Mechanisms of Substitution Reactions at Sulfinyl Sulfur. V. Halide and Acetate Ion Catalysis of the Solvolysis of Arylsulfinyl Sulfones in Acetic Acid–Water[1]

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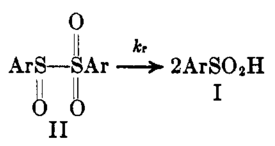
The solvolysis (eq 1) of arylsulfinyl sulfones (II) has been studied in acetic acid–water (5–40% water) in both the presence and absence of small amounts of added sulfuric acid. The results show that, in the absence of added sulfuric acid in solutions containing more than 10% water, an acetate ion catalyzed reaction, having the rate-determining step shown in eq 7, is the principal contributor to the solvolysis rate. In addition, the chloride and bromide ion catalyzed solvolyses of II have been studied in acetic acid–15% water and combination of these data with those for the acetate ion catalyzed reaction in the same solvent reveals how k_{Nu}, the rate constant for nucleophilic attack on the sulfinyl group of II (eq 6 or 7), depends on nucleophile structure in this solvent. Comparison of these data with those for the reactivity of the same nucleophiles in the same reaction in 60% dioxane shows that the change in solvent leads to interesting and significant changes in both relative and absolute reactivity. These are interpreted by considering the differences in the susceptibility of the various anions and transition states to stabilization by hydrogen-bonding interactions with a protic solvent and the fact that acetic acid is a better hydrogen bond donor than water. The uncatalyzed (or spontaneous) solvolysis of II in aqueous acetic acid has also been studied and it is concluded that its mechanism (eq 12) is the same as that of the uncatalyzed hydrolysis of II in aqueous dioxane.

We have previously carried out an extensive investigation of the solvolysis of arylsulfinyl sulfones (eq 1) in acetic acid–1% water solvent containing varying



$$\underset{\text{II}}{\mathrm{ArS(=O)-S(=O)_2Ar}} \xrightarrow{k_r} \underset{\text{I}}{2\mathrm{ArSO_2H}} \qquad (1)$$

amounts of added sulfuric acid (0.00–1.00 *M*).[2] Under these conditions the rate constant for solvolysis (k_r) can be expressed as the sum of an acid-independent and an acid-dependent term (eq 2). Because the

$$k_r = k + k'h_0{}^a \qquad (2)$$

$$a = 0.8\text{–}1.0 \text{ depending on Ar group in II}$$

acid-dependent term ($k'h_0{}^a$) is the dominant one in acetic acid–1% water solutions containing 0.20 *M* or greater H_2SO_4, almost all our attention in this earlier study was concentrated on the acid-catalyzed reaction. We did, however, measure a few solvolysis rates in acetic acid–5% water and these revealed that in this somewhat more aqueous medium the acid-catalyzed term was in general a much less important contributor to the over-all solvolysis rate. This indicated that the nonacid-catalyzed component of the solvolysis of II in this particular solvent system could be conveniently studied by examining the behavior of the solvolysis of II in the region of low sulfuric acid concentration (0.00–0.10 *M*) in this and more aqueous acetic acid.

The subsequent discovery[3] that acetate ion is one of the nucleophiles that can catalyze the hydrolysis of II in aqueous dioxane made a study of this kind imperative, because it raised the distinct possibility that all or part of the observed rate of solvolysis of II in aqueous acetic acid in the absence of added sulfuric acid might be due to an acetate-catalyzed reaction, the acetate ion coming from autoprotolysis of the solvent (eq 3). As outlined in the present paper, we

$$\mathrm{AcOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{AcO^-} + \mathrm{H_3O^+} \qquad (3)$$

have indeed found that an acetate-catalyzed reaction is an important contributor to the total hydrolysis rate of II under such conditions and we have studied this phenomenon in some detail.

