7. Nucleophilic Displacements in Organic Sulphites. Part VI.* Comparison of the Alkaline Hydrolyses of Cyclic and Open-chain Sulphites.

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The rates of alkaline hydrolysis of dimethyl and diethyl sulphite have been measured by conventional techniques at 0°. The reactions follow second-order kinetics and have the same rates whether measured by liberation of sulphur dioxide or uptake of alkali. By the use of oxygen-18, sulphur–oxygen bond-fission was found for dimethyl sulphite and is assumed for diethyl sulphite. The results are therefore qualitatively similar to those obtained earlier for the cyclic sulphites [1] and indicate that the mechanism of hydrolysis in the two systems is very similar. The rates of hydrolysis of trimethylene, diethyl, and dimethyl sulphites have been measured in alkaline buffers at 25°. The absence of buffer catalysis has been established. An approximate rate of hydrolysis has been obtained for the very reactive ethylene sulphite at 0° by conventional means and at 25° in buffer solutions. These results in conjunction with those of earlier studies on cyclic sulphites are compared with the corresponding data for cyclic and open-chain phosphates and carbonates.

IN Part III [1] it was shown that the alkaline hydrolyses of 1,2-cyclic sulphites were too rapid for convenient kinetic measurement, but the rates of hydrolysis of 1,3-sulphites could be measured with conventional techniques at 0°. The present paper provides similar data for two dialkyl sulphites. The reactions were followed in the two different ways previously described for the cyclic sulphites,[1] by measuring both the rate of uptake of alkali and the rate of liberation of sulphur dioxide. Two different indicators were used for the acid–base titrations, to one of which sulphurous acid acts as a monobasic acid and to the other as a dibasic acid.

The rates of alkaline hydrolysis of the dialkyl sulphites at 25° are too rapid for accurate measurement by either of the above methods unless the hydroxide-ion concentration is lower than 0·01M. Therefore a series of runs were carried out in alkaline buffer solutions, the sulphite concentration being sufficiently low not to exceed the buffer capacity. Since the buffer provides a constant hydroxide-ion concentration, the normally second-order hydrolysis becomes first order. The second-order rate coefficients are then calculated by use of the apparent hydroxide-ion concentration given indirectly by the measured pH of the buffer solution.

Under these conditions the possibility of buffer catalysis exists and this has been examined by measuring the rate of hydrolysis of the least reactive sulphite (diethyl) both in an alkaline buffer solution and by the conventional method.

The rate of hydrolysis of trimethylene sulphite at 25° in buffer solutions has also been measured. Approximate values of the rates of hydrolysis of ethylene sulphite at 0° by conventional means and in buffer solutions at 25° have been obtained.

These results enable a comparison to be made between the rates of hydrolysis of the cyclic and open-chain systems. The data for the sulphite esters may then be compared with those for the corresponding cyclic and open-chain phosphates and carbonates.

EXPERIMENTAL

The sulphites were prepared by standard methods.[2,3] Diethyl sulphite had b. p. 156°/750 mm., n_D^{25} 1·4130; dimethyl sulphite, b. p. 126°/760 mm., n_D^{25} 1·4070; ethylene sulphite, b. p. 73°/27 mm., n_D^{25} 1·4450; trimethylene sulphite, b. p. 89°/39 mm., n_D^{25} 1·4509.

* Part V, *J.*, 1959, 1766.

[1] Bunton, de la Mare, Lennard, Pearson, Pritchard, and Tillett, *J.*, 1958, 4761.
[2] Voss and Blanke, *Annalen*, 1931, **485**, 273.
[3] Carlson and Gretcher, *J. Amer. Chem. Soc.*, 1947, **69**, 1953.

Position of Bond-fission.—The alkaline hydrolysis was carried out in water enriched in oxygen-18 in the previously described manner.[4] The sample of methyl alcohol finally extracted, of b. p. 65—65·5°, n_D^{15} 1·3315, was isotopically analysed. The following values (atoms % excess of ^{18}O) were obtained: H_2O (solvent) 0·453, methyl alcohol 0·045.

Alkaline Hydrolysis of the Dialkyl Sulphites.—The following are examples of typical kinetic runs for each of the methods used.

