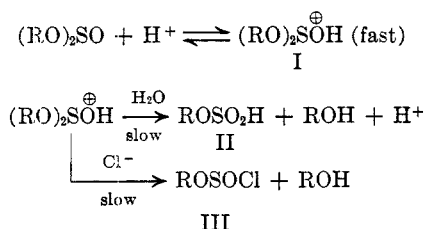# The Hydrolysis of Aryl Sulfites[1,2]

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Aqueous perchloric and sulfuric acid retard the hydrolysis of *o*-phenylene sulfite, because their negative salt effect overcomes a feeble acid catalysis. Hydrochloric acid at first retards hydrolysis, but at higher concentration speeds it, and the chloride ion is a specific nucleophilic catalyst for the acid hydrolysis. The spontaneous hydrolysis of diphenyl sulfite is relatively slow, but perchloric, sulfuric, and especially hydrochloric acid are catalysts at all concentrations. Most uniunivalent salts retard the hydrolysis of *o*-phenylene sulfite in water, but sulfates assist it. However, fluoride ion is a very effective catalyst, and apparently forms an intermediate with the sulfite ester. It does not catalyze the hydrolysis of diethyl sulfite, although this reaction is catalyzed by hydrogen fluoride.

The mechanism of the acid-catalyzed hydrolysis of dialkyl sulfites is well understood.[3-5] It falls into the A2 mechanistic category,[6] and the rate-limiting step of the reaction involves nucleophilic attack by water or a halide ion upon the conjugate acid (I) of the sulfite to give intermediates II and III, which decompose rapidly to products.

$$(RO)_2SO + H^+ \rightleftharpoons (RO)_2\overset{\oplus}{S}OH \text{ (fast)}$$
$$I$$

$$(RO)_2\overset{\oplus}{S}OH \xrightarrow[\text{slow}]{H_2O} ROSO_2H + ROH + H^+$$
$$II$$
$$\xrightarrow[\text{slow}]{Cl^-} ROSOCl + ROH$$
$$III$$

The position of the proton in I is not known; another reasonable structure for I involves protonation of the alkyl oxygen atom. Nucleophilic attack upon I could involve either prior addition or displacement, but isotopic exchange experiments give no evidence for a prior addition.[7]

Saturated cyclic and open-chain sulfites have similar reactivities in acid hydrolysis,[4] but Tillett made the very important observation that the behavior of *o*-phenylene sulfite (IV) was completely different from that of the alkyl sulfites.[5] He used aqueous dioxane as solvent and found that the spontaneous hydrolysis was unusually fast, but that perchloric and *p*-toluenesulfonic acid in low concentration slightly catalyzed the hydrolysis, but in high concentration retarded it. With sulfuric acid the rate increased to a maximum in 3 M acid and then decreased, and hydrochloric acid was a catalyst at all concentrations. It was found that lithium chloride, bromide, and perchlorate retarded the spontaneous hydrolysis, and therefore it was suggested that this unexpected kinetic form was the result of an acid catalysis superposed upon a negative salt effect of the electrolyte.

Aryl sulfites are more reactive than the cyclic or open-chain alkyl sulfites in initially neutral solution.[8] (An earlier report of their unreactivity arose because account had not been taken of their low solubility in water or aqueous alkali.[9]) However, there was no information on the acid hydrolysis of diphenyl sulfite, and we therefore examined this reaction in both aqueous dioxane and water, using low concentrations of ester. The kinetic form of hydrolysis was similar to that found for the saturated sulfites in that its spontaneous hydrolysis was very slow, but sulfuric and perchloric acids were catalysts, and hydrochloric acid was a very effective catalyst. We therefore also examined the hydrolysis of *o*-phenylene sulfite in water and found results broadly similar to those obtained by Tillett for hydrolysis in aqueous dioxane.[5]

## Experimental Section

**Materials.**—Diphenyl and *o*-phenylene sulfite were prepared by reaction between the phenol and purified thionyl chloride, in a pyridine–carbon bisulfide solution.[9,10] Diphenyl sulfite had bp 160° (8 mm), and *o*-phenylene sulfite had bp 90° (8 mm). Diethyl sulfite, prepared by the standard method,[10] had bp 157°. These compounds gave satisfactory analyses for sulfur. Dioxane was purified by standard methods,[11] and the fraction boiling between 100.5 and 101.5° was collected.

The salts were Analytical Reagent grade or were prepared in solution by neutralizing equivalent amounts of acid and base. Kinetic solutions of electrolytes in aqueous dioxane were made up so that the relative amounts of water and dioxane were constant.

**Kinetics.**—The reaction was followed by two methods.

**A.**—The liberated sulfur dioxide was estimated by titration with standard iodine (2–5 mM). Stoppered flasks were used for the faster runs at low temperatures, but sealed tubes were used for the slower runs, and at higher temperatures where loss of sulfur dioxide could be important. Plastic flasks and pipets were used for the experiments with potassium hydrogen fluoride and hydrofluoric acid.

**B.**—Reaction could be followed spectrophotometrically at 2760 A, where the absorption of sulfur dioxide is much higher than that of the esters. A Cary 14 or a PE-Hitachi spectrophotometer with a thermostatically controlled cell holder was used, and the temperature of the cell was checked with a thermocouple. The path length of the cell was 1 cm. The concentration of ester was approximately $10^{-4} M$ for the hydrolyses followed spectrophotometrically, $10^{-3} M$ for the hydrolyses in water followed titrimetrically, and $10^{-2} M$ for the hydrolyses in aqueous dioxane followed titrimetrically.

(3) H. F. van Woerden, *Chem. Rev.*, **63**, 557 (1963).

