

**954.** *Nucleophilic Displacements in Organic Sulphites. Part IX.<sup>1</sup>  
The Alkaline Hydrolysis of Some Aromatic Sulphites.*

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The rate-coefficients for alkaline hydrolysis at 25° in water containing 1% of dioxan are reported for diphenyl sulphite, and for the cyclic sulphites of 2,2'-dihydroxybiphenyl, 1,8-dihydroxynaphthalene, and catechol. The aromatic sulphites are considerably more reactive than simple aliphatic sulphites. Of the former, the cyclic sulphite of catechol is the most easily hydrolysed; it shows also a relatively high reactivity under neutral conditions and autocatalysis by the bisulphite ions produced in the reaction. The theoretical implications of these results are discussed.

In previous work, it was shown that the cyclic and open-chain sulphites are rapidly hydrolysed by alkali.<sup>2</sup> No quantitative measurements have, so far as we are aware, been elsewhere recorded for aromatic sulphites; but it has been stated<sup>3,4</sup> that diphenyl sulphite and 1,8-naphthylene sulphite are stable to alkali. It seemed to us likely that the observations indicated lack of solubility in the medium chosen for hydrolysis rather than intrinsically low reactivity; so we have re-investigated the reactions.

In fact, the hydrolyses of typical aromatic sulphites are far too rapid to be measured by conventional techniques in alkaline solution. The rates of reaction with hydroxide ion have, however, been evaluated by measurements made at different pH values, held constant through each kinetic run by an automatic titrator.

A preliminary account of the results has been given elsewhere.<sup>5</sup>

#### EXPERIMENTAL

Dioxan was purified by a standard method.<sup>6</sup> Ethylene sulphite and *o*-phenylene sulphite have been described previously.<sup>1,2</sup> 1,8-Dihydroxynaphthalene was prepared by the following method, for details of which we are indebted to Imperial Chemical Industries Limited, as we are

<sup>1</sup> Part VIII, Pagdin, Pine, Tillett, and van Woerden, *J.*, 1962, 3835.

<sup>2</sup> Bunton, de la Mare, Lennard, Llewellyn, Pearson, Pritchard, and Tillett, *J.*, 1958, 4761; Tillett, *J.*, 1960, 37.

<sup>3</sup> Richter, *Ber.*, 1916, 49, 2339.

<sup>4</sup> Green, *J.*, 1927, 2341.

<sup>5</sup> de la Mare, Tillett, and van Woerden, *Chem. and Ind.*, 1961, 1533.

<sup>6</sup> Hess and Frahm, *Ber.*, 1938, 71, 2627.

also for a generous gift of 8-aminonaphthalene-1-sulphonic acid. This sulphonic acid (224 g.) was heated with potassium hydroxide (400 g.) in water (370 g.), in a stainless steel autoclave at 240° for 7 hr. The mixture was then cooled and acidified. The free hydroxy-compound was precipitated and was filtered off and extracted with boiling water. The crude product separated on cooling. For the determination of the dissociation constant of this compound, a sample was recrystallised from water under a stream of sulphur dioxide. This yielded hair-like needles, m. p. 140—142°.

1,8-Naphthylene sulphite was prepared by the usual method (cf. ref. 4) and had m. p. 101° (Found: C, 58.2; H, 3.0; O, 23.4; S, 15.4. Calc. for C<sub>10</sub>H<sub>6</sub>O<sub>3</sub>S: C, 58.3; H, 2.9; O, 23.3; S, 15.5%). It was purified by recrystallisation from slightly acidified 40% aqueous alcohol. A sample thus obtained and used for kinetic work consisted of thin colourless needles, m. p. 102—103° (lit.,<sup>4</sup> 97°).

The infrared spectrum of this compound, and of the other sulphites discussed in this paper, all had strong absorption bands at *ca.* 1200 cm.<sup>-1</sup> characteristic of the S=O stretching frequency.

2,2'-Biphenylene sulphite was put at our disposal by Dr. D. M. Hall. It had been prepared from 2,2'-dihydroxybiphenyl by the action of thionyl chloride in benzene and had m. p. 72.5—74° (Found: C, 62.3; H, 3.5; S, 13.8. C<sub>12</sub>H<sub>8</sub>SO<sub>3</sub> requires C, 62.1; H, 3.5; S, 13.8%).

Diphenyl sulphite was prepared as described by Richter.<sup>3</sup> The crude yellow product was fractionally distilled through an efficient column. A main fraction was collected, having b. p. 154°/4 mm., *n*<sub>D</sub><sup>21</sup> 1.5718 (Found: C, 61.5; H, 4.1; O, 20.5; S, 13.6. Calc. for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S: C, 61.7; H, 4.3; O, 20.5; S, 13.7%).

*Kinetic Measurements.*—For the determination of reaction rates we used a Pye Autotitrator and a Pye Dynacap pH-meter. The principle of the instrumental arrangement was that the acid products liberated during the hydrolysis of the sulphite were neutralised automatically by the addition of alkali, at such a rate that the pH of the reaction mixture was maintained constant within the limits set by the instrument. The pH-meter was calibrated before each run with standard buffer solutions, made up from buffer tablets (Burroughs Wellcome & Co.).

