References and Notes

(1) (a) G. C. Bailey, *Catal. Rev.*, **3**, 37 (1969); (b) M. L. Khidelkel', A. D. Shebaldova, and I. V. Kalechits, *Russ. Chem. Rev.* (*Engl. Transl.*), **40**, 669 (1971); (c) R. L. Banks, *Top. Curr. Chem.*, **25**, 39 (1972); (d) N. Calderon, *Acc. Chem. Res.*, **5**, 127 (1972); (e) W. B. Hughes, *Organomet. Chem. Synth.*, **1**, 341 (1972); (f) G. Dall'Asta, *Rubber Chem. Tech.*, **47**, 511 (1974); (g) J. C. Mol and J. A. Moulijn, *Adv. Catal.*, **24**, 131 (1975); (h) R. J. Haines and G. J. Leigh, *Chem. Soc. Rev.*, **4**, 155, (1975); (i) R. Streck, *Chem. Ztg.*, **99**, 397 (1975); (j) L. Hocks, *Bull. Soc. Chim. Fr.*, 1893 (1975); (k) W. B. Hughes, *Chem. Tech.*, **5**, 486 (1975); (l) R. Taube and K. Seyferth, *Wiss. Z. Tech. Hochsch. Chem. "Carl Schorlemmer" Leuna-Merseburg*, **17**, 305 (1975).

(2) (a) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975); (b) T. J. Katz and R. Rothchild, *ibid.*, **98**, 2519 (1976); (c) C. P. Casey and T. J. Burkhardt, *ibid.*, **96**, 7808 (1974); (d) D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 927 (1972); (e) R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *J. Am. Chem. Soc.*, **98**, 3478 (1976); (f) B. A. Dolgoplosk et al., *Eur. Polym. J.*, **10**, 901 (1974), *Dokl. Chem.*, **216**, 380 (1974); (g) J. L. Hérisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970); (h) J.-P. Soufflet, D. Commereuc, and Y. Chauvin, *C. R. Acad. Sci., Ser. C*, **276**, 169 (1973).

(3) The metathesis of acetylenes is incompatible with the earlier mechanism.[2a] Isolable metal carbenes react stoichiometrically with olefins as in eq 3.[2c,d,4] Methyllithium[2h] and dimethylzinc[5] react with WCl_6 forming methane. Isolable metal carbenes initiate metatheses.[6] A fragment of the initiator has been detected at the start of polymer chains.[6c]

(4) C. P. Casey, H. E. Tuinstra, and M. C. Saemen, *J. Am. Chem. Soc.*, **98**, 608 (1976).

(5) E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975).

(6) (a) J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Am. Chem. Soc.*, **98**, 605 (1976); (b) T. J. Katz, J. McGinnis, and C. Altus, *ibid.*, **98**, 606 (1976); (c) S. J. Lee, J. McGinnis, and T. J. Katz, *ibid.*, **98**, 7818 (1976); (d) T. J. Katz, S. J. Lee, and N. Acton, *Tetrahedron Lett.*, 4247 (1976); (e) T. J. Katz and N. Acton, *ibid.*, 4251 (1976).

(7) (a) E. A. Zuech, *J. Chem Soc., Chem. Commun.*, 1182 (1968); (b) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. A. Kittleman, *J. Am. Chem. Soc.*, **92**, 528 (1970).

(8) During this experiment the "range" switch on the gas chromatograph was not changed between peaks. This was a mistake because the switch determines the resistance in parallel with the flame ionization detector and hence the voltage to the amplifier. This caused the weak signal from C_{16} to be below the range at which the amplifier responded linearly, and resulted in small peaks erroneously being measured smaller than they should have been. Thus $[C_{14}]/[C_{16}] = r_2$, and therefore $r_1 \times r_2$, were measured too large although r_1 was measured correctly. In experiment 3, in which the ratio of 2-butene to 4-octene was also high (see Table I) and in which this measurement could again have been made erroneously, the sensitivity was increased with the range switch tenfold between the time C_{12} and C_{14} eluted and tenfold again before C_{16} eluted. When this adjustment was not made the measurement of r_1 remained unchanged, but that of r_2 increased by 50%.