(4) C. A. Bunton, P. B. D. de la Mare, and J. G. Tillett, *J. Chem. Soc.*, 4754 (1958); C. A. Bunton, P. B. D. de la Mare, A. Lennard, D. R. Llewellyn, R. B. Pearson, J. G. Pritchard, and J. G. Tillett, *ibid.*, 4761 (1958); C. A. Bunton, P. B. D. de la Mare and J. G. Tillett, *ibid.*, 1766 (1959).

(5) J. G. Tillett, *ibid.*, 5138 (1960).

(6) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIV; (b) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(7) C. A. Bunton, P. B. D. de la Mare, P. M. Greaseley, D. R. Llewellyn, N. H. Pratt, and J. G. Tillett, *J. Chem. Soc.*, 4751 (1958).

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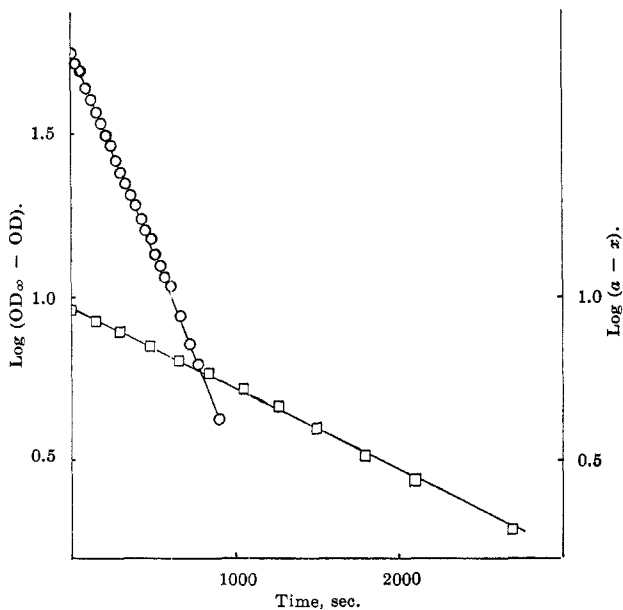
Figure 1.—Plot of log (sulfite) + constant vs. time: O, o-phenylene sulfite in 1.00 $M$ HCl in water at 25.0°, followed spectrophotometrically; and □, diphenyl sulfite in 1.66 $M$ HClO$_4$ in dioxane–water (60:40 v/v) at 25.0°, followed titrimetrically.
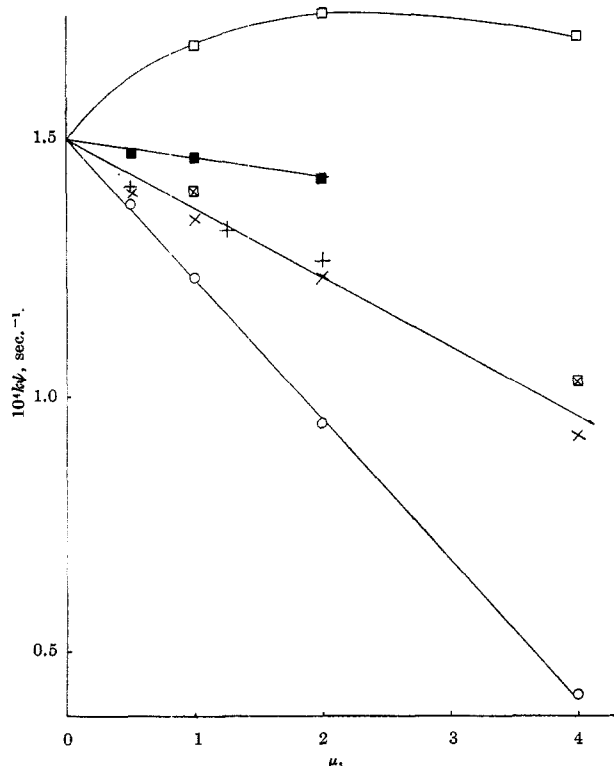


Figure 2.—Salt effects upon the hydrolysis of o-phenylene sulfite in water at 25°: ✕, LiCl; +, NaCl; ⊠, MgCl$_2$; O, LiCl$_4$O; □, Li$_2$SO$_4$; and ■, NaHSO$_4$.



Figure 3.—Hydrolysis of o-phenylene sulfite in aqueous acid at 25.0°: ✕, HCl; □, H$_2$SO$_4$; and O, HClO$_4$.
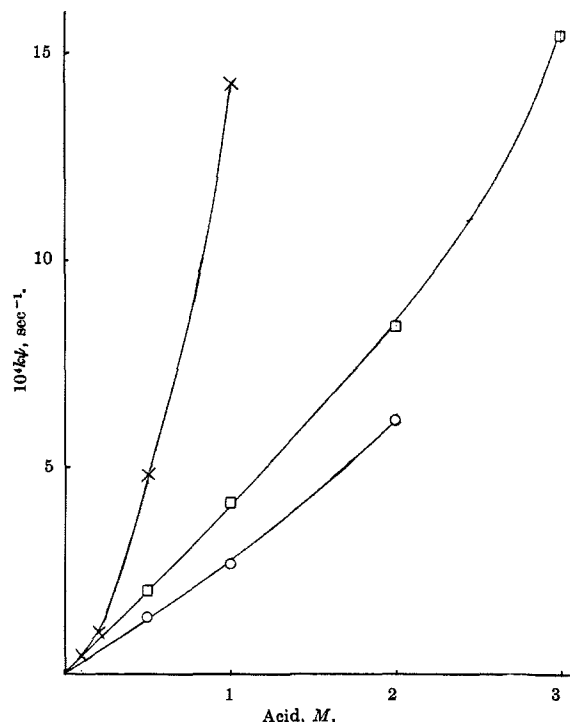


Figure 4.—Hydrolysis of diphenyl sulfite in aqueous acid at 25.0°: ✕, HCl; □, H$_2$SO$_4$; and O, HClO$_4$.