The reaction vessel was kept in a water-bath at 25° ± 0.1° and normally contained 250 ml. of reaction solution. The concentration of sulphite ranged from 10<sup>-3</sup> to 5 × 10<sup>-5</sup>M according to its solubility. At zero time a sample (1.00 ml.) was added from a stock solution of the sulphite in dioxan to the reaction vessel which contained a stirred mixture of dioxan and water from which carbon dioxide had been removed by bubbling out with nitrogen at the required pH. The final dioxan content of the aqueous solution was 1% v/v.\* A continuous stream of nitrogen was passed over the solutions during reaction to prevent uptake of carbon dioxide from the air. The consumption of sodium hydroxide (0.01—0.1N, depending on the concentration of sulphite) during hydrolysis of the sulphites was read on the burette at intervals. From these results the reaction rates were evaluated, it being assumed that, in 1% dioxan, reliable values for the concentration of hydroxide ion could be derived from the pH values.

Throughout these experiments, effects that might arise through locally high concentrations of added alkali were avoided by rapid stirring and by ensuring that the overall rate of reaction was not too fast. It was established that change in the concentration of alkali added to keep the pH constant, change in rate of stirring, and change in the concentration of added sulphite did not affect the measured rate-coefficients. In practice, the main source of spread in the second-order rate-coefficients was found to be due to errors in the pH reading. Fluctuations during the reaction, and deviations found on recalibration of the instrument after reaction, amounted together to about ±0.02 unit. This implies that there is an uncertainty of about ±5% in the concentration of hydroxide ion.

The method by which the rate coefficients were derived from the experimental data differed according to the pH at which the measurements had been made and the acidic dissociation constants of the products of reaction. Ethylene sulphite, for which measurements in a rather similar solvent had already been made<sup>2</sup> by conventional techniques, was first examined. The rate of hydrolysis of this compound was determined at a number of pH values over the range 8.58—9.36. First-order rate-coefficients were calculated from the equation:

$$\ln (v_{\infty} - v_t) = -kt + \text{Constant}, \quad (1)$$

\* With a more aqueous solvent it was difficult to ensure sufficiently rapid dissolution of all the sulphites. With a less aqueous solvent, the interpretation of the pH values would have been less certain.

where  $v_t$  is the volume of base added at time  $t$  and  $v_\infty$  is the infinity value, *i.e.*, the amount of titrant added on complete hydrolysis of the sulphite sample.

The following is a description of typical procedure. A sample of ethylene sulphite (*ca.* 20 mg.) was hydrolysed at pH 9.29. The volume ( $v_t$ ) of alkali (*ca.* 0.1N) consumed was recorded at intervals. The infinity value was found by a separate titration of an identical sample at pH 11.0 where hydrolysis was complete within a few minutes. This value (2.53 ml.) was slightly corrected, since the second dissociation constant,  $pK_2$ , of sulphurous acid is 7.2, to allow for the fact that at pH 9.29 somewhat less than two g.-equiv. of alkali will be titrated on hydrolysis of one mole of sulphite. A further correction was necessary to allow for the effect of dilution on the pH. The following results were obtained:

|                             |       |       |       |       |       |       |       |          |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|----------|
| Time (min.)                 | 0.75  | 1.50  | 3.00  | 4.50  | 6.00  | 7.50  | 10.00 | $\infty$ |
| $v_t$ (ml. of NaOH)         | 0.29  | 0.55  | 0.96  | 1.29  | 1.56  | 1.77  | 2.02  | 2.50     |
| $k_1$ (min. <sup>-1</sup> ) | 0.165 | 0.166 | 0.162 | 0.161 | 0.163 | 0.164 | 0.165 | —        |

Mean  $k_1 = 0.163$ ; from graph,  $k_1 = 0.165 \text{ min.}^{-1}$ .

The values for ethylene sulphite obtained in this way [procedure (a)], by using either the experimental or the calculated infinity value, are given in Table 1, together with second-order rate-coefficients,  $k_2^* = k_1/[\text{OH}^-]$  (l. mole<sup>-1</sup> min.<sup>-1</sup>), calculated from the pH values. The activity coefficient,  $f_{\text{OH}^-}$ , of the hydroxide ion was generally taken as unity; but for the measurements in 0.1M-potassium chloride a value of 0.766 was adopted; for runs in solutions with added inorganic sulphite, an approximate value was derived from the expression  $\log_{10} f_{\text{OH}^-} = -0.5 \sqrt{\mu}$  where  $\mu$  is the ionic strength.

For some measurements on some of the other sulphites, the value of  $pK_a$  for one or more of the products of hydrolysis was close to the pH chosen for examination. In these circumstances the infinity value would be subject to a large correction, and so Guggenheim's method <sup>7</sup>

TABLE 1.

Hydrolysis of ethylene sulphite.

|  |        |        |        |        |        |        |        |        |        |        |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| pH   | 8.58   | 9.09 † | 9.09   | 9.12 † | 9.19   | 9.25   | 9.29   | 9.30   | 9.31   | 9.36   |
| $k_1$ (min. <sup>-1</sup> )                              | 0.035  | 0.100  | 0.102  | 0.125  | 0.114  | 0.153  | 0.165  | 0.135  | 0.162  | 0.176  |
| $10^{-6}k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) | 0.0090 | 0.0080 | 0.0082 | 0.0080 | 0.0074 | 0.0087 | 0.0083 | 0.0067 | 0.0079 | 0.0077 |

† With 0.01M-Na<sub>2</sub>SO<sub>3</sub> and NaCl:  $f_{\text{OH}^-} = 0.85$ ; mean  $k_2 = 0.0080 \times 10^6 \text{ l. mole}^{-1} \text{ min.}^{-1}$ .