(9) (a) L. G. Parratt, "Probability and Experimental Errors in Science", Wiley, New York, N.Y., 1961, p 118; (b) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, pp 41–42.

(10) G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, *Makromol. Chem.*, **91**, 87 (1966), and later work.

(11) W. Ast and K. Hummel, *Naturwissenschaften*, **57**, 545 (1970).

(12) Sometimes disubstituted olefins have been said to give the products in 1:2:1 ratio.[2g,13]

(13) R. Rossi, P. Diversi, A. Lucherini, and L. Porri, *Tetrahedron Lett.*, 879 (1974).

(14) W. J. Kelly and N. Calderon, *J. Macromol. Sci., Chem.*, **9**, 911 (1975).

(15) M. T. Mocella, M. A. Busch, and E. L. Muetterles, *J. Am. Chem. Soc.*, **98**, 1283 (1976).

(16) J. Lal and R. R. Smith, *J. Org. Chem.*, **40**, 775 (1975).

(17) J. Shabtai, J. Herling, and E. Gil-Av, *J. Chromatogr.*, **11**, 32 (1963).

(18) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, N.Y., 1965, pp 69–72.

(19) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

(20) (a) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography", Varian Aerograph, Walnut Creek, Calif., 1967; (b) W. A. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1967); (c) L. S. Ettre, *J. Chromatogr.*, **8**, 525 (1962); (d) L. S. Ettre, "Practical Gas Chromatography", Perkin-Elmer, Norwalk, Conn., 1973, pp 4–23, and references cited therein.

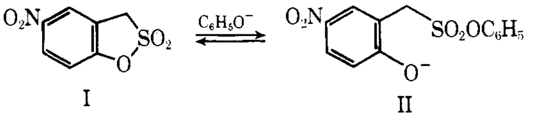
Intramolecular Nucleophilic Assistance in the Hydrolysis of Sulfonate Esters: Equilibrium Constant for Sultone Formation

Charles R. Farrar and Andrew Williams*

Contribution from the University Chemical Laboratories, Canterbury, Kent, England CT2 7NH. *Received September 24, 1976*

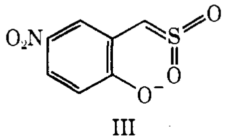
Abstract: The hydrolysis of phenyl 2-hydroxy-5-nitrophenylmethanesulfonate possesses a sigmoid pH dependence with a kinetic pK_a close to the thermodynamic value for the phenolic hydroxyl. This result is consistent with intramolecular nucleophilic participation by the hydroxyl group followed by hydrolysis of the intermediate sultone. Evidence supporting this conclusion is: (a) absence of buffer catalysis; (b) almost complete absence of a solvent deuterium oxide isotope effect; (c) a slightly positive entropy of activation; (d) the fast decomposition of the sultone compared with the observed rate constant for the sulfonate; (e) observation of an intermediate under conditions predicted from the sultone rate constant and that for the sulfonate; (f) the existence of a mass law effect on solvolyses carried out in solutions containing added phenol. The equilibrium constant for formation of the phenyl ester from sultone is 1.4×10^5 M^{-1}, which reflects the strained nature of the five-membered ring sultone. A crude estimate of the effective molarity gives a lower limit of 10^5 M, a relatively small value probably due to ring strain in the transition state of the intramolecular reaction.

It was argued recently that the observed absence of an E1cB mechanism in the hydrolysis of sultones (I)[1] is consistent with stereoelectronic considerations.[2,3] The demonstration of nucleophilic attack on sultones[3] indicates that, by the principle of microscopic reversibility, the reverse step will also not utilize the sulfene pathway (III), although it is well established that this mechanism predominates in the alkaline hydrolysis of aryl phenylmethanesulfonates (IV).[2,4] Reference to structure III confirms that cyclization will be a difficult process, since it requires a 90° rotation about a C=S double bond.