The first-order rate constants, $k_\psi$, were calculated from plots of log $(a - x)$ against time for the runs followed titrimetrically, or log (OD$_\infty$ − OD) against time, for runs followed spectrophotometrically. The concentration of ester at time $t$ is $a - x$ (in arbitrary units), and OD and OD$_\infty$ are the optical densities of the solution at times $t$ and $\infty$. Plots are shown in Figure 1.

The hydrolyses of o-phenylene and diphenyl sulfite were followed both spectrophotometrically and titrimetrically. The hydrolysis of diethyl sulfite was followed titrimetrically only. There is good agreement between the values of $k_\psi$ determined spectrophotometrically and titrimetrically. Our rate constants are not in general directly comparable with those of Tillett,
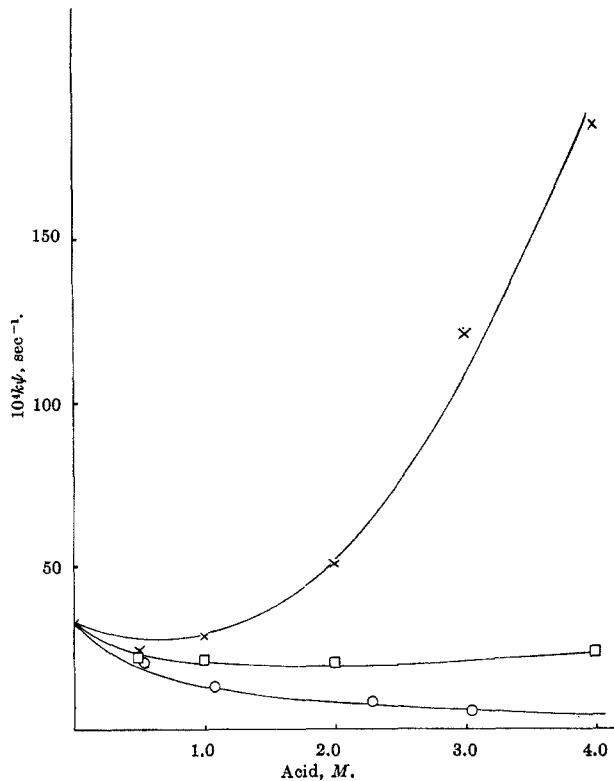
who used aqueous dioxane as solvent,[5] but a value of $25 \times 10^{-4}$ sec$^{-1}$ at 25° is reported for the rate constant for the spontaneous hydrolysis of o-phenylene sulfite in water containing 1% dioxane.[8] This rate constant is slightly smaller than our value for the hydrolysis in water.

## Results

o-**Phenylene sulfite.**—The first-order rate constants, $k_\psi$, for the hydrolysis in aqueous solutions of acids

TABLE I

HYDROLYSIS RATE, $10^4 k_\psi$ (SEC$^{-1}$), OF $o$-PHENYLENE SULFITE IN AQUEOUS MINERAL ACIDS[a]

| | | | 0.50 | 1.00 | 2.00 | 3.00 | 4.00 |
|---|---|---|---|---|---|---|---|
| 32.1 | 33.4 | 33.0[b] | 25.1, 23.8[b] | 28.7 | 50.7 | 122 | 184 |

HClO₄ concn, M

| 0.58 | 1.16 | 2.32 | 3.10 | 6.80 |
|---|---|---|---|---|
| 20.2 | 13.2, 12.8[b] | 8.73 | 5.91 | 3.05 |

H₂SO₄ concn, M

| 0.50 | 1.00 | 2.00 | 4.00 |
|---|---|---|---|
| 22.0, 22.3[b] | 21.5 | 20.4 | 23.1 |

| | 2 M acid, at 35.0° | | | 2 M acid, at 0° | |
|---|---|---|---|---|---|
| ... | HCl | HClO₄ | ... | HCl | HClO₄ |
| 60.4 | 91.2 | 18.3 | 3.51 | 3.32 | 0.88 |

[a] At 25.0°. Reaction followed spectrophotometrically unless specified.    [b] Reaction followed titrimetrically.

TABLE II

HYDROLYSIS OF $o$-PHENYLENE SULFITE[a]

$10^4 k_\psi$ (sec$^{-1}$) in Aqueous Salt Solutions

| Salt | Concentration, M | | | |
|---|---|---|---|---|
| | 0.5 | 1.0 | 2.0 | 4.0 |
| LiCl | 24.2 | 22.1 | 16.9 | 8.24 |
| NaCl | 25.7 | 21.0, 21.3[b] | 18.6 | |
| MgCl₂ | 25.6 | | 10.9 | |
| NaBr | 23.7 | 14.4 | | |
| LiClO₄ | 24.0, 23.8[b] | 17.4 | 9.02 | 2.62 |
| Li₂SO₄ | 48.1 | 56.2 | 50.2 | |
| Na₂SO₄ | 43.8 | | | |
| MgSO₄ | 44.9 | | | |
| NaHSO₄ | 29.9 | 29.7 | 27.0 | |

Fluoride Ion Catalyzed Hydrolysis

| [NaF], M | ... | 0.004 | 0.01 | 0.02 | 0.04 | 0.08 | 0.2 | 0.4 |
|---|---|---|---|---|---|---|---|---|
| $10^4 k_\psi$ sec$^{-1}$ | 32.5 | 80.0 | 129 | 202 | 279 | 306 | 293 | 278 |
| $10^4 k_F$, sec$^{-1}$ | | 47.5 | 96.5 | 169 | 246 | 273 | 260 | 245 |

| In Dioxane–Water (40:60 v/v) | | In Dioxane–Water (60:40 v/v) | | |
|---|---|---|---|---|
| [NaF], M | 0.0054 | ... | 0.005 | 0.01 |
| $10^4 k_\psi$, sec$^{-1}$ | 2.90,[b] 15.4, 15.5[c] | 0.36[d] | 26.2[b,c] | 52.8[b,c] |

[a] Determined spectrophotometrically and at 25.0° unless specified.    [b] At 0°.    [c] Reaction followed titrimetrically.    [d] Reference 5.