[procedure (b)] was preferred for the evaluation of rate-coefficients. Each burette reading,  $v_t$  at time  $t$ , was paired with a reading  $v'_t$  at time  $t + \delta$ , where  $\delta$  is a constant interval equal to 1–2 half-lives of the reaction. First-order rate-coefficients followed then from the expression

$$\ln (v'_t - v_t) = k_1 t + \text{Constant.} \quad (2)$$

The following is an example of the method, applied to diphenyl sulphite:

|                          |       |       |       |       |       |       |       |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| $t$ (min.)               | 1.00  | 2.00  | 4.00  | 6.00  | 8.00  | 10.00 | 12.00 |
| $v_t$ (ml.)              | 0.12  | 0.22  | 0.48  | 0.60  | 0.73  | 0.88  | 1.02  |
| $v'_t$ (ml.)             | 2.16  | 2.22  | 2.24  | 2.30  | 2.35  | 2.41  | 2.46  |
| $\log_{10} (v'_t - v_t)$ | 1.310 | 1.301 | 1.246 | 1.230 | 1.210 | 1.185 | 1.158 |
| $t$ (min.)               | 14.00 | 16.00 | 18.00 | 20.00 | 22.00 | 24.00 |       |
| $v_t$ (ml.)              | 1.15  | 1.27  | 1.39  | 1.50  | 1.61  | 1.68  |       |
| $v'_t$ (ml.)             | 2.51  | 2.56  | 2.61  | 2.65  | 2.69  | 2.71  |       |
| $\log_{10} (v'_t - v_t)$ | 1.134 | 1.111 | 1.086 | 1.061 | 1.033 | 1.021 |       |

From the graph,  $k_1 = 0.0282 \text{ min.}^{-1}$ .

Other values for diphenyl sulphite are given in Table 2; they were derived by procedure (b), except for the measurements at pH 5.51 and 5.94 for which the calculated infinity value [procedure (a)] was used.

<sup>7</sup> Guggenheim, *Phil. Mag.*, 1926, 2, 538.

2,2'-Biphenylene sulphite was investigated in the pH range 5.04—7.65 (Table 3). Except for three runs at low pH, for which procedure (a), based on infinity titrations at pH 8.6,\* was used, all evaluations were carried out by procedure (b).

1,8-Naphthylene sulphite was investigated in the pH range 4.33—6.37 (Table 4). Procedure (b) was applied, except for measurements below pH 5.3, for which procedure (a), with an infinity value determined by a titration at pH 9.2, was used. This titration gave approximately three times the value for  $v_\infty$  applicable to the kinetic measurements, since one mole of this sulphite, when hydrolysed at this pH, liberates two equivalents of sulphurous acid and one equivalent of 1,8-dihydroxynaphthalene which is titrated as a monobasic acid of  $pK_a$  6.58.

*o*-Phenylene sulphite was investigated in the pH range 2.55—3.82 (Table 5). Method (b)

TABLE 2.

| Hydrolysis of diphenyl sulphite.  |        |        |        |        |        |       |
|---|--------|--------|--------|--------|--------|-------|
| pH .....  | 5.51   | 5.94   | 6.38   | 6.73   | 6.82   | 6.96  |
| $k_1$ (min. <sup>-1</sup> ) .....                                       | 0.0057 | 0.0152 | 0.0282 | 0.0686 | 0.0820 | 0.138 |
| $10^{-6}k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) ...            | 1.75   | 1.80   | 1.17   | 1.22   | 1.22   | 1.50  |
| pH .....  | 7.09   | 7.23   | 7.39   | 7.33   | 7.48   | 7.64  |
| $k_1$ (min. <sup>-1</sup> ) .....                                       | 0.193  | 0.200  | 0.255  | 0.258  | 0.383  | 0.500 |
| $10^{-6}k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) ...            | 1.55   | 1.16   | 1.04   | 1.23   | 1.26   | 1.14  |
| Mean $k_2 = 1.3 \times 10^6$ l. mole <sup>-1</sup> min. <sup>-1</sup> . |        |        |        |        |        |       |

TABLE 3.

| Hydrolysis of 2,2'-biphenylene sulphite.                                |        |        |       |       |       |       |       |       |       |       |      |
|---|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| pH .....  | 5.04   | 5.52   | 5.69  | 6.07  | 6.34  | 6.51  | 6.70  | 6.94  | 7.07  | 7.32  | 7.65 |
| $k_1$ (min. <sup>-1</sup> ) .....                                       | 0.0034 | 0.0096 | 0.017 | 0.037 | 0.053 | 0.107 | 0.135 | 0.288 | 0.300 | 0.455 | 1.20 |
| $10^{-6}k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> ) ...            | 3.06   | 2.9    | 3.4   | 3.1   | 2.4   | 3.3   | 2.7   | 3.4   | 2.5   | 2.2   | 2.6  |
| Mean $k_2 = 2.9 \times 10^6$ l. mole <sup>-1</sup> min. <sup>-1</sup> . |        |        |       |       |       |       |       |       |       |       |      |