Rate of disappearance of alkali. The sulphite (*ca.* 0·10 ml.) was added to 0·0500N-sodium hydroxide (100 ml.) at 0°. 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 (5 ml.) were withdrawn with ice-cooled pipettes of 3 sec. drainage time and quenched rapidly in excess of 0·0100N-hydrochloric acid (25 ml.) in stoppered flasks which had been bubbled-out with nitrogen. The excess of acid was then back-titrated against 0·00993N-sodium hydroxide with a mixture of phenolphthalein and α-naphtholphthalein as indicator, titrations being carried out with a slow stream of nitrogen passing over the solution. Results are in Table 1.

TABLE 1.

Time (min.)	0	1·50	3·27	7·00	9·97	15·11	20·63	∞
Titre (ml.)	0·00	1·47	2·50	4·29	5·56	6·89	8·08	11·79
10^3x (M)	0·00	1·17	2·20	3·97	5·29	6·56	7·74	11·50
10^2[NaOH] *	4·942	4·708	4·502	4·148	3·884	3·630	3·394	2·642
10^2 [sulphite] †	1·150	1·033	0·930	0·753	0·621	0·494	0·376	0·00
k_2 (l. mole^{-1} min.$^{-1}$)	—	1·49	1·38	1·43	1·34	1·33	1·36	—

* 10^2[NaOH] = $10^2(b - 2x)$. † 10^2[sulphite] = $10^2(a - x)$.

Second-order coefficients are calculated from

$$k_2 = 2·303 \{\log_{10} [a(b - 2x)/b(a - x)]\}/t(b - 2a)$$

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. Measurements were also made with a mixture of Methyl Red and Bromocresol Green as indicator. In this case also the above formula was used to calculate the rate-coefficients.

Rate of liberation of sulphur dioxide. To 0·02288N-sodium hydroxide at 0° (100 ml.) was added dimethyl sulphite (*ca.* 0·03 ml.) as described above. The solution was well shaken and at intervals samples (10 ml.) were withdrawn and quenched in a mixture of 0·1N-hydrochloric acid (10 ml.) and 0·0100N-potassium iodate in potassium iodide (25 ml.). The excess of iodine was back-titrated with 0·01102N-sodium thiosulphate. Results are in Table 2.

TABLE 2.

Time (min.)	0	10·46	20·67	35·70	50·67	70·29	110·6	∞
Titre (ml.)	0·00	1·71	2·68	3·83	4·51	5·01	5·66	6·00
x (M)	0·00	9·43	14·73	21·13	24·88	27·65	31·21	33·00
10^3[sulphite] *	3·310	2·367	1·835	1·197	0·822	0·545	0·189	0·00
10^2[NaOH] †	2·288	2·099	1·993	1·865	1·790	1·735	1·664	1·626
k_2 (l. mole^{-1} min.$^{-1}$)	—	1·48	1·36	1·40	1·40	1·34	1·42	—

* 10^3[sulphite] = $10^2(a - x)$. † 10^2[NaOH] = $10^2(b - 2x)$.

Values of the second-order rate coefficients were calculated by the formula given above. Values obtained by the different methods are compared in Table 3. Iodometry was used unless otherwise specified.

Hydrolysis in Alkaline Buffers at 25°.—The buffer solution used was the universal buffer mixture of Britton and Welford [5] which is 0·02857M with respect to diethylbarbituric acid, citric acid, potassium dihydrogen phosphate, and boric acid, neutralised with a specified quantity of 0·2N-sodium hydroxide. All solutions were prepared with freshly boiled-out distilled water.

[4] Bunton, de la Mare, Greaseley, Llewellyn, Pratt, and Tillett, *J.*, 1958, 4751.
[5] Britton and Welford, *J.*, 1937, 1848.