TABLE III

ACID HYDROLYSIS, $10^4 k_\psi$ (SEC$^{-1}$), OF DIPHENYL SULFITE IN WATER AND AQUEOUS DIOXANE[a,b]

| Water, vol % | HCl concn, M | | | | |
|---|---|---|---|---|---|
| | 0.1 | 0.2 | 0.3 | 0.5 | 1.0 |
| 100 | 0.43 | 1.00 | ... | 4.83 | 14.1, 14.4[c] |
| 90 | ... | ... | ... | 9.89, 10.1[c] | 19.3 |
| 80 | ... | ... | ... | 17.8[c] | 35.7[c] |
| 60 | 1.96[c] | 4.49[c] | ... | 19.4[c] | ... |
| 40 | 2.12[c] | 5.41[c] | 16.4[c] | | |

| Water, vol % | HClO₄ concn, M | | | H₂SO₄ concn, M | | | |
|---|---|---|---|---|---|---|---|
| | 0.5 | 1.0 | 2.0 | 0.5 | 1.0 | 2.0 | 3.0 |
| 100 | 1.37, 1.41[c] | 2.67 | 6.13 | 2.05 | 4.17 | 8.40 | 15.4 |
| 90 | 1.51[c] | 2.52[c] | 8.13[c] | 1.42[c] | 5.36, 5.31[c] | 8.34 | ... |
| 80 | 1.80, 1.83[c] | 3.02[c] | 8.83[c] | 1.34 | 3.78 | 8.83 | ... |
| 60 | 0.58[c] | 2.30[c] | 8.05, 8.08[c] | 0.82 | 1.84 | ... | ... |
| 40 | 0.59[c] | 2.32[c] | 8.04 | ... | 1.36 | 9.31 | ... |

| Water, vol % | Temp, °C | 0.2 M HCl | 2 M HClO₄ | 2 M H₂SO₄ |
|---|---|---|---|---|
| 40 | 0 | 0.532[c] | 0.691[c] | 0.854[c] |
| 40 | 35.0 | 12.2[c] | 20.2[c] | 23.1[c] |

[a] At 25.0°. Reaction followed spectrophotometrically unless specified.    [b] In water at 25.0°, $10^4 k_\psi$ = 0.03 sec$^{-1}$.    [c] Reaction followed titrimetrically.

and salts are given in Tables I and II. For reaction in aqueous salt solution, plots of log $k_\psi$ against ionic strength are shown in Figure 2. The rate constants for the fluoride ion catalyzed reactions are also given in Table II. Figure 3 shows a plot of $k_\psi$ for hydrolysis

of $o$-phenylene sulfite against acid concentration in water.

**Diphenyl Sulfite.**—The rate constants for the acid-catalyzed hydrolysis in water and aqueous dioxane are given in Table III, and for hydrolysis in aqueous

acid are plotted against acid concentration in Figure 4.

**Diethyl Sulfite.**—The rate constants for hydrolysis in aqueous fluorides and hydrofluoric acid are in Table IV, together with a literature value for hydrolysis in aqueous perchloric acid.

TABLE IV

HYDROLYSIS OF DIETHYL SULFITE IN WATER[a]

| Reagent | KF | NaHF$_2$ | HF | HClO$_4$ |
|---------|-----|----------|--------|---------|
| [Reagent], $M$ | 1.0 | 0.37, 0.50 | 0.42, 1.08 | 1.08 |
| $10^5 k_\psi$, sec$^{-1}$ | $\approx 0$ | 4.76, 9.35 | 3.90, 6.60 | 64[b] |

[a] At 35.0°. [b] Reference 4.

**Influence of Temperature.**—Values of the Arrhenius parameters $A$ and $E$, and the entropy of activation, $\Delta S^*$, calculated using Eyring's equation,[12] are given in Table V. For the acid-catalyzed reaction the values of $\Delta S^*$ are calculated using 1 $M$ acid at 25° as the standard state.

TABLE V

ARRHENIUS PARAMETERS OF HYDROLYSES

| Substrate | o-Phenylene | Diphenyl | | |
|-----------|-------------|----------|---|---|
| Solvent | Water | Dioxane–water (60:40 v/v) | | |
| Reagent | ... | 0.2 $M$ HCl | 2 $M$ H$_2$SO$_4$ | 2 $M$ HClO$_4$ |
| $E$, kcal mole$^{-1}$ | 14.3[a] | 15.0 | 15.4 | 16.2 |
| Log $A$ | 6.9 | 8.3 | 7.9 | 8.4 |
| $\Delta S^*$, eu | −29 | −23.5 | −24.5 | −22 |

[a] Measured from 0 to 25°; for the range 25–35°, $E \approx 11.5$ kcal mole$^{-1}$.

For the spontaneous hydrolysis of o-phenylene sulfite in water, the energy of activation is somewhat larger and the entropy of activation less negative than that found by Tillett for hydrolysis in dioxane–water (60:40 v/v).[5] Because of the large contribution of the spontaneous hydrolysis of o-phenylene sulfite, we could not calculate Arrhenius parameters for the hydrolysis catalyzed by hydrochloric acid, but the rate constant in 2 $M$ hydrochloric acid is greater, relative to that in water, at the higher temperatures (Table I), showing that hydrolysis catalyzed by hydrochloric acid has a higher activation energy than the spontaneous hydrolysis. Similarly the relative rate retardation by perchloric acid is greater at low temperatures than high. For the hydrolysis of carboxylic anhydrides, the activation energy of the acid hydrolysis is larger than that of the spontaneous hydrolysis.[13,14]

The activation energy for the spontaneous hydrolysis of o-phenylene sulfite decreases slightly with increasing temperature, this form of deviation from the simple Arrhenius equation is typical of hydrolyses in which the transition state is highly solvated,[15] and in which its formation requires reorientation of several water molecules.