TABLE 4.

| Hydrolysis of 1,8-naphthylene sulphite.                                  |        |        |        |        |        |       |       |       |       |
|--|--------|--------|--------|--------|--------|-------|-------|-------|-------|
| pH .....   | 4.33   | 4.64   | 4.95   | 5.24   | 5.29   | 5.62  | 5.92  | 6.22  | 6.37  |
| $k_1$ (min. <sup>-1</sup> ) .....  | 0.0040 | 0.0073 | 0.0192 | 0.0273 | 0.0302 | 0.057 | 0.115 | 0.240 | 0.403 |
| $10^{-6}k_2$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )                 | 17.7   | 16.6   | 20.9   | 15.7   | 15.3   | 13.6  | 13.7  | 14.3  | 17.2  |
| Mean $k_2 = 16.0 \times 10^6$ l. mole <sup>-1</sup> min. <sup>-1</sup> . |        |        |        |        |        |       |       |       |       |

was used for measurements below pH 3.0; for the remainder, method (a) was used, with an infinity value determined by titrating at pH 5.2. The hydrolysis of this compound was complicated by (i) a relatively high rate of reaction in neutral solution, and (ii) autocatalysis by the products of hydrolysis. Results were calculated as initial rates, based on calculated infinity values. The following is an example of a typical kinetic run, with 0.1M-potassium chloride and 0.040M-sodium hydrogen sulphite.

|  |     |      |      |      |      |      |      |          |
|--|-----|------|------|------|------|------|------|----------|
| $t$ (min.) .....   | 0   | 0.42 | 1.08 | 1.58 | 2.08 | 2.75 | 3.42 | $\infty$ |
| $v_t$ (ml. of NaOH) .....  | 0.0 | 0.58 | 1.23 | 1.67 | 1.93 | 2.20 | 2.41 | 2.88     |
| $k_1$ (min. <sup>-1</sup> ) .....  | —   | 0.54 | 0.52 | 0.55 | 0.53 | 0.53 | 0.53 | —        |
| Mean $k_1 = 0.53$ min. <sup>-1</sup> ; from graph, $k_1 = 0.54$ min. <sup>-1</sup> . |     |      |      |      |      |      |      |          |

Fig. 1 shows that there is a linear dependence of the initial rate on the concentration of hydroxide ion. The intercept ( $k_{H_2O} = 0.15$  min.<sup>-1</sup>) represents the neutral rate; and from the slope, the rate of the alkali-catalysed reaction is  $k_2 = 2 \times 10^9$  l. mole<sup>-1</sup> min.<sup>-1</sup>. Table 5 shows that neither neutral nor alkaline rates were influenced by the presence of 0.01M-ammonium thiocyanate or 0.1M-potassium chloride, the reduced activity coefficient of the hydroxide ion in these solutions being taken into account.

In view of the autocatalysis, the reaction was studied in solutions which had been prepared

\* At this pH the correction for incomplete dissociation of sulphurous acid is approximately compensated by that for the increase in the dissociation of 2,2'-dihydroxybiphenyl, two equivalents of acid being titrated.

by adding sodium sulphite and then hydrochloric acid to attain the desired pH. In the pH region investigated, the mixtures then contained equivalent amounts (in the range  $1-6 \times 10^{-3}M$ ) of bisulphite ions and chloride ions, with only small amounts of sulphite ions. The concentration of *o*-phenylene sulphite was varied over the range  $0.5-1 \times 10^{-3}M$ . First-order rate-coefficients at a large number of pH values were obtained from the logarithmic plots of liberated acid against time. For those runs where the amount of bisulphite ions liberated during hydrolysis added considerably to the concentration already present at the start, only the initial rate was taken.

In Fig. 2, the values of the second-order rate-coefficients are plotted as a function of bisulphite ion concentration. It is seen that the overall rate,  $k_{obs}$ , is satisfactorily represented by equation (3):

$$k_{obs} = k_{H_2O} + k_2[OH^-] + k_{auto}[OH^-][HSO_3^-], \quad (3)$$

where  $k_2 = 2 \times 10^9 \text{ l. mole}^{-1} \text{ min.}^{-1}$ ,  $k_{H_2O} = 0.15 \text{ min.}^{-1}$ , and  $k_{auto} = 1.4 \times 10^{12} \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$ .

The autocatalysed reaction was satisfactorily represented by these values.

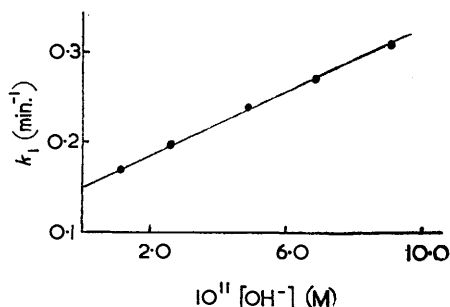


FIG. 1. Hydrolysis of *o*-phenylene sulphite.