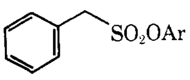


(1)

I II



III



IV

Studies of the reverse step of eq 1 are likely to be complicated by the hydrolysis of sultone (I), which is a relatively labile species, and by a possible direct and general-base-catalyzed formation of product from II. If it is possible to measure the rate constant for the reverse step then we may estimate the equilibrium constant for the ring opening reaction because we know the forward rate constant.[3] The high rate constants for hydrolysis of five-membered sultones compared with their acyclic analogues have been attributed to strain energy[5] and x-ray crystallography indicates a small value for the ring angle around the sulfur atom (96.1°)[6] compared with a more usual value of approximately 107°.[7] This work seeks to confirm the existence of strain in the five-membered ring sultone from a thermodynamic standpoint and also presents the first example of an intramolecular nucleophilic catalysis of sulfonate ester hydrolysis by a phenolate oxyanion. Further, the results of this study confirm the conclusions of Kaiser and his co-workers[1] concerning direct attack in sultone hydrolysis as opposed to the E1cB mechanism.

Experimental Section

Materials. Phenyl 2-hydroxy-5-nitrophenylmethanesulfonate was synthesized by adding a solution of 2-hydroxy-5-nitrophenylmethanesulfonic acid sultone (I, from a previous study,[3] 2.15 g, 10 mmol) in an ethanol/acetonitrile solution (25 mL) to a solution of sodium phenolate (1.16 g, 10 mmol) in ethanol (10 mL). The mixture was stirred at room temperature for 15 min, acidified with ethanolic HCl, and evaporated in vacuo to give an oil which solidified on treatment with water. The solid was recovered by filtration, washed with water, and recrystallized from benzene as a white powder, mp 141-143 °C. Anal. Calcd for $C_{13}H_{11}NSO_6$: C, 50.5; H, 3.6; N, 4.5. Found: C, 50.5; H, 3.7; N, 4.6. Analyses were carried out by Mr. G. M. J. Powell using a Hewlett-Packard Model 185 CHN analyzer. Infrared spectra (Unicam SP 200), NMR spectra (Perkin-Elmer R 10), and mass spectra (AEI MS 902) confirmed the identity of the compound.

Buffers and other materials were of analytical reagent grade or were recrystallized before use. Deuterium oxide (99.8% D) was obtained from Ryvan Chemical Co. and water used throughout the work was doubly distilled from glass.

Methods. Kinetics were measured by following the reactions spectrophotometrically at the appropriate wavelength previously determined using a repetitive scanning instrument (Unicam SP 800). The stock solution of sulfonate in ethanol (~50 μL) was placed on the flattened tip of a glass rod and introduced into the buffer (2.5 mL) in a silica cell in the thermostated cell compartment of a Unicam SP 800, 600, or Beckman DBG spectrophotometer equipped with a servoscribe recorder. The trace was activated at the instant the glass rod entered the solution; first-order rate constants were estimated from the recorder traces from plots on two-cycle logarithmic paper utilizing infinity readings.

The pH of buffer solutions was measured after each kinetic run using a Pye-Dynacap pH meter accurate to ±0.01 units and calibrated with EIL standard buffers accurate to the same tolerances.

The estimation of thermodynamic pK_a's of species was carried out spectrophotometrically at an appropriate wavelength in buffer solutions with pH spanning the pK_a. Since the sulfonate undergoes hydrolysis at alkaline pH's the absorbance at zero time for a particular pH was obtained by extrapolation. The experimental data $(A_{pH} - A_L)/(A_H - A_L)$ were plotted vs. pH on two-cycle logarithmic paper and the best theoretical line was drawn through the points using a normalized line

$$y = 1/(1 + 10^{-\Delta pK_a}) \qquad (2)$$

to the same scale on tracing paper. The parameter A_{pH} represents the observed optical density, A_L and A_H the invariant optical densities at pH's lower and higher than that corresponding to the pK_a. The same technique was used to determine k_{lim} and $pK_a^{kinetic}$ for the plot of $\log_{10} k$ vs. pH (Figure 1) for the hydrolysis data. The 2-hydroxy-5-nitrophenylsulfonic acid (for pK_a determination) was prepared by dissolving the sultone (I) in a few drops of acetonitrile, adding a few drops of ethanol, and diluting to 5 mL with 0.1 M KOH. The solution was kept for 2 h to ensure hydrolysis and then used as a stock solution to determine the pK_a spectrophotometrically.

