The Mechanism of the Acid Hydrolysis of Sodium Aryl Sulfates[1]

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Abstract: The solvent isotope effect (k_{D_2O}/k_{H_2O} = 2.43), the dependence of rate on acidity (log $k_\psi = -H_0$ + constant), and the effect on the rate of changing per cent dioxane in dioxane–water mixtures have been determined for the acid-catalyzed hydrolysis of sodium phenyl sulfate. The results are compared with the corresponding data for the hydrolysis of sodium methyl selenate, a reaction which is known to proceed *via* an A-2 type mechanism. The comparison strongly indicates that the hydrolysis of the aryl sulfate ion involves the A-1 type mechanism shown in eq 4. An explanation of how the observed effect of Ar group structure on rate of hydrolysis of $ArOSO_3^-$ can be accommodated to this mechanism is presented.

In aqueous solution sodium aryl sulfates (I) undergo an acid-catalyzed hydrolysis (eq 1) leading to the formation of sodium bisulfate and the appropriate phenol. Some years ago Burkhardt, Ford, and Singleton[2] conducted a kinetic study of the reaction in dilute

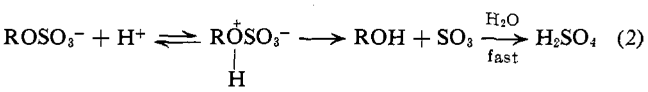
$$\underset{\text{I}}{ArOSO_3^-Na^+} + H_2O \xrightarrow{H^+} ArOH + Na^+HSO_4^- \qquad (1)$$

aqueous hydrochloric acid solution. Besides establishing the following rate law:

$$\text{rate} = k_\psi(H^+)(ArOSO_3^-)$$

they also found that the rate was accelerated by the presence of electron-withdrawing substituents in the aromatic ring, a plot of log k_ψ *vs.* log K_a for the ionization of the corresponding phenol ArOH being linear with a slope of about 0.25.

One commonly suggested[3-5] mechanism for the acid-catalyzed hydrolysis of the corresponding alkyl sulfates $ROSO_3^-$ is the following A-1 type process



$$ROSO_3^- + H^+ \rightleftharpoons \underset{H}{R\overset{+}{O}SO_3^-} \longrightarrow ROH + SO_3 \xrightarrow[\text{fast}]{H_2O} H_2SO_4 \qquad (2)$$

and indeed there are a number of cogent arguments[3,4] that can be advanced in its support. However, the parallel between the hydrolysis rate of $ArOSO_3^-$ and the acidity of ArOH,[2] coupled with the fact that sodium aryl sulfates[2] appear to hydrolyze considerably faster in acid solution than sodium alkyl sulfates,[5] led us to wonder if perhaps the aryl compounds were hydrolyzing, not by the mechanism in eq 2, but rather by the following A-2 type mechanism (eq 3).

$$ArOSO_3^- + H^+ \overset{\text{fast}}{\rightleftharpoons} ArOSO_3H \qquad (3a)$$

$$ArOSO_3H + H_2O \xrightarrow{\text{slow}} ArO^- + H_2\overset{+}{O}\text{-}SO_3H \xrightarrow{\text{fast}} ArOH + H_2SO_4 \qquad (3b)$$

Fortunately there would appear to be a relatively straightforward way to resolve this question. Bunton and Hendy[4] have established that the acid-catalyzed hydrolysis of sodium alkyl selenates, $ROSeO_3^-Na^+$, almost certainly involves an A-2 type mechanism. If the aryl sulfate ion hydrolysis is also of the A-2 type one might expect that its (1) solvent isotope effect, (2) dependence of rate on acidity of the medium, and (3) response of rate to changes in dioxane content in dioxane–water mixtures would be very similar to those observed by Bunton and Hendy[4] for the selenate system. On the other hand, if hydrolysis of the sulfate involves an A-1 mechanism of the type shown in eq 2 it will: (1) exhibit a considerably larger value of k_{D_2O}/k_{H_2O} than that found for the selenate reaction; (2) show a more pronounced increase in rate with increasing acidity; and (3) probably also give a greater acceleration of rate with increasing dioxane content in dioxane–water mixtures.

Results

Hydrolysis of Sodium Phenyl Sulfate. At 277 mμ the extinction coefficient for the phenyl sulfate ion is much smaller than that for phenol. This means that the rate of acid-catalyzed hydrolysis of $C_6H_5OSO_3^-$ can be conveniently followed spectrophotometrically by observing the increase with time of the absorbance at this wavelength. Plots of log $(A_\infty - A)$ *vs.* time showed excellent linearity for all reaction conditions. Experimental first-order rate constants for the hydrolysis, k_ψ, are tabulated in Table I.