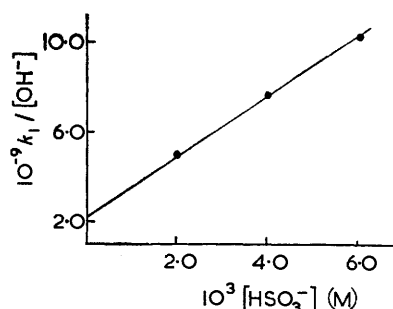


FIG. 2. Hydrolysis of *o*-phenylene sulphite with added sodium hydrogen sulphite.

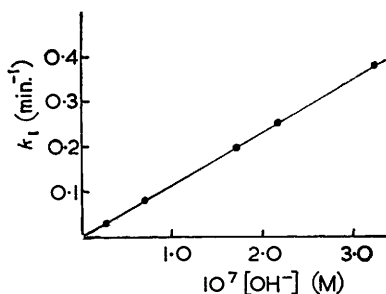
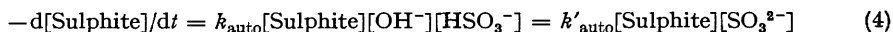


FIG. 3. Hydrolysis of diphenyl sulphite.

The rates of hydrolysis of *o*-phenylene sulphite were determined also at  $15.0^\circ$  and at  $0.4^\circ$ . The appropriate coefficients of equation (3) were evaluated as previously described. The activity coefficients of the hydroxide ion were evaluated by Larsson's method.<sup>8</sup> Allowance was made for the variation with temperature of the ionic product of water, and in calculating the infinity values the variation in the first dissociation constant of sulphurous acid with temperature was also taken into account. The results are summarised in Table 6.

Values of  $k'_{auto}$  included in this Table involve the assumption that the autocatalysis can be represented by a kinetic term of the form  $k'_{auto}[\text{Sulphite}][\text{SO}_3^{2-}]$ , *i.e.*, the kinetic form of the autocatalysis reaction involved is:



<sup>8</sup> Larsson, *Acta Chem. Scand.*, 1957, **11**, 1131.

TABLE 5.

Hydrolysis of *o*-phenylene sulphite.

(a) Without added sodium hydrogen sulphite.

| pH   | $f_{OH^-}$ | $10^{11}[OH^-]$<br>(M) | $k_1$<br>(min. <sup>-1</sup> ) | pH   | $f_{OH^-}$ | $10^{11}[OH^-]$<br>(M) | $k_1$<br>(min. <sup>-1</sup> ) |
|------|------------|------------------------|--------------------------------|------|------------|------------------------|--------------------------------|
| 3.82 | 0.766      | 8.8                    | 0.31 *                         | 3.27 | 0.766      | 2.5                    | 0.20 *                         |
| 3.79 | 0.89       | 7.1                    | 0.28 †                         | 2.99 | 0.96       | 1.1                    | 0.17 †                         |
| 3.72 | 0.766      | 6.9                    | 0.27 *                         | 2.76 | 0.95       | 0.62                   | 0.17 †                         |
| 3.73 | 0.766      | 7.3                    | 0.25 *                         | 2.76 | 0.95       | 0.62                   | 0.16 †                         |
| 3.73 | 0.766      | 7.3                    | 0.28 *                         | 2.75 | 0.89       | 0.63                   | 0.16 †                         |
| 3.72 | 0.766      | 6.9                    | 0.28 *                         | 2.60 | 0.94       | 0.43                   | 0.14 †                         |
| 3.57 | 0.766      | 4.9                    | 0.24 *                         | 2.55 | 0.766      | 0.47                   | 0.15 *                         |

\* With 0.1M-KCl. † With 0.01M-NH<sub>4</sub>CNS. ‡ No salts added.

(b) With added sodium hydrogensulphite.

| $10^8[NaHSO_3]$<br>(M) | pH   | $f_{OH^-}$ | $10^{11}[OH^-]$<br>(M) | $k_1$<br>(min. <sup>-1</sup> ) | $10^8[NaHSO_3]$<br>(M) | pH   | $f_{OH^-}$ | $10^{11}[OH^-]$<br>(M) | $k_1$<br>(min. <sup>-1</sup> ) |
|------------------------|------|------------|------------------------|--------------------------------|------------------------|------|------------|------------------------|--------------------------------|
| 1.00                   | 3.91 | 0.94       | 9.0                    | 0.45                           | 4.00                   | 3.68 | 0.90       | 5.3                    | 0.61                           |
| 1.00                   | 3.84 | 0.94       | 7.7                    | 0.41                           | 4.00                   | 3.64 | 0.90       | 4.9                    | 0.50                           |
| 1.00                   | 3.82 | 0.94       | 7.2                    | 0.41                           | 4.00                   | 3.59 | 0.90       | 4.3                    | 0.50                           |
| 1.00                   | 3.74 | 0.94       | 6.0                    | 0.36                           | 4.00                   | 3.58 | 0.90       | 4.3                    | 0.49                           |
| 1.00                   | 3.58 | 0.94       | 4.1                    | 0.30                           | 4.00                   | 3.58 | 0.90       | 4.3                    | 0.51                           |
| 1.00                   | 3.45 | 0.94       | 3.1                    | 0.25                           | 4.00                   | 3.58 | 0.766      | 5.1                    | 0.54 *                         |
| 2.00                   | 3.90 | 0.92       | 8.5                    | 0.60                           | 4.00                   | 3.48 | 0.766      | 4.0                    | 0.46 *                         |
| 2.00                   | 3.83 | 0.92       | 7.3                    | 0.55                           | 4.00                   | 3.47 | 0.90       | 3.3                    | 0.39                           |
| 2.00                   | 3.75 | 0.92       | 6.1                    | 0.46                           | 4.00                   | 3.33 | 0.90       | 2.4                    | 0.34                           |
| 2.00                   | 3.63 | 0.92       | 4.9                    | 0.39                           | 4.00                   | 3.30 | 0.766      | 2.6                    | 0.39 *                         |
| 2.00                   | 3.54 | 0.92       | 3.8                    | 0.34                           | 4.00                   | 3.20 | 0.766      | 2.1                    | 0.36 *                         |
| 2.00                   | 3.31 | 0.92       | 2.2                    | 0.24                           | 6.00                   | 3.57 | 0.88       | 4.2                    | 0.61 †                         |
| 4.00                   | 3.72 | 0.92       | 5.8                    | 0.58                           | 6.00                   | 3.46 | 0.88       | 3.3                    | 0.48                           |