Deuterium oxide buffers were prepared from solutions of sodium carbonate in D_2O and made up to 1 M ionic strength with KCl. The pD was estimated according to the equation[7b]

$$pD = pH_{(\text{meter reading})} + 0.37 \qquad (3)$$

from measured pH readings.

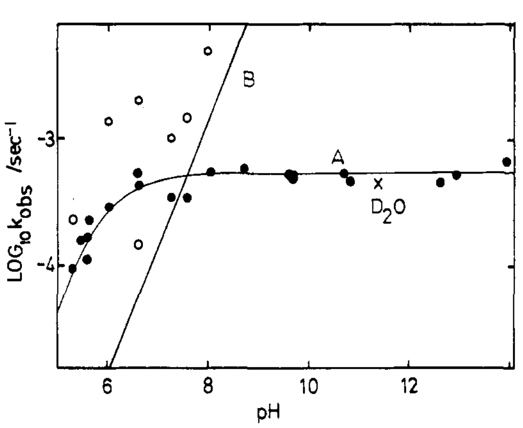


Figure 1. The pH dependence of the hydrolysis of phenyl 2-hydroxy-5-nitrophenylsulfonate at 25 °C and ionic strength made up to 1 M with KCl (line A, filled circles). Line B represents the hydroxide ion catalyzed hydrolysis of the sultone (I) and the open circles are the rate constants for the reaction of the sultone in the buffers used for hydrolysis of the sulfonate. Line A is theoretical according to eq 4 and the parameters given in Table II.

Results

The rates of reaction of the phenyl sulfonate (II) obeyed good first-order kinetics and the product was shown to be the same as that from the sultone under the same conditions by comparison with the final absorbance of an equivalent amount of the latter (I) at 400 nm in the same buffer. The rate constants were independent of the type of buffer and of the buffer concentration employed, although this is not true of sultone hydrolysis.[3] The pH dependence of the rate constants is illustrated in Figure 1 and a sigmoid kinetic law is obeyed

$$k = k_{lim}/(1 + a_{H^+}/K_a^{kinetic}) \qquad (4)$$

The results are given in Table I and the parameters k_{lim} and $pK_a^{kinetic}$ are $(5.2 \pm 0.6) \times 10^{-4}\ s^{-1}$ and 6.0 ± 0.1, respectively. In selected kinetic experiments (see Figure 1) the rate constant for sultone reaction was measured and found to exceed the phenyl sulfonate (II) value under the same conditions of pH, buffer concentration, temperature, and ionic strength. The hydroxide component to the sultone reaction is represented by the line of unit slope derived from data already published from this laboratory.[3] The buffer component of the sultone reaction was dependent on the buffer concentration and on the nature of the buffer itself.

The absence of a hydroxide term to the kinetic equation for the hydrolysis is consistent with the low reactivity of phenyl phenylmethanesulfonate to hydroxide attack; the effect of the 2-oxyanion in II is likely to exceed that of the 5-nitro group and make its alkaline hydrolysis slower than that of the former compound. The value of k_{OH} for phenyl phenylmethanesulfonate $(4.9 \times 10^{-5}\ M^{-1}\ s^{-1})$[8a] gives rise to a pseudo-first-order rate constant of $4.9 \times 10^{-5}\ s^{-1}$ at 1 M NaOH, which is an upper limit for the hydrolysis of II and is well below the observed plateau rate constant (k_{lim}).

The temperature dependence of k_{lim} was measured with carbonate buffers from 25 to 50 °C and the results given in Table I together with the deuterium oxide solvent isotope effect on this parameter. The pK_a's determined spectrophotometrically by the method given in the Experimental Section come close to the expected values and are reported in Table II.