The dramatic increase in the rate of many S$_N$2 substitution reactions which occurs on going from protic to aprotic polar solvents and the equally interesting alterations in the relative reactivities of a series of nucleophiles toward a given substrate which often accompany the same change in solvent have been amply documented[4,5] and have sparked much interest[6,7] in the general question of solvation phenomena involving reactants and transition state in such reactions. In this connection, it is also of interest to examine the effect on various nucleophilic substitutions of a change from water to another protic solvent, such as acetic acid, which is capable of more effective hydrogen-bonding solvation of an anion. By measuring the reactivity toward II of several other nucleophiles besides acetate ion in a solvent such as 85% acetic acid and comparing the results with our previous data[3] for nucleophilic attack by the same species on this substrate in 60% dioxane, we can provide just this sort of information.

Results

The solvolysis of the sulfinyl sulfones was studied at 21.4° in acetic acid–water mixtures ranging from 5 to 40% in water content. Rates were followed by measuring the disappearance of II spectrophotometrically. Two different arylsulfinyl sulfones, the *p*-anisyl compound (IIa, Ar = *p*-$CH_3OC_6H_4$) and the *p*-tolyl compound (IIb, Ar = *p*-$CH_3C_6H_4$), were studied. The solvolysis rate constants (k_r) were obtained from the slopes of first-order plots of sulfinyl sulfone disappearance. These plots showed excellent linearity in every case. The results for all of the runs,

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-106-65.

[2] J. L. Kice and G. Guaraldi, *J. Org. Chem.*, **31**, 3568 (1966).

[3] J. L. Kice and G. Guaraldi, *Tetrahedron Letters*, 6135 (1966).

[4] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[5] (a) A. J. Parker, *J. Chem. Soc.*, 1328, 4398 (1961); (b) L. Friedman and H. Shecter, *J. Org. Chem.*, **25**, 877 (1960).

[6] (a) E. A. S. Cavell and J. A. Speed, *J. Chem. Soc.*, 226 (1961); (b) J. A. Leary and M. Kahn, *J. Am. Chem. Soc.*, **81**, 4173 (1961); (c) A. J. Parker, *Australian J. Chem.*, **16**, 585 (1963).

[7] (a) B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc., Sect. B*, 152 (1966); (b) A. J. Parker, *ibid., Sect. A*, 220 (1966); (c) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

TABLE I

SOLVOLYSIS OF SULFINYL SULFONES IN ACETIC ACID–WATER[a]

Sulfinyl sulfone[b]	Solvent[c]	$[H_2SO_4] \times 10^2$, M	$k_r \times 10^3$, sec^{-1}
IIa	HOAc–5% H_2O	0.00	0.43
		0.11	0.31
		0.28	0.33
		0.94	0.33
		4.6	0.46
	HOAc–15% H_2O	0.00	7.2
		0.10	5.1
		0.20	4.0
		0.40	3.2
		1.25	2.0
		2.5	1.6
		5.0	1.4
	HOAc–20% H_2O	0.00	21
		0.00[d]	20
		1.0	9.0
		2.0	5.2
		5.0	3.8
		10.0	3.2
		27.0	3.1
		45.0	3.4
		90.0	4.8
	HOAc–40% H_2O	10.0	41
		20.0	34
		50.0	24
		100	26
IIb	HOAc–5% H_2O	0.00	0.69
		0.11	0.64
		0.95	0.55
		5.7	0.61
		10.0	0.80
	HOAc–15% H_2O	0.10	12.5
		0.20	9.7
		0.40	6.8
		0.63	5.6
		5.0	2.9
	HOAc–20% H_2O	0.00	51
		1.0	20
		2.0	13
		5.0	9.4
		10.0	6.6
		27.0	6.2
		45.0	6.2

[a] All data at 21 4°. [b] Initial II concentrations: IIa, 1.3–1.7 × 10^{-4} M; IIb, 1.3–2.4 × 10^{-4} M. [c] Per cent H_2O refers to grams of water per 100 ml of solution. [d] Ia added initially, 1.7 × 10^{-4} M.

except those involving the use of halide ions as catalysts, are shown in Table I. The data for the halide ion catalyzed reactions are summarized in Table II.