\* With 0.1M-KCl. †  $f_{OH^-}$  approximated from  $-\log_{10} f_{OH^-} = 0.51\sqrt{\mu}$ .

(c) At 15° in 0.1M-KCl.

| pH     | $f_{OH^-}$ | $10^{11}[OH^-]$<br>(M) | $k_1$<br>(min. <sup>-1</sup> ) |
|--------|------------|------------------------|--------------------------------|
| 2.96   | 0.765      | 0.54                   | 0.08                           |
| 3.91   | 0.765      | 4.90                   | 0.14                           |
| 3.59   | 0.765      | 2.26                   | 0.11                           |
| 3.40   | 0.765      | 1.46                   | 0.093                          |
| 3.76   | 0.765      | 3.46                   | 0.123                          |
| 3.62 * | 0.765      | 2.46                   | 0.173                          |

(d) At 0.4° in 0.1M-KCl.

| pH      | $f_{OH^-}$ | $10^{11}[OH^-]$<br>(M) | $k_1$<br>(min. <sup>-1</sup> ) |
|---------|------------|------------------------|--------------------------------|
| 3.14    | 0.770      | 0.21                   | 0.018                          |
| 3.96    | 0.770      | 1.42                   | 0.030                          |
| 4.50    | 0.770      | 4.87                   | 0.064                          |
| 4.98    | 0.770      | 14.1                   | 0.175                          |
| 4.75    | 0.770      | 8.66                   | 0.105                          |
| 4.90 †  | 0.98       | 9.42                   | 0.125                          |
| 4.36 †† | 0.93       | 2.93                   | 0.127                          |

\* With added NaHSO<sub>3</sub> (0.002M). † Without KCl. ‡ With added NaHSO<sub>3</sub> (0.002M).

TABLE 6.

Temperature-coefficients and Arrhenius parameters \* for hydrolysis of *o*-phenylene sulphite.

| Temperature                             | $k_{H_2O}$<br>(min. <sup>-1</sup> ) | $10^{-9}k_2^{OH^-}$<br>(l. mole <sup>-1</sup> min. <sup>-1</sup> ) | $10^{-12}k_{auto}$<br>(l. <sup>2</sup> mole <sup>-2</sup> min. <sup>-1</sup> ) | $10^{-5}k'_{auto}$<br>(l. mole <sup>-1</sup> min. <sup>-1</sup> ) † |
|---|-------------------------------------|--|--|---|
| 0.4°                                    | 0.014                               | 1.1  | 1.44   | 0.05  |
| 15.0                                    | 0.073                               | 1.4  | 1.30   | 0.49  |
| 25.0                                    | 0.15                                | 2.0  | 1.60   | 2.6   |
| $E_a$ * (kcal. mole <sup>-1</sup> ) ... | 15.7                                | 4.5  | —  | —   |
| $\log_{10} B$ * .....                   | 8.94                                | 12.6   | —  | —   |

\* Calculated by using the equation  $k = B \exp(-E/RT)$ . The values of the ionic product of water used were 1.01, 0.45, and  $0.12 \times 10^{-14}$  at 25°, 15°, and 0.4°, respectively.<sup>9</sup>

† The second dissociation constant of sulphurous acid at various temperatures was calculated from the values <sup>10, 11</sup> at 25° and 18°, it being assumed that there is an Arrhenius type of variation. The values used were 6.24, 12.2, and  $35.9 \times 10^{-8}$  at 25°, 15°, and 0.4°, respectively.

<sup>9</sup> Harned and Robinson, *Trans. Faraday Soc.*, 1941, **37**, 971.

<sup>10</sup> Tarter and Garretson, *J. Amer. Chem. Soc.*, 1941, **63**, 808.

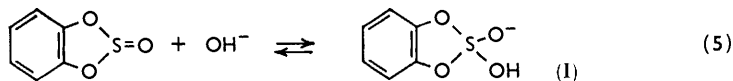
<sup>11</sup> Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531.