Demonstration of Sultone Intermediate. We examined the reaction of the sulfonate (II) under conditions where sultone (I) is produced faster than it decomposes, namely in the pH region 6-7 with nonnucleophilic buffers. 2,6-Lutidine is a suitable species as it acts as a general base on the sultone rather than as a nucleophile and is only weakly catalytic.[3] Addition

Table I. Kinetic Data for the Hydrolysis of Phenyl 2-Hydroxy-5-nitrophenylmethanesulfonate and the Corresponding Sultone (I)[a]

pH	Buffer	$k/s^{-1} \times 10^4$, sulfonate (II)[c]	k/s^{-1}, sultone (I) (405 nm)
13.94	NaOH	6.7	
12.94	NaOH	5.2	
12.61	NaOH	4.7	
11.37 (pD)	Carbonate	4.7 (D_2O)	
10.80	Carbonate	4.6	
10.7	Carbonate	5.4	
9.70	Carbonate	5.2	0.13
9.69	Carbonate	4.8	
9.63	Triethylamine	1.3 (with 0.05 M phenol)	
9.59	Triethylamine	5.2	0.16
8.71	Carbonate	5.9	
8.04	Tris[d]	5.5	4.9×10^{-4}
7.55	Tris	3.3	1.5×10^{-3}
7.27	Tris	3.5	1.0×10^{-3}
6.62	Phosphate	4.3[b]	2.0×10^{-3}
6.02	Phosphate	2.9[b]	1.4×10^{-3}
6.57	Lutidine	5.2[b]	
5.63	Acetate	2.3[b]	
5.59	Phosphate	1.7[b]	
5.58	Phosphate	1.1[b]	
5.46	Acetate	1.6[b]	
5.29	Acetate	0.94[b]	2.3×10^{-4}
9.65 (31.1 °C)	Carbonate	12.5, 11.7	
9.65 (36.7 °C)	Carbonate	18.7, 18.8	
9.65 (43.4 °C)	Carbonate	40.4, 38.4	
9.65 (49.4 °C)	Carbonate	73.6, 74.7	

[a] Conditions: 25 °C (except for the temperature studies), ionic strength made up to 1 M with KCl. [b] At 400 or 405 nm. [c] At 440 nm. [d] Trishydroxymethylaminomethane.

Table II. Collection of Rate and Thermodynamic Data for the Hydrolysis of Phenyl 2-Hydroxy-5-Nitrophenylmethanesulfonate[a]

pK_a^{kinetic}	6.0 ± 0.1	$\Delta G^{\ddagger}$	19.6 ± 0.9 kcal/mol
$pK_a^{\text{thermodynamic}}$	6.0 ± 0.1 (440 nm)	$\Delta H^{\ddagger}$	20.1 ± 0.8 kcal/mol
pK_a (sulfonic acid)	6.8 ± 0.1 (440 nm)	$\Delta S^{\ddagger}$	1.7 ± 5 eu/mol
k_{lim}/s^{-1}	$(5.2 \pm 0.6) \times 10^{-4}$		
$k_{\mathrm{lim}}^{H_2O}/k_{\mathrm{lim}}^{D_2O}$	0.97 ± 0.05		

[a] Parameters for 25 °C and ionic strength made up to 1 M with KCl.

Figure 1. The pH dependence of the hydrolysis of phenyl 2-hydroxy-5-nitrophenylsulfonate at 25 °C and ionic strength made up to 1 M with KCl (line A, filled circles). Line B represents the hydroxide ion catalyzed hydrolysis of the sultone (I) and the open circles are the rate constants for the reaction of the sultone in the buffers used for hydrolysis of the sulfonate. Line A is theoretical according to eq 4 and the parameters given in Table II.

of sulfonate (II) to the lutidine buffer at pH 6.6 initiated a large decrease in absorbance (405 nm) caused by sultone formation. The rate constant for this decrease (5.15×10^{-4} s^{-1}) comes close to that expected from eq 4 using the kinetic parameters quoted earlier. Very slowly the absorbance returned and the first-order rate constant for this ($(7.8 \pm 1) \times 10^{-5}$ s^{-1}) is close to that for the hydrolysis of the sultone in the same buffer ($(6.1 \pm 1) \times 10^{-5}$ s^{-1}) calculated from data already acquired.[3]