## Discussion

**Spontaneous and Acid-Catalyzed Hydrolysis. o-Phenylene Sulfite.**—The spontaneous hydrolysis is much faster than that of diphenyl sulfite or of the alkyl sulfites.[4,5,8] Uniunivalent salts of strong acids retard this hydrolysis, and therefore an acid could, acting as an electrolyte, also retard this hydrolysis, and for sulfuric and perchloric acid this retardation may be greater than the rate enhancement due to acid catalysis. Perchlorate ion retards the spontaneous hydrolysis more than does the hydrogen sulfate ion, and perchloric acid retards hydrolysis more than does sulfuric. Perchloric acid, even at 6.8 $M$, retards hydrolysis, but with sulfuric acid the rate constant goes through a shallow minimum at 2 $M$ acid and then increases slightly. This behavior of o-phenylene sulfite is very similar to that of succinic anhydride in water, where, except at high concentration, the electrolyte effect of the acid overcomes a feeble acid catalysis, and perchloric acid retards hydrolysis more than does sulfuric.[16,17]

Halogen acids are more effective catalysts in the acid hydrolysis of sulfite esters simply because the halide ions can attack the conjugate acid of the substrate.[4,5] It is interesting to note that, except for fluoride ion, they have the typical negative salt effect upon the spontaneous hydrolysis of o-phenylene sulfite (Table II), showing that chloride and bromide ions are only weakly nucleophilic towards the sulfur atom of an uncharged sulfite ester.

Our results on the hydrolysis of o-phenylene sulfite are generally similar to those found by Tillett for the hydrolysis in aqueous dioxane,[5] although there are detailed differences in the kinetic forms of the hydrolyses. Most of Tillett's work was done at 0°, and this temperature difference complicates rate comparisons, but it seems that the catalysis by hydrochloric acid is much more important in aqueous dioxane than in water, because there is no minimum in plots of rate constant against hydrochloric acid concentration in aqueous dioxane,[5] whereas we observe one in water (Table I and Figure 3). These results suggest that hydrochloric acid is a better catalyst in aqueous dioxane than in water, and our observations on the hydrolysis of diphenyl sulfite in water and aqueous dioxane (Table III) support these conclusions. The high catalytic efficiency of hydrochloric acid depends in part upon the nucleophilicity of the chloride ion, which should increase as the water content of the solvent is reduced,[18] provided that the solvent is sufficiently aqueous to support the ionization of hydrochloric acid. This condition is met in dioxane–water (60:40 v/v).[19]

One obvious difference between our results and those of Tillett is that in aqueous dioxane the nonhalogen acids at first increase the rate slightly, and a rate maximum is followed by a sharp decrease, whereas we find no rate maximum with low concentrations of aqueous perchloric and sulfuric acid (Figure 3). These systems

(12) S. Glasstone, K. J. Laidler and H. Eyring," Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 199.
(13) J. Koskikallio, D. Pouli, and E. Whalley, Can. J. Chem., **37**, 1360 (1959); C. A. Bunton and S. Perry, J. Chem. Soc., 3070 (1960).
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(15) E. A. Moelwyn Hughes, Proc. Roy. Soc. (London), **A164**, 295 (1938); J. R. Hulett, Quart. Rev. (London), **18**, 227 (1964), and references cited therein.

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(19) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 11.

are complicated, particularly in aqueous dioxane, and it is difficult to separate the effects of mineral acids as proton donors and as electrolytes. Rate maxima with increasing acidity, or irregular variation of rate with acidity are well known for reactions of weakly basic substrates such as amides,[20,21] but it seems highly improbable that the rate maxima observed for acid hydrolysis in aqueous dioxane are caused by protonation of the substrate, particularly one as weakly basic as o-phenylene sulfite, when no maxima have ever been observed with aliphatic sulfites.[4] There are now many examples of hydrolyses of both carboxylic and inorganic esters and related compounds for which rate maxima, and sometimes minima, are observed in acid, and were the effects are not caused by complete protonation.[16,17,21-24]

The electrolyte effects upon the rate of the spontaneous hydrolysis of o-phenylene sulfite in water depend upon the differential salt effects upon the activity coefficients $f_s$ and $f_*$ of the initial and transition states in the Brønsted–Bjerrum rate equation ($n$ is the formal order with respect to water).

$$k_\psi = k_0 \frac{f_s}{f_*} a_{H_2O}^n$$

We do not know how the activity coefficient of o-phenylene sulfite varies with added electrolyte, but large ions salt in ethylene sulfite (decrease $f_s$), and small ions, e.g., chloride, salt it out.[25] The effects of sulfates were not studied, but we expect them to salt out the sulfite strongly. We should also expect solubilities of ethylene and o-phenylene sulfites to vary similarly with added electrolyte. Typically large anions, e.g., perchlorate, salt in such polar nonelectrolytes as ketones, esters, and anhydrides, and small anions, or those of high charge density, e.g., chloride or sulfate, salt them out.[26,27] Salt effects upon the spontaneous hydrolysis of carboxylic anhydrides can be explained on the basis that perchlorates decrease both $f_s$ and $a_{H_2O}^n/f_*$, chlorides increase $f_s$, but decrease $a_{H_2O}^n/f_*$ more, and for sulfates the increase in $f_s$ overcomes the decrease in $a_{H_2O}^n/f_*$.[27] We assume that the same pattern will apply to the spontaneous hydrolysis of o-phenylene sulfite. As for the hydrolysis of carboxylic anhydrides, and of the conjugate acid of N-acetylimidazole,[21] the salt effects seem to depend upon the nature of the anion rather than the cation (Table II), and plots of log $k_\psi$ against ionic strength are approximately linear, except for the sulfates (Figure 2). For the hydrolysis of o-phenylene sulfite in dioxane–water (60:40 v/v) at 25°, $10^4 k_\psi = 2.61$ sec$^{-1}$, i.e., it is approximately one-twelfth as fast as in water.[5] Solvent effects of this magnitude are commonly observed for reactions