## DISCUSSION

1,8-Naphthylene sulphite (Table 4), 2,2'-biphenylene sulphite (Table 3), and diphenyl sulphite (Table 2) were investigated in the pH regions 4.3—6.4, 5.0—7.7, and 5.5—7.7, respectively. When the logarithms of the first-order rate-coefficients are plotted against pH, straight lines of approximately unit slope are obtained. Similarly, if first-order rate-coefficients are plotted against concentrations of hydroxide ion derived from pH values, straight lines are obtained, passing through the origin (*e.g.*, Fig. 3). These results imply that the reaction rates can be expressed by the equation:  $k_{\text{obs}} = k_2[\text{OH}^-]$ . In these regions of pH the rate is proportional to the concentration of hydroxide ion; the neutral rate (*i.e.*, the rate of reaction with water molecules) is negligible.\* No autocatalysis was obtained for any of these compounds; and the presence of inorganic sulphite in amount five times the concentration arising from the hydrolysing samples had no significant effect on the rate of reaction.

*o*-Phenylene sulphite, alone of the compounds studied, had a rate of reaction with water significant in comparison with the hydroxide-catalysed reaction in the pH range that we studied. It was also unique in that autocatalysis by bisulphite ions was important. Other anions (*e.g.*, chloride, thiocyanate) had no significant effect.

The autocatalysis did not seriously interfere with determination of the rate of alkaline hydrolysis. The kinetic form of the reaction involved is indicated in equation (4). It is clear that S—O fission will be observed with all these compounds; and by analogy with the effect of added nucleophiles on the rate of acid-catalysed hydrolysis, it appears reasonable to suppose that autocatalysis arises through attack by sulphite ions,  $\text{SO}_3^{2-}$ , on the organic sulphite to form an unstable species which rapidly undergoes further reaction. If this is so, the rate-coefficient can be calculated to be  $k'_{\text{auto}} = 2.6 \times 10^5 \text{ l. mole}^{-1} \text{ min.}^{-1}$  when allowance is made for the equilibrium constant ( $K'_a = 6.24 \times 10^{-8}$ ) for the second dissociation of sulphurous acid. The reactivity with hydroxide ions ( $k_2^{\text{OH}^-} = 2 \times 10^9 \text{ l. mole}^{-1} \text{ min.}^{-1}$ ) is greater, but the corresponding value for anions such as chloride and thiocyanate must be very much smaller, and we have no explanation for the apparently very great nucleophilic power of the sulphite ion.



It is possible that in this system there is a build-up of the intermediate (I). This intermediate may then react with bisulphite ion leading to a sequence of reactions which give the products of hydrolysis. This does not help to explain the autocatalysis, but it suggests a possible route to the transition state, and one which might be tested by examining the exchange of oxygen between the medium and the S=O group.

We hope to examine the aromatic sulphites in this way, and to repeat the earlier<sup>12</sup> measurements on ethylene sulphite, which we interpreted as failing to show with certainty any incorporation of  $^{18}\text{O}$  into the sulphite by exchange with solvent in the course of partial hydrolysis. Davis<sup>13</sup> has recently interpreted our results as indicating significant exchange, but we do not think that this can be regarded as established by our experiments.

The variation with temperature in rate of alkaline hydrolysis of *o*-phenylene sulphite shows no particularly abnormal feature. The reaction is very rapid, the rates having been determined with the nucleophile in concentration of the order of  $10^{-11}\text{M}$ ; and in accordance with this the Arrhenius energy of activation is *ca.* 5 kcal. mole<sup>-1</sup>. This result is subject to a little uncertainty (probably about  $\pm 0.5$  kcal. mole<sup>-1</sup>) since the rate of neutral hydrolysis

\* This was confirmed for naphthylene sulphite by measurements at 100° in 60% dioxan. By iodometric titrations of liberated sulphite (sealed tube technique), a low neutral rate,  $2.5 \times 10^{-3} \text{ min.}^{-1}$  was established.

<sup>12</sup> Bunton, de la Mare, Greaseley, Llewellyn, Pratt, and Tillet, *J.*, 1958, 4751.

<sup>13</sup> Davis, *J. Amer. Chem. Soc.*, 1962, **84**, 599.

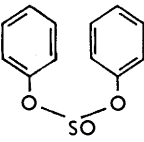
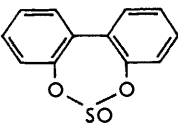
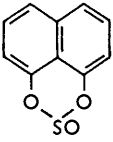
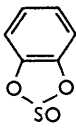
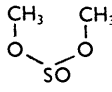
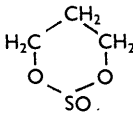
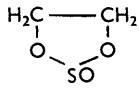
and the rate of the autocatalysed reaction have both to be allowed for. The value is consistent with the simplest mechanism which accords with the kinetic behaviour, namely, that hydroxide ion is involved in nucleophilic attack on sulphur; and it does not help to confirm or eliminate the possibility (reaction 5) that the attack is a two-stage process with the first stage reversible.

It is interesting that a compound, the reaction of which with nucleophile derived from water is so great, should be relatively stable in the sense that it is easily isolated, purified, and stored. Unlike the aliphatic sulphites which are easily soluble in water, aromatic sulphites seem to dissolve only to a very limited extent, and to be virtually non-hygroscopic.

*Structural Effects.*—In Table 7 are given the relative rates of hydrolysis of the sulphites with which this work is concerned. Our results for ethylene sulphite and dimethyl sulphite

TABLE 7.