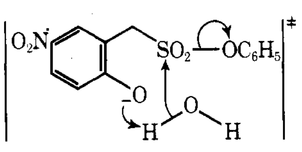
Mass Law Effect with Added Phenol. If the hydrolysis of II proceeds via the sultone then added phenol might decrease the overall rate constant for depletion of the sulfonate. Since we know the rate constant for phenol attack on sultone (I)[3] and may accurately determine the rate of reaction of sultone under the conditions of the experiment we calculate that a measurable decrease should be observed. The rate constant for sulfonate decomposition is given by the expression

$$k = k_{\mathrm{lim}}k_2/(k_2 + k_B[C_6H_5\bar{O}]) \qquad (5)$$

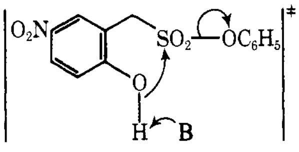
where k_{lim} is the rate constant for formation of sultone, k_2 is that for decomposition of sultone under the prevailing conditions, and k_B that for phenolate attack.[3] In an experiment at pH 9.7 with triethylamine buffers (0.1 M, 1 M ionic strength made up with KCl) containing 0.05 M phenolate the rate constant ($(1.3 \pm 0.1) \times 10^{-4}$ s^{-1}) was observed. The value of k_2 measured under the same conditions of the experiment (0.16 ± 0.03 s^{-1}) together with k_B and k_{lim} gave, using eq 5, a value of $(1.1 \pm 0.2) \times 10^{-4}$ s^{-1}, which is equal to the observed quantity within the experimental error limits.

Discussion

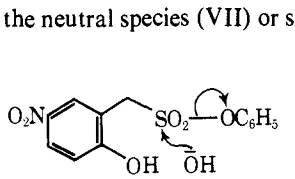
The hydrolysis of phenyl 2-hydroxy-5-nitrophenylmethanesulfonate (II) involves direct nucleophilic attack of the 2-phenoxyanion and not intramolecular general-base catalyzed attack of water (V). Evidence consistent with this hypothesis is as follows: (a) The intermediate sultone (I) decomposes under the conditions of all the experiments faster than the observed rate attributed to the intramolecular nucleophilic attack. Figure 1 illustrates this for selected pH's; sultone decomposition entails nucleophilic catalysis[3] and regular hydroxide catalysis predominates only in the high pH region. In the pH range corresponding to the ionization of the substrate the sultone decomposition is fast, owing to buffer catalysis. (b) Hydrolysis of the sulfonate (II) is independent of buffer concentration or type and there is too small a solvent deuterium oxide isotope effect to support either mechanism V or VI. General-base-catalyzed hydrolysis in VI is not in any case expected because intramolecular attack by the 2-oxyanion group would be more efficient and the latter group is present at higher concentrations than the conjugate acid in the pH region corresponding to the plateau. (c) The enthalpy of activation for the reaction of the conjugate base of the sulfonate (II) comes close to that expected for oxyanion attack on aromatic sulfonate esters.[9] The slightly positive entropy of activation favors an intramolecular reaction rather than an intermolecular process. (d) An intermolecular mechanism consistent with the observed rate law is attack of hydroxide ion on the neutral species (VII) or sulfene formation (VIII). Using the pK_a of the 2-hydroxyl group (6.0) and the value for k_{lim} (5.2×10^{-4} s^{-1}) we can estimate the rate constant to be 5.2×10^4 M^{-1} s^{-1}. This value is some nine orders of magnitude larger than the rate constant for hydrolysis of phenyl phenylmethanesulfonate (IV) in alkali; even allowing for the possible noncompensatory effects of the 5-nitro and 2-hydroxyl substituents this rate constant difference is too large to support the same mechanism. The pathway for alkaline hydrolysis of IV involves sulfene formation[1,2,8] and the direct attack of alkali