Table I. Kinetics of the Acid-Catalyzed Hydrolysis of Sodium Phenyl Sulfate

Temp, °C	Solvent	Acid, *M*	$k_\psi \times 10^4$, sec^{-1}
40.1	H_2O	HCl, 5.81	17.4
		4.97	9.08
		4.36	5.93
		2.91	1.63
		2.00	0.87
		1.00	0.32
60.7	H_2O	HCl, 0.86	2.80[a]
	D_2O	DCl, 0.86	6.80[a]
30.1	40% dioxane–60% H_2O (v/v)	$HClO_4$, 0.50	0.49
30.1	60% dioxane–40% H_2O (v/v)	$HClO_4$, 1.81	10.3
		1.21	6.06
		0.81	3.80
		0.60	3.43
		0.50	2.47
		0.40	2.19
		0.24	1.57
15.1	80% dioxane–20% H_2O (v/v)	$HClO_4$, 0.50	4.85
20.2	80% dioxane–20% H_2O (v/v)	$HClO_4$, 0.50	9.1

[a] Average of several runs.

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[1] This research was supported by the National Institutes of Health under Research Grant No. GM-12104.

[2] G. N. Burkhardt, W. G. K. Ford, and E. Singleton, *J. Chem. Soc.*, 17 (1936).

[3] E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963).

[4] C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, 3130 (1963).

[5] S. Burstein and S. Liberman, *J. Am. Chem. Soc.*, **80**, 5235 (1958).

Hydrolysis of Pyridinium *p*-Nitrophenyl Sulfate. To check that the rate of hydrolysis does indeed show the dependence on aryl group structure claimed by Burkhardt, Ford, and Singleton[2] we measured the rate of hydrolysis of *p*-nitrophenyl sulfate ion under a number of the same reaction conditions for which k_ψ had been determined for the phenyl sulfate ion. Because it was easier to prepare, and because study of the closely related acid hydrolysis of aryl Bunte salts[6] has indicated that the rate is not changed by having pyridinium rather than sodium as the cationic portion of the salt, we used pyridinium *p*-nitrophenyl sulfate, rather than sodium *p*-nitrophenyl sulfate, for these studies.

Rates were followed spectrophotometrically at 320 mμ using the same type of procedure as for the phenyl sulfate ion. The rate constants obtained under the various reaction conditions are given in Table II.

Table II. Kinetics of the Acid-Catalyzed Hydrolysis of Pyridinium *p*-Nitrophenyl Sulfate

Temp, °C	Solvent	Acid, *M*	$k_\psi \times 10^4$, sec^{-1}
39.7	H_2O	HCl, 4.39	25.9
		2.92	6.98
		1.98	3.36
		1.00	1.28
30.1	60% dioxane–40% H_2O (v/v)	$HClO_4$, 0.81	14.3
		0.61	10.3
		0.40	7.57
		0.24	5.39

Comparison of these data with those for the phenyl sulfate ion in the same solvents indicates that both hydrolyses show the same dependence of rate on the acidity of the medium. The ratio $(k_\psi^{p\text{-NO}_2}/k_\psi^{p\text{-H}})$ is also not greatly changed by a change from water to 60% dioxane as solvent.

Our average value of $(k_\psi^{p\text{-NO}_2}/k_\psi^{p\text{-H}})$ in water as solvent at 39.7° is 4.3. The value previously obtained by Burkhardt, *et al.*,[2] at 48.6° in water was 5.0. Although we seem to find somewhat less rate enhancement for the *p*-nitro compound than they did, the results are still closely enough comparable so that we conclude that their data on the effects of substituents on hydrolysis rate are basically reliable.

Discussion

Solvent Isotope Effect. The acid-catalyzed hydrolysis of sodium phenyl sulfate shows a solvent isotope effect, (k_{D_2O}/k_{H_2O}) = 2.43. This is in the range (1.9–2.6) considered[7] typical of A-1 type hydrolyses and is much larger than the value of 1.36 observed[4] for the A-2 type hydrolysis of methyl selenate ion. The solvent isotope effect thus definitely points toward an A-1 mechanism for the aryl sulfate ion hydrolysis.