in which a water molecule attacks a formally unsaturated electrophilic atom, as in the spontaneous hydrolyses of derivatives of organic and inorganic acids.[13,17,22,28,29] The transition states for these reactions are strongly solvated by water, and therefore added salts decrease $a_{H_2O}^n/f_*$,[27] and this strong solvation is apparently associated with large solvent deuterium isotope effects.[28,30] Tillett found a large solvent deuterium isotope effect of $k_{H_2O}/k_{D_2O} = 6$, for the hydrolysis of o-phenylene sulfite in aqueous dioxane.[5] Solvolyses in which formation of the transition state requires orientation of a number of water molecules typically have activation energies which increase with decreasing temperature,[15,31a] as is found for o-phenylene sulfite.

**Diphenyl Sulfite.**—The behavior of diphenyl sulfite is very similar to that of the saturated cyclic and openchain sulfites in that its spontaneous hydrolysis is slow, but that acids catalyze the hydrolysis and halogen acids are particularly effective in this respect.[4] For hydrolysis in aqueous sulfuric and perchloric acid, the rate at first increases linearly with acid concentration (Figure 4). This kinetic form is frequently, but not always, found for A2 reactions, and has been used as a mechanistic test.[6b,31b] However, typically for the saturated sulfites the rate increases more rapidly than does acid concentration,[4] and we therefore ascribe no especial significance to the linear variation of rate with acid concentration. If we follow Bunnett's calculation of $w$ or $w^*$ values to indicate the extent of involvement of water in the transition state, we estimate $w^*$ to be approximately zero, and $w$ to be approximately 7.5 for both sulfuric and perchloric acids. These values are somewhat larger than those found for acid hydrolyses of the saturated sulfites.[31b]

For hydrolysis catalyzed by sulfuric and perchloric acid, addition of dioxane to the water at first increases the rate slightly, but then retards it. The effect of the dioxane depends upon the concentration of mineral acid. These small effects of added dioxane are very similar to those found for the corresponding hydrolysis of diethyl and ethylene sulfite[4,5] and seem to be typical of A2 hydrolyses of esters and related compounds.[13,32]

Again hydrochloric acid behaves differently from the other acids, because the rate of hydrolysis increases steadily with addition of dioxane as for the hydrolysis of o-phenylene sulfite.

The rates of the acid hydrolysis of diphenyl and the saturated sulfites are similar,[4] e.g., in 1 M HClO$_4$ at 25°, for diphenyl sulfite $10^3 k_\psi = 2.67$ sec$^{-1}$, and for diethyl sulfite 4 sec$^{-1}$. This similarity of reactivity in understandable because, although electronic withdrawal by the phenyl groups should make diphenyl sulfite less basic than a saturated sulfite, it should assist nucleophilic attack upon the sulfur atom and sulfur-oxygen bond breaking. The energies and entropies of activation are also similar and are in the range

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(29) J. Koskikallio, *Ann. Acad. Sci. Fennicae*, [AII] **57**, 1 (1954).

(30) C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3207 (1961).

(31) (a) V. Gold, *Trans. Faraday Soc.*, **44**, 506 (1948); (b) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961).

(32) R. P. Bell, A. L. Dowding, and J. A. Noble, *J. Chem. Soc.*, 3106 (1955); C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *ibid.*, 2327 (1957).

generally associated with A2 hydrolyses.[33] Typically, for acid hydrolysis of dialkyl sulfites, the energy of activation decreases and the entropy becomes more negative as the solvent is changed from water to aqueous dioxane.[4,5]

However, there is, as expected, a large difference in the rates of the spontaneous hydrolyses of diphenyl and saturated sulfites. There is little evidence on the rates of the spontaneous hydrolyses of the latter, except that for ethylene sulfite at 44.6° $10^6 k_\psi = 0.11$ sec$^{-1}$ in water,[4] whereas at 25° for diphenyl sulfite $10^3 k_\psi = 3$ sec$^{-1}$.

**Comparison of o-Phenylene and Diphenyl Sulfite.—** In the spontaneous hydrolysis o-phenylene sulfite is approximately a thousand times as reactive as diphenyl sulfite (Tables I and III). Tillett, finding o-phenylene sulfite to be much more reactive than ethylene sulfite in neutral solution, had considered the possibility that strain in o-phenylene sulfite might be responsible for this difference,[5] but the heats of hydrolysis of cyclic and open-chain aryl and alkyl sulfites are very similar,[8,34] suggesting that these rate differences are not caused by release of strain energy during hydrolysis, although in phosphate esters there is a large energetic difference between the open-chain and the five-membered cyclic phosphate esters, which may be responsible for the high reactivity of the latter,[35] and the structures of these phosphates have been examined recently in attempts to test this hypothesis.[36]

It is possible that a gain in entropy during ring opening is in part responsible for the higher reactivity of o-phenylene over diphenyl sulfite in neutral solution, and in general of the more rigid over the less rigid sulfites in alkali.[8] The evidence is not clearcut: Allinger and Falkow note that entropy effects on the rates of ring-opening reactions should be small,[37] and this generalization holds fairly well for hydrolyses of some carboxyl derivatives,[38] but Koskikallio and Whalley concluded that entropy effects were important in the acid hydrolysis of epoxides.[39]

The sulfite group is probably electron withdrawing, and some assistance to the spontaneous hydrolysis could arise by electronic relay through the aromatic ring of o-phenylene sulfite, but it is difficult to estimate the size of such an effect because as yet we have no
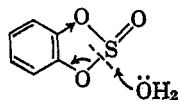
information on substituent effects for the spontaneous hydrolyses of diaryl sulfites.