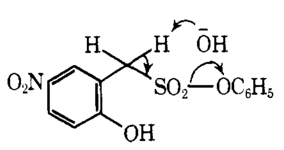
V



VI

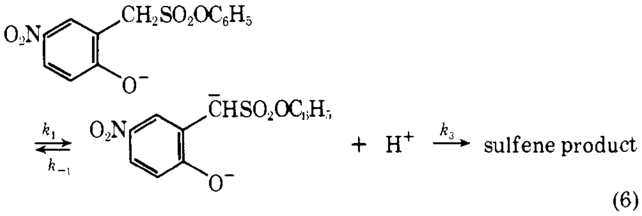


VII



VIII

on the sulfur (VII) would involve an even larger rate constant difference. It is apparent from earlier studies[10] that hydroxide attack on esters is not enhanced sufficiently by neighboring electrophiles, even when located correctly for maximum interaction with the carbonyl oxygen, for such large rate differences to be explained in this way. (e) Rate limiting proton transfer from the methylene group (eq 6) is a possible mech-



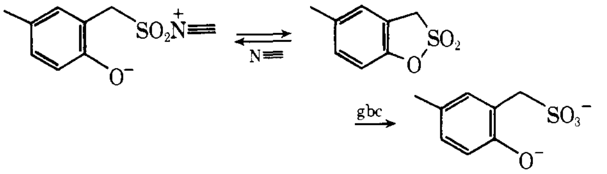
(6)

anism, but it is unlikely that the decomposition of the carbanion (k_3) to yield sulfene would be faster than the intramolecular donation of a proton from the 2-hydroxyl group to the carbanion. The former rate constant would be approximately the same as that for IV, the unsubstituted ester (2.9×10^4 s^{-1}),[8a] and the latter (k_{-1}) is presumably a diffusion-limited rate constant ($\sim 10^{10}$ s^{-1}). The overall first-order rate constant for this mechanism may be estimated from data already available[8a] to be $K_{SH}k_3/K_a$, where K_{SH} and K_a are the ionization constants for the carbanion and 2-hydroxyl group, respectively. If we can assume, as before, that the 5-nitro and 2-hydroxyl electronic effects cancel, then we may use K_{SH} and k_3 for the reaction of IV[8a] (respectively $10^{-22.8}$ and 2.9×10^4 s^{-1})[8a] to give an estimated rate constant via this mechanism of 4.6×10^{-13} M^{-1} s^{-1}, some eight orders of magnitude lower than the observed value. (f) Direct evidence for intramolecular nucleophilic attack is the observation of the sultone intermediate (I) followed by its decomposition. Experiments at pH 6.6 with 2,6-lutidine buffers indicate that an intermediate is formed in an initial relatively fast step and the large decrease in absorbance at 405 nm for decay of the intermediate is within the confidence limits the same as the decay of sultone (I) in the same buffer. (g) The mass law effect of added phenol on the rate constant for the decomposition of the phenyl sulfonate (II) provides further conclusive evidence for the proposed mechanism.

The equilibrium constant for formation of the phenyl sulfonate from sultone and the phenolate anion, derived from the forward and reverse rate constants from eq 1, indicates that the sulfonate is the more stable state ($K = 1.4 \times 10^5$ M^{-1}). Some of this stability must be due to the phenolate state being essentially less stable than the *p*-nitrophenolate as judged from the difference in pK_a's between 4-nitrophenol and phenol; this probably contributes some 1000 to the equilibrium constant. Since the reaction should involve an entropy loss due to the formation of single species from two reactants the equilibrium constant for formation might be expected to be unfavorable, especially as the component groups in reactants and products are similar. The favorability of the reaction is judged to be further evidence of strain in five-membered ring sultones.[5,6]