Evidence for Acetate Ion Catalyzed Solvolysis of II.—Examination of Table I shows that the addition of the first small amounts of sulfuric acid to the various acetic acid–water media leads to a pronounced *decrease* in the rate of solvolysis of both sulfinyl sulfones studied. However, once a certain sulfuric acid concentration is reached (the exact value depends on the amount of water in the solvent), further increases in sulfuric acid concentration lead to no further decrease in rate and k_r levels off at a value which remains constant until one gets to higher sulfuric acid concentrations, at which point the previously studied[2] acid-catalyzed solvolysis reaction begins to be a significant factor and the rate starts to increase.

TABLE II

HALIDE ION CATALYZED SOLVOLYSIS OF IIa IN ACETIC ACID–15% WATER[a]

Catalyst	$[X^-] \times 10^4$, M	$[H_2SO_4] \times 10^2$, M	$k_r \times 10^3$, sec^{-1}	$k_X = \left[\frac{k_r - k_r^0}{[X^-]}\right]^b$
Br^-	1.98	3.8	56	2.7 × 10^2
		2.5	57	2.8 × 10^2
		1 25	56	2.7 × 10^2
Cl^-	18.8	0.20	39	19
	9.4	0.20	22	18
		1.25	21	20

[a] All data at 21.4°; initial concentration of IIa, 1.4 × 10^{-4} M. [b] k_r^0 equals rate of solvolysis of IIa in the absence of halide ion under otherwise identical conditions. For values used see Table I.

Since the addition of a strong acid will decrease the concentration of acetate ion by repressing the autoprotolysis equilibrium shown in eq 3, a decrease in k_r accompanying the initial addition of sulfuric acid to the solvent is qualitatively what one would expect to observe if an acetate ion catalyzed reaction is an important contributor to k_r in the absence of added acid. The next question to ask is whether the decrease in k_r correlates quantitatively with the decrease in acetate ion with increasing sulfuric acid concentration.

If an acetate ion catalyzed reaction is responsible for the decrease in k_r with increasing $C_{H_2SO_4}$, then, in media of acidity low enough so that the acid-catalyzed solvolysis of II[2] can be neglected, k_r should be given by eq 4, where k_u equals the uncatalyzed

$$k_r = k_u + k_{OAc}[AcO^-] \qquad (4)$$

(or spontaneous) rate of solvolysis of II in that particular acetic acid–water solvent. The acetate ion concentration will be governed by the relationships

$$[AcO^-][H^+] = K_{aut}$$

(K_{aut} = autoprotolysis constant for $AcOH-H_2O$ solvent used)

$$[H^+] = C_{H_2SO_4} + [AcO^-]$$

For solutions where $C_{H_2SO_4} \gg [AcO^-]$, one will have $[AcO^-] = K_{aut}/C_{H_2SO_4}$, but for smaller concentrations of sulfuric acid $[AcO^-]$ must be calculated using

$$[AcO^-] = \frac{\sqrt{C^2_{H_2SO_4} + 4K_{aut}} - C_{H_2SO_4}}{2}$$

The value of K_{aut} for acetic acid–15% water is 2.4 × 10^{-6}.[8] Using this we have calculated $[AcO^-]$ for each sulfuric acid concentration in acetic acid–15% water and in Figure 1 we have plotted the k_r data for both IIa and IIb in this medium against these calculated acetate ion concentrations. As required by eq 4 both plots are nicely linear.

Unfortunately K_{aut} is not known for acetic acid–20% water. However, by restricting ourselves to data for solutions containing enough sulfuric acid (10^{-2} M or greater) so that $C_{H_2SO_4} > [AcO^-]$, we can, by plotting k_r *vs.* $1/C_{H_2SO_4}$, still test the agreement

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[8] K. B. Wiberg and R. J. Evans, *J. Am. Chem. Soc.*, **80**, 3019 (1958).