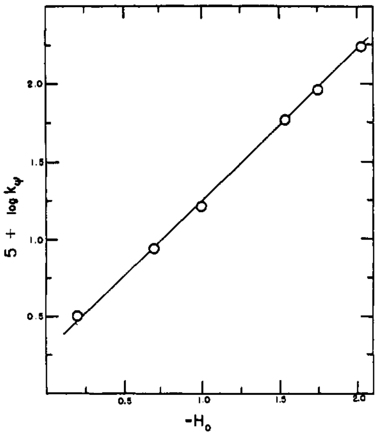
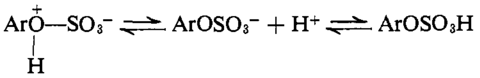


Figure 1. Log k_ψ *vs.* $-H_0$ for the hydrolysis of sodium phenyl sulfate in 1.00 to 5.81 *N* hydrochloric acid.

Dependence of Hydrolysis Rate on Acidity. Figure 1 shows a plot of log k_ψ for the hydrolysis of sodium phenyl sulfate in aqueous hydrochloric acid solutions *vs.* the Hammett acidity function, $-H_0$, for the same media. The plot is linear with a slope of 0.99. In contrast, Bunton and Hendy[4] found that a plot of log k_ψ for the hydrolysis of sodium methyl selenate *vs.* $-H_0$ was a smooth curve whose slope decreased with increasing acidity. Instead, for the selenate system a plot of log k_ψ *vs.* log (H^+) was approximately linear with a slope of about 0.9.

Clearly, then, the rate of hydrolysis of the aryl sulfate ion responds to changes in acidity in strongly acid solution in a very different way than does the hydrolysis of the methyl selenate ion. The nature of the difference in behavior is such as to suggest *considerably less* involvement of water in the transition state for the hydrolysis of the aryl sulfate ion. Furthermore, given the results of Fuller, Hughes, and Ingold,[8] which show that the H_- function calculated from the protonation of $ArSO_3^-$ ions by hydrochloric and perchloric acids is parallel to H_0 for acid concentrations between 1.5 and 6 *M*, the dependence of rate on acidity observed for the hydrolysis of the aryl sulfate ion is that expected for an A-1 type hydrolysis.

Effect of Dioxane Content on Rate of Hydrolysis in Dioxane–Water Mixtures. The dissociation constant (K_a) of any neutral acid HA decreases markedly with increasing dioxane content in 40–80% dioxane–water mixtures.[9] This means that for a given hydrogen ion concentration the fraction of aryl sulfate ion present at equilibrium as either II or III should *increase* markedly with increasing dioxane content of the medium. The same would be true for the fraction of methyl selenate ion present as CH_3OSeO_3H or $CH_3\overset{+}{O}(H)SeO_3^-$.



$$Ar\overset{+}{\underset{H}{O}}{-}SO_3^- \rightleftharpoons ArOSO_3^- + H^+ \rightleftharpoons ArOSO_3H$$

II III

Because of this, in dioxane–water solutions containing a fixed hydrogen ion concentration, the rate constant for an A-1 type hydrolysis should rise quite sharply with increasing per cent dioxane. The increase in the rate of an A-2 type hydrolysis for the same change in dioxane content would presumably be more modest,

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(6) J. L. Kice, J. M. Anderson, and N. E. Pawlowski, *J. Am. Chem. Soc.*, **88**, 5245 (1966).

(7) (a) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956); **80**, 4162 (1958); (b) C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 3207 (1961).

(8) Unpublished results of Fuller, Hughes, and Ingold (Fuller, Thesis, London, 1961) quoted by Bunton and Hendy.[4]

(9) See, for example, data for acetic acid given by A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

however, since the concomitant decrease in water concentration will at least partly counterbalance the favorable effect of having a larger percentage of the substrate present as II or III.

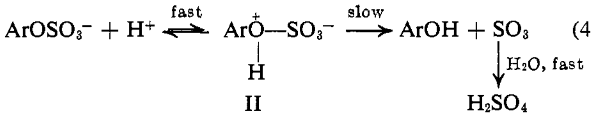
Table III compares the effect of changes in per cent dioxane on the rates of hydrolysis of sodium phenyl sulfate and sodium methyl selenate. We see that a given increase in dioxane content produces a considerably larger increase in the hydrolysis rate of the sulfate. Given the indications from the solvent isotope and acidity studies that the hydrolysis of the aryl sulfate ion is an A-1 process while that of the selenate is an A-2 reaction, this is just the sort of behavior that the discussion in the preceding paragraph would lead us to expect. The data in Table III thus seem to provide further significant support for the idea that the hydrolysis of sodium phenyl sulfate occurs *via* an A-1 mechanism.