It is not possible at present to obtain an accurate estimate of the effective molarity because the intermolecular reaction of a phenolate anion (of pK_a ~6) with a phenyl sulfonate ester is far too slow to measure. Data from the laboratory of Vizgert[9] for high temperatures allow us to calculate the rate constant for hydroxide attack on phenyl benzenesulfonate (3.2×10^{-5} M^{-1} s^{-1}). The only evidence available so far to enable us to estimate the rate constant for phenolate attack is the Brønsted type plot for attack of nucleophiles on sultone (I).[3] Enough oxyanion data are available to give a rough estimate that the phenoxide ion of pK_a = 6 is some 10^4-fold less reactive than hydroxide ion. The value could well be larger for benzenesulfonates, as these esters are very unreactive compared with sultone (I), and this leads to an upper limit of 3.2×10^{-9} M^{-1} s^{-1} for the rate constant for attack of phenoxide on phenyl benzenesulfonate. The effective molarity estimated from this ($>10^5$ M) is well in the region expected for an intramolecular covalent bond formation and might be higher for an unstrained sultone. In any case the high value for the effective molarity is yet further evidence against an intramolecular general-base assisted attack on the sulfonate (V).[11] So far as we are aware the only examples of neighboring group participation in sulfonic acid chemistry to be studied thoroughly, namely sulfonamide hydrolysis catalyzed by carboxylic acid,[12] do not allow as yet the estimation of an effective molarity to compare with our lower limit.

The results of this investigation for ring closure of the sulfonate provide us with an explanation for the observation in sultone hydrolysis of general-base catalysis with tertiary amines as opposed to the operation of a nucleophilic pathway:[3] (eq 7). General-base catalysis results in a high deuterium oxide



(7)

solvent isotope effect for tertiary amines and also a bimolecular rate constant some tenfold less than expected from the Brønsted plot for secondary and primary amine attack (after due consideration of steric hindrance effects). The phenolate leaving group is predicted to be poor in comparison with the amine leaving group derived from the quaternary nitrogen derivatives; in the series $CH_3CON^+R_3$ and $CH_3COOC_6H_5$[13] the rate constant difference for hydrolysis in water is some five or six orders of magnitude for groups of similar pK_a. Thus, although the high energy intermediate may be formed it rapidly returns to sultone and the equilibrium constant for formation is sufficiently low, especially for weakly basic amines, for there to be little effect on the overall rate.

Acknowledgment. We thank the Royal Society for an equipment grant and the University of Kent for a Studentship for C.R.F.

References and Notes

(1) P. Müller, D. F. Mayers, O. R. Zaborsky, and E. T. Kaiser, *J. Am. Chem. Soc.*, **91**, 6732 (1969).
(2) A. Williams, K. T. Douglas, and J. S. Loran, *J. Chem. Soc., Chem. Commun.*, 689 (1974).
(3) T. Deacon, A. Steltner, and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1778 (1975).
(4) (a) J. F. King and R. P. Beatson, *7th International Symposium on Sulfur Chemistry*, Bangor, July 1974, Abstract B20; (b) *ibid., Tetrahedron Lett.*, 973 (1975).
(5) (a) E. T. Kaiser, *Acc. Chem. Res.*, **3**, 145 (1970); (b) O. R. Zaborsky and E. T. Kaiser, *J. Am. Chem. Soc.*, **88**, 3084 (1966).
(6) E. B. Fleischer, E. T. Kaiser, P. Langford, S. Hawkinson, A. Stone, and R. Dewar, *Chem. Commun.*, 197 (1967).
(7) (a) "Tables of Interatomic Distances and Configurations in Molecules", *Chem. Soc., Spec. Publ.*, **No. 11**, 1 (1958); **No. 18**, 1 (1965); (b) A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 947 (1975).
(8) (a) M. B. Davy, K. T. Douglas, J. S. Loran, A. Steltner, and A. Williams, *J. Am. Chem. Soc.*, in press; (b) K. T. Douglas, A. Steltner, and A. Williams, *J. Chem. Soc., Chem. Commun.*, 353 (1975).
(9) R. V. Vizgert, *Russ. Chem. Rev.*, (*Engl. Transl.*), **32**, 1 (1963).
(10) A bibliography of work on hydroxyl assistance is given in A. Williams and G. Salvadori, *J. Chem. Soc., Perkin Trans. 2*, 883 (1972).
(11) M. I. Page, *Chem. Soc. Rev.*, **2**, 295 (1975).
(12) A. Wagenaar, A. J. Kirby, and J. B. F. N. Engberts, *Tetrahedron Lett.*, 3735 (1975); 489 (1976).
(13) (a) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960); (b) A. Williams, *ibid.*, **98**, 5645 (1976).