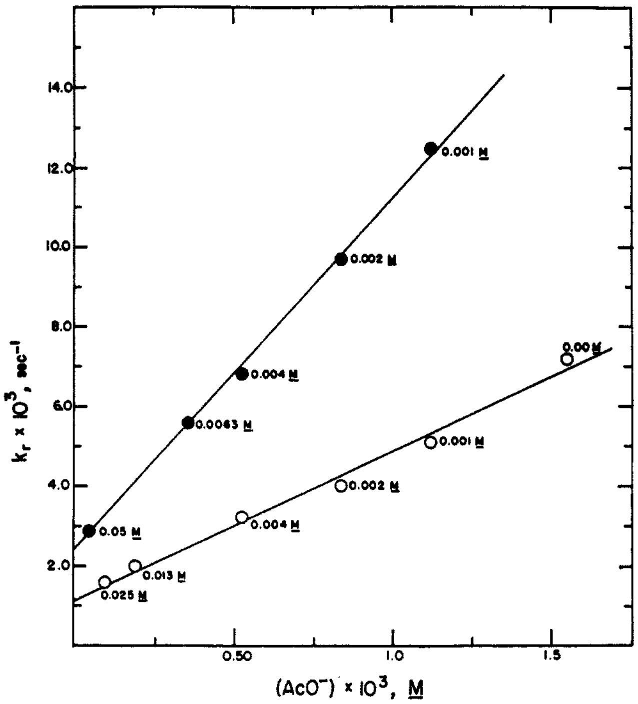


Figure 1.—Log k_r *vs.* $[AcO^-]$ for runs in acetic acid–15% water: ○, IIa; ●, IIb. Concentrations shown on graph refer to concentrations of sulfuric acid added to the various solutions.

of the data with eq 4. Such plots for the AcOH–20% H_2O data are shown in Figure 2. They also are satisfactorily linear.

We conclude, therefore, that the decrease in k_r upon addition of sulfuric acid does indeed correlate quantitatively with the decrease in acetate ion concentration and that an acetate ion catalyzed reaction is the *principal* contributor to the over-all rate of solvolysis of II in the absence of sulfuric acid in acetic acid–15–40% water. In less aqueous media, such as acetic acid–5% water, where K_{aut} is much smaller,[8] it is, while still detectable, much less important.

Unequivocal confirmation of the ability of acetate ion to catalyze the solvolysis of II was provided by two runs with IIb in acetic acid–5% water in which small amounts of sodium acetate were added to that solvent. The rate of solvolysis was found to increase linearly with the amount of added acetate, as indicated by the following data [concentration of added NaOAc ($k_r \times 10^3$, sec^{-1})]: 0.00 *M* (0.69); 5×10^{-4} *M* (3.74); 1×10^{-3} *M* (6.90).

The slopes of the plots in Figure 1 give us k_{OAc}, the second-order rate constant for the acetate ion catalyzed reaction in AcOH–15% H_2O. For IIa, k_{OAc} is 3.7; for IIb, it is 8.8.[9–11]

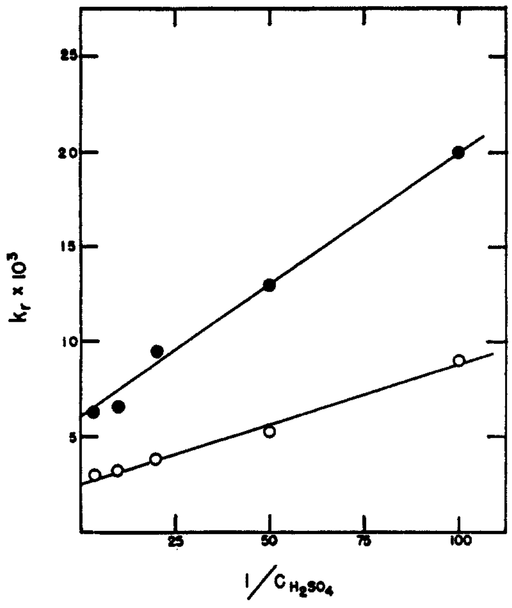


Figure 2.—Log k_r *vs.* $1/C_{H_2SO_4}$ for runs in acetic acid–20% water: ○, IIa; ●, IIb.