Typical Run.—Trimethylene sulphite (*ca.* 1·0 ml. of 0·1M stock solution) was added to a buffer solution of measured pH 11·79 (100 ml.) at 25·0°. Nitrogen was bubbled through as described above. The solution was well shaken and samples withdrawn rapidly and pipetted into a mixture of 0·2N-hydrochloric acid (25 ml.) and 0·00100N-potassium iodate in iodide (25 ml.). The excess of iodine was back-titrated with 0·00129N-sodium thiosulphate. The pH of the solution was measured on a Cambridge pH-meter with calomel and glass electrodes. Values of the first-order rate coefficient (k_1) were calculated from the usual formula $k_1 = k_2[\text{OH}^-]$ by using the value of the hydroxide-ion concentration calculated from the measured pH of the buffer solution. The value of the ionic product of water used was $1·008 \times 10^{-14}$ at 25°.[6] Results are in Table 4.

TABLE 3. *Alkaline hydrolyses of diethyl and dimethyl sulphites at 0°.*

10^2[Diethyl sulphite] (M) ...	1·48	1·48	1·53	1·45	1·47	1·50	0·984	0·746
10^2[Sodium hydroxide] (M)	4·92	5·89	8·00	9·85	19·9	4·87	2·40	4·81
k_2 (l. mole^{-1} min.$^{-1}$)	0·366	0·348	0·354	0·354	0·354	0·348	0·360	0·348
10^2[Diethyl sulphite] (M) ...	1·53	0·793	1·46	1·40	0·935 *a*	0·938 *b*	1·51 *a*	4·31 *b*
10^2[Sodium hydroxide] (M)	9·87	2·39	4·82	39·8	2·30	2·31	4·83	4·68
k_2 (l. mole^{-1} min.$^{-1}$)	0·336	0·348	0·360	0·336	0·354	0·366	0·336	0·342
10^2[Dimethyl sulphite] (M)	1·39	0·783	0·417	1·029	1·008	0·764	0·479	0·256
10^2[Sodium hydroxide] (M)	4·80	4·87	4·94	2·51	2·51	2·51	2·51	2·43
k_2 (l. mole^{-1} min.$^{-1}$)	1·42	1·45	1·46	1·46	1·48	1·42	1·46	1·39
10^2[Dimethyl sulphite] (M)	0·500	0·331	0·915	0·286	1·15 *a*	1·15 *b*	0·972 *a*	0·963 *b*
10^2[Sodium hydroxide] (M)	2·50	2·29	8·81	10·0	4·94	4·94	2·16	2·14
k_2 (l. mole^{-1} min.$^{-1}$)	1·38	1·40	1·49	1·51	1·40	1·40	1·44	1·47

a Followed by acid–base titration with phenolphthalein and α-naphtholphthalein. *b* Followed by acid–base titration with Methyl Red and Bromocresol Green.

TABLE 4.

Time (min.)	0	1·72	3·68	5·87	9·11	11·90	14·87	∞
Titre (ml.)	20·71	15·89	12·20	9·60	7·50	5·98	5·22	4·31
$10k_1$ (min.$^{-1}$)	—	2·00	1·95	1·88	1·74	1·86	1·81	—
k_2 (l. mole^{-1} min.$^{-1}$)	—	32·7	31·2	30·1	27·8	29·8	30·0	—

Iodometric Titrations.—The end-point for the iodine–thiosulphate titration with solutions of concentration 0·001N was determined electrometrically using the " dead-stop " method of Foulk and Bawden.[7,8]

Runs in alkaline buffer solutions are summarised in Table 5.

TABLE 5. *Hydrolyses in alkaline buffer solutions at 25·0°.*

Sulphite	pH	10^3[OH$^-$]	k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)	Sulphite	pH	10^3[OH$^-$]	k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)
Dimethyl ...	11·60	4·00	0·0366	9·20	Diethyl ...	11·60	4·00	0·0101	2·50
,, ...	11·79	6·25	0·0630	10·0	,, ...	11·79	6·25	0·0160	2·56
Trimethylene	11·60	4·00	0·119	29·9	Ethylene...	10·50	0·313	1·62	5200
,,	11·79	6·25	0·193	30·9	,, ...	10·79	0·625	3·78	6050

Results of runs followed by conventional means are in Table 6.

