.) containing 2 equiv. of sodium hydroxide. The reaction was completed by heating the mixture to 100° for 4 hr. Most of the water was then removed by fractional distillation, first through a fractionating column and then under high vacuum. Finally the diol was evaporated under the vacuum provided by a mercury-vapour pump, and collected in a cooled trap. Benzene (25 ml.) was added to the distillate and the mixture was distilled. This procedure was repeated until the distillate was clear. The residue (usually *ca.* 5 ml.) was redistilled at a pressure of *ca.* 10 mm.; first and last fractions were rejected. The resulting product had the correct refractive index, and was used for isotopic analysis. Hydrolyses of the 1 : 2-sulphites were complete in ½ hr. at room temperature.

Hydrolysis in acid solution. The following method was used for trimethylene sulphite, and with slight modification was satisfactory for the other cyclic sulphites. The sulphite (*ca.* 20 g.) was heated under reflux for about 8 hr. with enriched water (100 ml.) and perchloric acid (usually 0·2—0·5M), a stream of nitrogen being passed through the solution continuously to remove the liberated sulphur dioxide. The resulting solution was neutralised (phenolphthalein), and the diol was recovered as described above.

Isotope Analysis.—The diol was pyrolysed to carbon monoxide on red-hot carbon at low pressure in a radio-frequency heater. The carbon monoxide was analysed mass-spectrometrically. The results, both for acidic and for alkaline hydrolysis, are given in Table 1.

TABLE 1. *Hydrolysis of cyclic sulphites in isotopically enriched water.*

	^{18}O-Abundance (atoms % excess)			
	Alkaline hydrolysis		Acidic hydrolysis	
Sulphite	H_2O (solvent)	Diol (recovered)	H_2O (solvent)	Diol (recovered)
Ethylene	0·410	0·005	0·300 *	0·006 *
	0·860	0·000	0·935 †	0·001 †
Propylene	0·663	0·003	0·350	0·000
meso-2 : 3-Butylene	0·395	0·000	0·350	0·033
Tetramethylethylene	0·935	0·011	0·600	0·024
Trimethylene	0·365	0·002	0·966	0·015
1 : 3-Butylene	0·350	0·001	0·350	0·025

* With 2·0M-$NaClO_4$ and 0·5M-$HClO_4$. † With 6·0M-HCl.

TABLE 2. *Isotopic analyses of sulphites recovered after partial hydrolyses.*

			^{18}O-Abundance (atoms % excess) *	
Experiment	Sulphite	Conditions	H_2O (solvent)	Sulphite (recovered)
(*a*)	Ethylene	Alkaline	0·940	0·016
(*f*)	Ethylene	Alkaline †	0·000	0·052
(*c*)	Ethylene	Acidic	1·07	0·016
(*d*)	Ethylene	Acidic	0·997	0·000
(*e*)	Ethylene	Initially neutral	0·997	−0·004
(*b*)	Trimethylene	Alkaline	0·997	−0·002

* Relative to a sample of carbon monoxide obtained by pyrolysis of oxalic acid.

† In this experiment, the sulphite (^{18}O-abundance, 0·055 atom % excess) was enriched isotopically on the exocyclic oxygen atom.

Recovery, and Isotopic Analysis, of Sulphites after Partial Reaction.—Since isotopic exchange between the oxygen atom of the $S{=}O$ group and the solvent is a possible process with important mechanistic consequences, experiments were performed to test whether this exchange occurred. (*a*) Ethylene sulphite (9·8 g.) was allowed to react with sodium hydroxide (3·7 g., the amount required for decomposition of half of the sulphite) in $H_2{}^{18}O$ (100 ml.). When reaction was complete, the ethylene sulphite was recovered by extraction with ether and fractional distillation. The product had b. p. 58°/8 mm., n_D^{25} 1·4446, and the isotopic abundances are shown in Table 2. Similar experiments were performed (*b*) for trimethylene sulphite; (*c*), (*d*) for ethylene sulphite in 0·1M-perchloric acid, the reaction mixture being allowed to stand at 73° for approximately one half-life; and (*e*) in initially neutral solution. A final check (*f*) was made by preparing ^{18}O-labelled ethylene sulphite. Sulphur dioxide was bubbled into enriched water, to give an aqueous solution of $S^{18}O_2$. This was heated, and the $S^{18}O_2$ was passed into phosphorus pentachloride. The mixture was fractionally distilled, to give $S^{18}OCl_2$, b. p. 78°. From this was prepared by the usual method ^{18}O-labelled ethylene sulphite. This was treated with sufficient alkali to hydrolyse half of it in isotopically normal water, and the recovered sulphite was examined. The results of these isotopic analyses are also given in Table 2; values for the sulphites were determined by passing the sulphite through a red-hot carbon tube heated *in vacuo* by a radio-frequency furnace. This procedure differed from that normally used in that there was no liquid-nitrogen trap in the vacuum system. Thus oxides of sulphur formed by decomposition were not removed by condensation, but were reduced by the carbon. We know that this method can detect ^{18}O-labelling of the sulphur-oxygen atom but we have no guarantee that it can do this quantitatively.

DISCUSSION

In all the reactions studied, whether under acidic or alkaline conditions, the diol produced in reaction in isotopically enriched solvent was isotopically normal. Hence sulphur–oxygen bond-fission occurs in all these cases, even under alkaline conditions with ethylene sulphite, structurally the most favourable situation for bimolecular attack on carbon; and under acidic conditions with tetramethylethylene sulphite, structurally the most favourable situation for unimolecular C–O heterolysis.

The exchange reaction of the type shown in the equation does not occur in significant competition with the hydrolysis, either under acidic or alkaline conditions, with either ethylene or trimethylene sulphite.

Elucidation of the mechanisms prevailing in these reactions requires consideration also of the kinetics of hydrolysis: these are described in the accompanying papers.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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