Table III. Effect of Per Cent Dioxane on Relative Rate of Hydrolysis in Dioxane–Water Mixtures

	$k/k_{40\%\ \text{diox}}$	
Solvent	Aryl sulfate hydrolysis[a]	Methyl selenate hydrolysis[b]
40% dioxane	(1.0)	(1.0)
60% dioxane	5.0	1.6
80% dioxane	67[c]	6.3

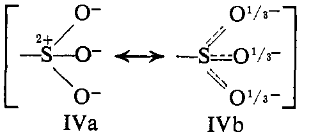
[a] Data are for 30.1° for solutions 0.5 *M* in perchloric acid. [b] Data are for 25.1° for solutions 0.10 *M* in perchloric acid. Data from ref 4. [c] Extrapolated from data at lower temperatures.

Mechanism of the Acid-Catalyzed Hydrolysis. We have seen that each comparison of data for the aryl sulfate ion hydrolysis with similar data for the hydrolysis of sodium methyl selenate[4] has pointed toward an A-1 mechanism being operative in the hydrolysis of the sulfate. The only reasonable mechanism of this type that can be written is the one shown in eq 4 involving the zwitterion II as the key intermediate.[10]



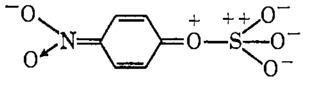
$$\mathrm{ArOSO_3^-} + \mathrm{H^+} \overset{\text{fast}}{\rightleftharpoons} \underset{\text{II}}{\mathrm{Ar}\underset{\mathrm{H}}{\overset{+}{\mathrm{O}}}\mathrm{—SO_3^-}} \xrightarrow{\text{slow}} \mathrm{ArOH} + \underset{\mathrm{H_2SO_4}}{\underset{\downarrow\ \mathrm{H_2O,\ fast}}{\mathrm{SO_3}}} \qquad (4)$$

We must now explain how the observed[2] dependence of hydrolysis rate on structure can be accommodated to the A-1 mechanism in eq 4. Translated into present-day terminology Burkhardt, Ford, and Singleton's[2] observations regarding the relationship between the hydrolysis rate of $\mathrm{ArOSO_3^-}$ and the acidity of ArOH would be stated as follows. The rate of hydrolysis of $\mathrm{ArOSO_3^-}$ is correlated better by σ_- constants than by σ constants and exhibits a ρ of about +0.5. What this says is that the electron density on the phenolic oxygen is slightly greater in the transition state of the rate-determining step than in the aryl sulfate ion and that in the transition state there is greater resonance interaction between this oxygen and an electron-withdrawing *para* substituent than in $\mathrm{ArOSO_3^-}$. At first glancet his seems somewhat surprising. However, one should recall that there is ample evidence[11] $\mathrm{SO_3^-}$ can act as a rather strong electron-withdrawing group when *immediately adjacent* to a reaction site. This is due to the presence of a large positive charge on sulfur as a result of the contribution of structure IVa to the resonance hybrid. This will both decrease the electron density on



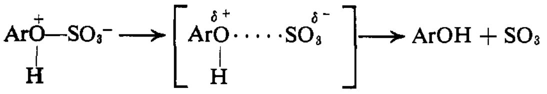
IVa IVb

the phenolic oxygen in $\mathrm{ArOSO_3^-}$ and also render unimportant any resonance interaction with a *para* substituent such as $\mathrm{NO_2}$, due to the unfavorable energetics associated with the contributing structure



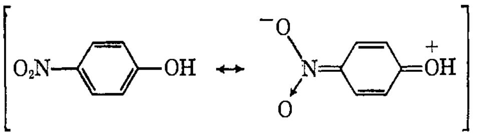
as a result of the positive charges on the adjacent sulfur and oxygen atoms.