**Fluoride Ion Catalyzed Hydrolysis of o-Phenylene Sulfite.—** Salts generally retard the spontaneous hydrolysis, and even sulfates, which speed reaction, have
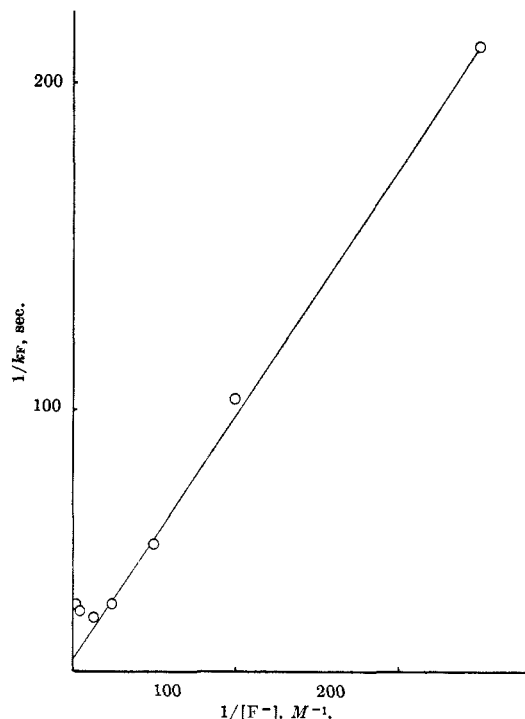


Figure 5.—Fluoride ion catalyzed hydrolysis of o-phenylene sulfite in water at 0°.

only a small effect. However, relatively small amounts of fluoride ion increase the reaction rate sharply, and at 0.08 $M$ sodium fluoride the rate is almost four times that in water (Table II). At higher fluoride ion concentrations, the rate levels off and then falls slightly, but this fall could well be caused by a small negative salt effect of sodium fluoride.

The fluoride ion is almost certainly acting as a nucleophilic catalyst, either by converting the sulfite
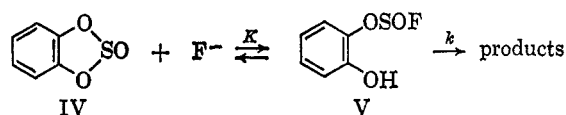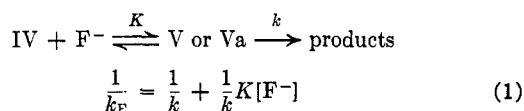


into a fluorosulfinate (V) or by adding to the sulfur atom to give Va.
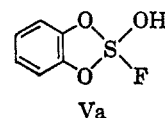


Fluoride ion is nucleophilic towards alkyl[18,40] and acyl[41] carbon atoms, although not especially so, and it is not known whether its attacks upon acyl carbon atoms, as in reactions of ethyl chloroformate or p-nitrophenyl acetate, proceed by direct displacement or by prior addition.

If we assume that we can neglect the effect of the fluoride ion as an electrolyte (except at the higher concentrations), and that it and o-phenylene sulfite are in equilibrium with an intermediate, e.g., V or Va, we can apply eq 1 (where $k_F$ is the increase of $k_\psi$ caused by

(33) L. L. Schaleger and F. A. Long, Advan Phys. Org. Chem., 1, 1 (1963).

(34) R. E. Davis, J. Am. Chem. Soc., 84, 599 (1962).

(35) P. C. Haake and F. H. Westheimer, ibid., 83, 1102 (1961); J. R. Cox, R. E. Wall, and F. H. Westheimer, Chem. Ind. (London), 929 (1959); E. T. Kaiser, M. Panar, and F. H. Westheimer, J. Am. Chem. Soc., 85, 602 (1963).

(36) D. A. Usher, E. A. Dennis, and F. H. Westheimer, ibid., 87, 2320 (1965); T. A. Steitz and W. N. Lipscomb, ibid., 87, 2488 (1965).

(37) N. L. Allinger and V. Falkow, J. Org. Chem., 25, 701 (1960).

(38) C. A. Bunton, N. A. Fuller, S. G. Perry, and V. J. Shiner, J. Chem. Soc., 2918 (1963), and references cited; O. H. Wheeler and E. E. G. de Rodriquez, J. Org. Chem., 29, 1227 (1964).

(39) J. Koskikallio and E. Whalley, Trans. Faraday Soc., 55, 815 (1959).

(40) F. L. M. Pattison and J. E. Millington, Can. J. Chem., 34, 757 (1956); E. D. Bergmann and I. Shahak, Chem. Ind. (London), 157 (1958); R. F. Hudson, Chimia (Aarau), 16, 173 (1962).

(41) M. Green and R. F. Hudson, Proc. Chem. Soc., 149 (1959); J. Chem. Soc., 1055 (1962); W. P. Jencks and J. Carriuolo, J. Am. Chem. Soc., 83, 1743 (1961); J. O. Edwards and R. G. Pearson, ibid., 84, 16 (1962).

$$IV + F^- \underset{}{\overset{K}{\rightleftharpoons}} V \text{ or } Va \overset{k}{\longrightarrow} \text{products}$$

$$\frac{1}{k_F} = \frac{1}{k} + \frac{1}{k}K[F^-] \qquad (1)$$

added fluoride ion) to the fluoride-catalyzed reaction (*cf.* ref 42).