TABLE 6. *Conventional runs .*

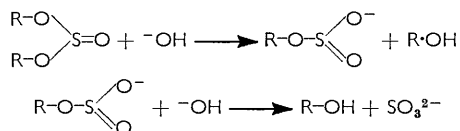| Temp.	10^3[OH$^-$]	10^3[Ester]	k_2 (l. mole^{-1} min.$^{-1}$)	Temp.	10^3[OH$^-$]	10^3[Ester]	k_2 (l. mole^{-1} min.$^{-1}$)
		Ethylene sulphite				Diethyl sulphite	
25·0°	1·00	0·347	*ca.* 7,000	25·0°	48·6	5·49	2·58
0	1·00	0·305	*ca.* 1,000	25·0	23·6	4·65	2·68

DISCUSSION

Hydrolysis of the Dialkyl Sulphites.—The good agreement between the rate constants obtained by the different methods as indicated in Table 3 shows that the decrease in

[6] Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 4496.
[7] Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045.
[8] Evans, *Analyst*, 1947, No. 852, **72**, 99.

concentration of hydroxide ion followed by acid–base titration with either indicator is the same as the increase in concentration of sulphur dioxide followed by titration with iodine.   The results obtained are thus qualitatively similar to those recorded for the cyclic sulphites [1] and by analogous reasoning it may be assumed that the intermediate sulphinate ion does not build up to bulk concentration during the reaction but reacts instantaneously.   The most probable reaction sequence is a two-stage process

$$R-O \diagdown \atop R-O \diagup \!\!\!\!> S{=}O + {}^-OH \longrightarrow R-O-S \diagup^{O^-} \diagdown_O + R{\cdot}OH$$

$$R-O-S \diagup^{O^-} \diagdown_O + {}^-OH \longrightarrow R-OH + SO_3{}^{2-}$$

where the first step is slow and rate-determining and the second step is fast.

   Comparison of Open-chain and Cyclic Sulphites.—Tables 5 and 6 show that the rate of alkaline hydrolysis of diethyl sulphite is the same in alkaline buffer solutions as in weakly alkaline unbuffered solutions.   This indicates that there is no buffer catalysis.   The values of the second-order rate coefficients of the open-chain and cyclic sulphites can then be compared :

Temp.	Sulphite:	Ethylene	Trimethylene	Dimethyl	Diethyl
0°		*ca.* 1000	4·8	1·4	0·35
25		*ca.* 6000	30	10	2·6

   Thus ethylene sulphite is hydrolysed about 10^2 times more rapidly than trimethylene sulphite which, although being hydrolysed faster than the open-chain sulphites, has a rate which is still roughly of the same order of magnitude.

   It is of interest to compare these results with those obtained for the phosphate esters. The five-membered ethylene phosphate is hydrolysed about 10^6 times more rapidly than dimethyl phosphate in alkaline solution.[9]   Trimethylene phosphate is hydrolysed less than ten times more rapidly than dimethyl phosphate.[10,11]   The order of reactivity in the sulphite esters is therefore the same as that observed for the phosphates, *i.e.*, five-membered ring $\gg$ six-membered ring $\approx$ open-chain ester, although the ratio of the rates for five- and six-membered rings is reduced from 10^6 to *ca.* 10^2.

   Westheimer [12] has suggested that the very high reactivity of ethylene phosphate is not entirely due to conventional ring strain but is due also to 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.

   It has been suggested [13] that the reactivity sequence in the sulphite esters can be explained by the existence of similar repulsions.

   The idea that such repulsions may exist is supported by the data on organic carbonates. Ethylene carbonate [14] is hydrolysed about fifty times faster than dimethyl carbonate.[15] Thus the same type of reactivity sequence is observed for phosphates, sulphites, and carbonates.

   [9] Kumanoto, Cox, and Westheimer, *J. Amer. Chem. Soc.*, 1956, **78**, 4858.
   [10] Khorana, Tener, Wright, and Moffatt, *J. Amer. Chem. Soc.*, 1957, **79**, 430.
   [11] Cox, unpublished results, quoted by Westheimer in ref. 12.
   [12] Westheimer, *Chem. Soc. Special Publ.*, No. 8, 1957, 1.
   [13] Bunton, de la Mare, and Tillett, *J.*, 1959, 1766.
   [14] Kempa and Lee, *J.*, 1959, 1576.
   [15] Skrabal and Baltadschieiva, *Monatsh.*, 1924, **45**, 95.