The rate-determining step in the hydrolysis mechanism is the dissociation of zwitterion II to phenol and sulfur trioxide, *i.e.*



$$\mathrm{Ar}\underset{\mathrm{H}}{\overset{+}{\mathrm{O}}}\mathrm{—SO_3^-} \longrightarrow \left[\mathrm{Ar}\underset{\mathrm{H}}{\overset{\delta+}{\mathrm{O}}}\cdots\cdots\overset{\delta-}{\mathrm{SO_3}}\right] \longrightarrow \mathrm{ArOH} + \mathrm{SO_3}$$

If the O–S bond is assumed to be almost completely broken by the time the transition state is reached in this reaction, the electron density on the phenolic oxygen will be essentially the same as in phenol itself and could therefore well be somewhat greater than in the starting aryl sulfate ion. Furthermore, *para* substituents such as $\mathrm{NO_2}$ could contribute to mesomeric stabilization of this transition state in the same way that they stabilize the phenol, *i.e.*



Thus, provided the structure of the transition state for the dissociation of II is assumed to be considerably closer to (ArOH + $\mathrm{SO_3}$) than to II, one can account for both the small positive ρ value and the fact that the rates are correlated better by σ_- than by σ constants.

This picture can also explain why aryl sulfate ions are hydrolyzed so much more rapidly than alkyl sulfate ions.[11a] As noted earlier, we do not feel there is any stabilization of the aryl sulfate ion *via* resonance interaction of an unshared pair on the phenolic oxygen with the aromatic ring. On the other hand, the picture of the transition state which we have just developed would suggest that the transition state will receive some stabilization as a result of an interaction of this type, just as a phenol does. This will cause the activation energy

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[10] An A-1 mechanism involving the sulfonate-protonated form III seems most unrealistic since heterolysis of the ArO–S bond and expulsion of $\mathrm{ArO^-}$ should be easier in the unprotonated form $\mathrm{ArOSO_3^-}$ than in $\mathrm{ArOSO_3H}$. On the other hand, in the mechanism in eq 4 involving II the proton facilitates heterolysis of the ArO–S bond by converting ArO to the better leaving group $\mathrm{Ar\overset{+}{O}(H)}$–.

[11] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 99–102, and references cited therein.

[11a] NOTE ADDED IN PROOF. From recent data on the rate of hydrolysis of $\mathrm{CH_3OSO_3^-}$ in aqueous perchloric acid (B. D. Batts, *J. Chem. Soc., Sect. B*, 551 (1966)) and the data in Table I for $\mathrm{C_6H_5OSO_3^-}$ we calculate that the aryl sulfate hydrolyzes approximately 500 times faster than the alkyl compound at 40°.

for the hydrolysis of the aryl sulfate ion to be somewhat less than would otherwise be the case. Since no such resonance stabilization of the transition state is possible in the case of the hydrolysis of alkyl sulfate ions, we can see why aryl sulfate ions should hydrolyze considerably faster than their alkyl counterparts.

Experimental Section

Preparation and Purification of Materials. Sodium phenyl sulfate was prepared by the procedure of Burkhardt and Lapworth.[12] It was purified by several recrystallizations from ethanol and after each recrystallization was triturated with diethyl ether. Analysis indicated that the product so obtained is a hydrate, $C_6H_5OSO_3Na\cdot0.5H_2O$. *Anal.* Calcd for $C_6H_5OSO_3Na\cdot0.5H_2O$: C, 35.13; H, 2.95. Found: C, 35.20; H, 3.14.

Pyridinium *p*-Nitrophenyl Sulfate. This was prepared by a modification of the procedure of Burkhardt and Lapworth.[12] A mixture of 20 g (0.125 mole) of pyridiniumsulfonic acid[13] and 100 ml of dry benzene was placed in a three-necked flask which had been fitted with a reflux condenser and drying tube and a stirrer. After the mixture had been brought to 70°, 10 g (0.072 mole) of *p*-nitrophenol was added, and the reaction mixture was stirred for 4 hr at reflux.

The pyridinium *p*-nitrophenyl sulfate was then filtered off and recrystallized twice from water. After each recrystallization the dried salt was triturated with a small amount of ether. The salt was finally dried under reduced pressure over calcium chloride; mp 76°. *Anal.* Calcd for $C_{12}H_{10}N_2O_6S$: C, 44.29; H, 3.38. Found: C, 44.23; H, 3.29.

Solvents. Dioxane was purified by the procedure suggested by Wiberg.[14]

Procedure for Kinetic Runs. The reaction vessel was of a type previously described[15] in connection with kinetic study of the disproportionation of sulfinic acids. Its construction is such that an aliquot may be withdrawn without exposing the remainder of the solution to the atmosphere.