A plot of $1/k_F$ against $1/[F^-]$ is linear (Figure 5), except towards the intercept where the negative salt effect of sodium fluoride may be important. From the value at the intercept we calculate $10^2k = 4.5$ sec$^{-1}$ for breakdown of the intermediate to products, and from it and the slope we calculate an equilibrium constant $K = 30$ l. mole$^{-1}$.

Fluoride ion also catalyzes the hydrolysis in aqueous dioxane; comparison with Tillett's results for hydrolysis in dioxane–water (60:40 v/v) at 0°, where $10^4k_\psi = 0.36$ sec$^{-1}$, shows that 0.005 $M$ potassium fluoride increases the rate 70-fold.[5] This reaction was not studied in detail in aqueous dioxane, but fluoride ion is a much more effective catalyst in these solvents than in water, presumably because it is less solvated than in water.[18]

Because of solubility problems, the fluoride ion catalyzed hydrolysis of diphenyl sulfite was not studied in detail, but spectrophotometric measurements suggest that fluoride ion catalyzes the spontaneous hydrolysis. However, the hydrolysis of diethyl sulfite is not catalyzed by fluoride ion, and potassium hydrogen fluoride is a relatively ineffective catalyst, and hydrogen fluoride is less effective than the strong mineral acids (Table IV and ref 4). Therefore, it

(42) F. R. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1947).

seems that ethoxy is not a good enough leaving group to be displaced by fluoride ion, just as neither it, nor aryloxy, are displaced by chloride ion from sulfur. Wiberg has made the generalization that, for substitutions at a carbonyl carbon atom, one base will not displace appreciably stronger bases,[43] and this generalization apparently applies also to sulfite hydrolysis.

The high nucleophilicity of fluoride ion towards *o*-phenylene sulfite and the relatively high stability of the intermediate (V or Va) are not unexpected, because sulfur–fluorine bonds are strong; *e.g.*, sulfonyl fluorides are much less reactive than the chlorides towards water.[44]

Despite the unreactivity of fluoride ion toward diethyl sulfite, hydrogen fluoride is a much more effective catalyst than would be expected if it acted solely as a proton donor, because it is only slightly dissociated,[45] and its protonating power, as measured by Hammett's acidity function, is considerably less than that of a strong acid; *e.g.*, for 1 $M$ acids perchloric acid protonates a nitroamine approximately 30 times more strongly than does hydrofluoric acid.[46]

The catalyzed reaction presumably involves attack of the hydrogen bifluoride ion upon the conjugate acid of the ester.

(43) K. B. Wiberg, *ibid.*, **77**, 2519 (1955).
(44) C. G. Swain and C. B. Scott, *ibid.*, **75**, 246 (1953).
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(46) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

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# The Mechanism of the Alkyl Sulfide–Sulfinic Acid Reaction. The Direction of Cleavage of Unsymmetrical Sulfides[1a]

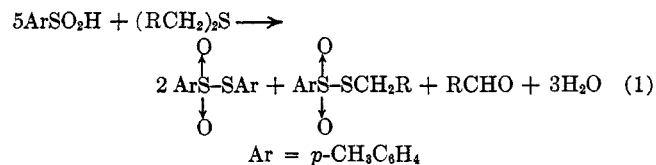JOHN L. KICE, BRUCE R. TOTH, DAVID C. HAMPTON,[1b] AND JAMES F. BARBOUR

*Department of Chemistry, Oregon State University, Corvallis, Oregon*

In the recently discovered reaction of alkyl sulfides with *p*-toluenesulfinic acid the alkyl sulfide is cleaved and one of its alkyl groups is oxidized (eq 1). Previous studies have suggested that the rate-determining step of this reaction is an elimination (eq 2) which is formally similar to the key step in the pyrolysis of either sulfoxides or amine oxides. We have now determined the preferred direction of cleavage, and, therefore, of elimination, for a series of unsymmetrical sulfides by measurement of the relative amounts of the two possible alkyl thiolsulfonates formed as products in the different cases. The results are compared with those of Cope, *et al.*, for the pyrolytic elimination of a series of unsymmetrical amine oxides and are found to be surprisingly similar. The significance of this finding for the mechanism of the rate-determining step of the sulfide–sulfinic acid reaction is discussed, and it is concluded that eq 7 is probably a more accurate representation of that step than is eq 2.

A new reaction between alkyl sulfides and *p*-toluenesulfinic acid has recently been described.[2] In this reaction the sulfide is cleaved and one of its alkyl groups is oxidized, the over-all course of the reaction being as shown in eq 1. Previous study[2b] of the mechanism of the reaction has suggested that the rate-determining step is the unimolecular elimination shown in eq 2. The formal relationship of reaction 2 to such other eliminations as the pyrolyses of amine oxides[3,4] (eq 3) and sulfoxides[5,6] (eq 4) is readily apparent.

$$5ArSO_2H + (RCH_2)_2S \longrightarrow$$

$$2 \underset{O}{\overset{O}{Ar\overset{\uparrow}{\underset{\downarrow}{S}}}}-SAr + \underset{O}{\overset{O}{Ar\overset{\uparrow}{\underset{\downarrow}{S}}}}-SCH_2R + RCHO + 3H_2O \quad (1)$$

$$Ar = p\text{-}CH_3C_6H_4$$

(2) (a) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2390 (1962); (b) J. L. Kice and E. H. Morkved, *ibid.*, **85**, 3472 (1963); (c) J. L. Kice and E. H. Morkved, *J. Org. Chem.*, **29**, 1942 (1964).
(3) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **76**, 5740 (1954).
(4) (a) A. C. Cope, T. T. Foster, and P. H. Towle, *ibid.*, **71**, 3929 (1949); (b) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957); (c) A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).
(5) D. J. Cram and C. A. Kingsbury, *ibid.*, **82**, 1810 (1960).
(6) C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964).