Rates  $k_2$  (l. mole<sup>-1</sup> min.<sup>-1</sup>) of alkaline hydrolysis of organic sulphites in aqueous (1%) dioxan solution at 25°.

|   |   |  |  |
|---|---|--|--|
|  |  |   |  |
| (II)  | (III)   | (IV)   | (V)  |
| $10^{-6}k_2$  | 1.3   | 2.9  | 16   |
|  |  |  |  |
| (VI)  | (VII)   | (VIII)   |  |
| $10^{-6}k_2$  | 0.000010  | 0.000030   | 0.0080   |

differ slightly from those of Davis.<sup>13</sup> We are unable to explain this discrepancy, although it does not affect the general order of reactivity. For the aliphatic sulphites, it has been established that the reaction involves nucleophilic attack on sulphur, and that the second stage of hydrolysis (involving a second attack on sulphur to liberate sulphur dioxide as inorganic sulphite) follows rapidly on the first. It is assumed that the mechanism adopted by the aromatic sulphites is essentially similar. For these compounds must react by S-O bond fission; and (i) if the rates of the two stages of hydrolysis had been similar, a disturbance in the kinetic form of hydrolysis would have been observed when rate-coefficients were calculated on the basis of the liberation of a molecule of sulphur dioxide for each molecule of hydroxide ion attacking the organic compound; (ii) if the first stage of hydrolysis had been very rapid and was followed by slow decomposition of the half-hydrolysed ester, a sudden change in pH would have been observed when the compounds were dissolved in the reaction solution. Neither of these phenomena was observed. So the ring-opening is the first rate-determining step, and the differences in measured rate represent differences in ease of attack on sulphur.

Comparing the various ring systems in the two series, we find that 2,2'-biphenylene sulphite (III) and trimethylene sulphite (VII) are only about three times more reactive than their open-chain analogues (II) and (VI). In both systems the molecules can adjust by internal rotation to the geometrical requirements of the sulphite group. For 1,8-naphthylene sulphite (IV), in which the oxygen atoms are held in a much more rigid position, reactivity is increased by a further factor of five. The two five-membered-ring

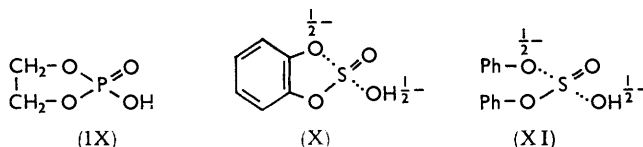


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molecules, *o*-phenylene sulphite (V) and ethylene sulphite (VIII), show reactivities with alkali about  $10^3$  times greater than diphenyl sulphite and dimethyl sulphite, respectively.

Examination of the cyclic di-esters of phosphoric acid has shown that ethylene phosphate (IX) is much more labile with alkali than its open-chain analogues; and that this high reactivity involves P-O fission and is associated with a high heat of hydrolysis.<sup>14</sup> It has been suggested that the internal strain revealed in this way results from interaction between the polar P-O bonds and the lone pair of electrons on phosphorus (cf. ref. 14).

The situation in the sulphites is at first sight analogous, in that high reactivity with alkali seems to be associated with rigidity of the ring, and especially with the geometrical situation to which the sulphite group is constrained in *o*-phenylene sulphite (V). Measurements of the heat of hydrolysis,<sup>1</sup> however, show that the difference in reactivity between diphenyl sulphite (II) and *o*-phenylene sulphite (V) is not determined by strain in the initial state. Davis<sup>13</sup> has reached a similar conclusion for ethylene sulphite and dimethyl sulphite. It seems that the transition state (X) for attack on sulphur in *o*-phenylene sulphite is particularly favoured relative to that for attack on diphenyl sulphite (XI).



It must be presumed that, for four-covalent sulphur with twelve electrons in the valency shell (which can be presumed to be the electronic arrangement in the transition state for attack by a nucleophile on a sulphite), the geometry imposed by the *o*-phenylene system is more favourable for S-O bond-breaking than that in its less strained analogues; but that differential ring-strain is not similarly introduced for the electronic situation in the sulphite itself, namely, molecules having three-covalent sulphur with ten electrons in the valency shell.

*Neutral Hydrolysis.*—The high reactivity of *o*-phenylene sulphite in alkaline hydrolysis is maintained in its reaction with other nucleophiles; its rate of neutral hydrolysis ( $k_{H,O}$ ) at 25° is 0.15 min.<sup>-1</sup>, the activation energy is 16 kcal. mole<sup>-1</sup>, and the non-exponential term in the Arrhenius equation, calculated on the basis that water and the sulphite are concerned in a bimolecular reaction, is  $B = 8.9 \times 10^8$  l. mole<sup>-1</sup> min.<sup>-1</sup>, a value which is not inconsistent with this interpretation.

We are indebted to Dr. C. A. Bunton for unpublished observations on diphenyl sulphite and to Dr. D. M. Hall for a sample of 2,2'-biphenylene sulphite. We also thank the Netherlands Organisation for the Advancement of Pure Research (Z.W.O.) for the award of a NATO Fellowship to H. F. van W., and Mr. R. Mitchell for technical assistance.

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<sup>14</sup> Westheimer, *Chem. Soc. Special Publ.* No. 8, 1957, 1; Kumamoto, Cox, and Westheimer, *J. Amer. Chem. Soc.*, 1956, **78**, 4858.