To initiate a run a weighed amount of the aryl sulfate salt was dissolved in a measured volume of the proper solvent containing the desired amount of perchloric or hydrochloric acid. The resulting solution was placed in the reaction vessel and deaerated for 5 to 10 min with prepurified nitrogen. While being deaerated the solution was cooled in an ice bath. After the solution was deaerated, the reaction vessel was placed in a constant temperature bath. The reaction was then followed by removing 1- or 2-ml aliquots, diluting these aliquots to 50 ml with 95% ethanol, and measuring the optical density of the resulting solutions at either 277 mμ (for the phenyl sulfate ion hydrolysis) or 320 mμ (for the *p*-nitrophenyl sulfate ion hydrolysis).

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[12] G. N. Burkhardt and A. Lapworth, *J. Chem. Soc.*, 684 (1926).

[13] P. Baumgarten, *Ber.*, **59**, 1166 (1926).

[14] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 245.

[15] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

The Mechanism of the Acid Hydrolysis of Bunte Salts (S-Alkyl and S-Aryl Thiosulfates)[1]

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Abstract: The rates of acid-catalyzed hydrolysis (eq 1) of a series of S-aryl and S-alkyl thiosulfates (Bunte salts) have been measured under a variety of reaction conditions in water and various dioxane–water mixtures. The data on the variation of the hydrolysis rate with the acidity of the medium and on the increase in rate accompanying an increase in the dioxane content of dioxane–water mixtures have been compared with corresponding data for two closely related acid-catalyzed hydrolyses: (1) that of sodium aryl sulfates (a reaction thought to proceed by an A-1 mechanism) and (2) that of sodium methyl selenate (a reaction presumably proceeding by an A-2 mechanism). This comparison shows that the response of the Bunte salt hydrolysis to these particular reaction variables is very closely comparable to that of the sulfate hydrolysis and very different from that of the selenate hydrolysis, and it strongly suggests that the Bunte salt hydrolysis proceeds by an A-1 mechanism. It is shown that the observed solvent isotope effect for the Bunte salt hydrolysis ($k_{D_2O}/k_{H_2O} = 1.4$) and the variation of rate with Ar for $ArSSO_3^-$ ($\rho \cong -0.5$) are also compatible with the particular A-1 mechanism shown in eq 3. This mechanism involves an initial reversible protonation of the Bunte salt on the divalent sulfur followed by rate-determining unimolecular dissociation of the zwitterion intermediate to thiol and sulfur trioxide. It is thus the same type of mechanism proposed for the sulfate hydrolysis. A tentative explanation is advanced to explain why the Bunte salt and sulfate hydrolyses, although proceeding by the same basic mechanism, show somewhat different response of rate to changes in alkyl or aryl group structure.

On being heated in aqueous acid Bunte salts (S-alkyl or S-aryl thiosulfates) are hydrolyzed to bisulfate and the appropriate mercaptan (eq 1).[2-4] The reaction

$$\mathrm{R{-}S{-}SO_3^- + H_2O \xrightarrow{H^+} R{-}SH + HSO_4^-} \qquad (1)$$

is one of a sizeable group of hydrolyses of sulfate derivatives (eq 2) which involve replacement of the group Y originally bonded to the sulfate sulfur by OH. Some other members of the group are the following hydrolyses: sulfamic acid[5] (eq 2, Y = NH_2); aryl sulfates[6]

$$\mathrm{Y{-}SO_3^- + H_2O \longrightarrow HO{-}SO_3^- + Y{-}H} \qquad (2)$$

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[1] This research was supported by the National Institutes of Health under Research Grant GM-12104.

[2] T. S. Price and D. F. Twiss, *J. Chem. Soc.*, **95**, 1725 (1909).

[3] (a) Z. El-Heweki and E. Taeger, *J. Prakt. Chem.*, **7**, 191 (1958); (b) P. Baumgarten, *Ber.*, **63**, 1330 (1930).

[4] (a) H. E. Westlake and G. Dougherty, *J. Am. Chem. Soc.*, **63**, 658 (1941); (b) H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, 20, 475 (1955); (c) U. Weiss and S. Sokol, *J. Am. Chem. Soc.*, **72**, 1687 (1950); (d) B. Saville, *J. Chem. Soc.*, 1730 (1960).

[5] J. P. Candlin and R. G. Wilkins, *ibid.*, 4236 (1960).

[6] (a) G. N. Burkhardt, W. G. K. Ford, and E. Singleton, *ibid.*, 17 (1936); (b) J. L. Kice and J. M. Anderson, *J. Am. Chem. Soc.*, **88**, 5242 (1966).