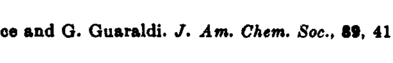
Halide Ion Catalyzed Solvolyses.—The data in Table II show that the presence of small amounts of chloride or bromide ion markedly accelerates the rate of solvolysis of II in acetic acid–15% water. This is similar to what has been observed[3] in 60% dioxane. Two runs at different chloride ion concentrations show that the quantity ($k_r - k_r^0/[Cl^-]$) is independent of chloride ion concentration, indicating that, just as in 60% dioxane,[3] the halide ion catalyzed reaction is first order in halide ion. In the presence of halide ion, k_r can therefore be expressed by eq 5, where k_r^0 equals the rate of solvolysis of II in the absence of added halide ion under otherwise identical conditions and k_X is the second-order rate constant for the halide ion catalyzed reaction. Experiments

$$k_r = k_r^0 + k_X[X^-] \qquad (5)$$

varying the sulfuric acid concentration (Table II) show that k_X is not dependent on $C_{H_2SO_4}$ in the region of low sulfuric acid concentration, a result which is also in accord with previous experience in 60% dioxane.[3,12]

Discussion

Mechanism of the Acetate Ion Catalyzed Solvolysis of II.—In the absence of added strong acid an acetate ion catalyzed reaction is the principal contributor to the rate of solvolysis of II in aqueous acetic acid containing more than about 10% water. In AcOH–15% H_2O the second-order rate constant, k_{OAc}, for this reaction shows the following dependence on sulfinyl sulfone structure: ($k_{OAc}^{IIb}/k_{OAc}^{IIa}$) = 2.4. This is very similar to the values of ($k_{Nu}^{IIb}/k_{Nu}^{IIa}$) observed previously[3,12] in 60% dioxane for the relative reactivities of IIa and IIb in nucleophilic substitutions of the type


(6)

$$Nu^- + Ar\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-\underset{\underset{O}{\|}}{S}Ar \xrightarrow{k_{Nu}} Ar\underset{\underset{O}{\|}}{S}Nu + ArSO_2^- \qquad (6)$$

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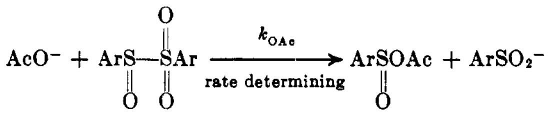
[9] Accurate values of k_{OAc} cannot be determined for AcOH–20% H_2O or AcOH–40% H_2O because K_{aut} is not known for these two media. In the case of AcOH–5% H_2O, K_{aut} has been reported by two groups of workers,[8,10] but there is uncertainty about its exact value.[11] In AcOH–5% H_2O we can, however, make use of the two runs with added sodium acetate to estimate k_{OAc} for IIb in that solvent. The value of k_{OAc} so obtained, 6.1, suggests that k_{OAc} for a given sulfinyl sulfone decreases with an increase in the percentage acetic acid in the solvent. It might also be noted that, given this value of k_{OAc} for IIb in AcOH–5% H_2O, the data in Table I on the decrease of k_r with increasing sulfuric acid concentration in AcOH–5% H_2O are in much better agreement with the value of K_{aut} given by Kilpi and Lindell[10] than with the one estimated by Wiberg and Evans.[8]

[10] S. Kilpi and E. Lindell, *Ann. Acad. Sci. Fiennicae. Series II*, **121**, 1 (1963); *Chem. Abstr.*, **59**, 9388*h* (1963).

[11] Wiberg and Evans[8] give K_{aut} for acetic acid-5% water as 4×10^{-8}. Kilpi and Lindell,[10] on the other hand, estimate the same quantity as 4×10^{-9}.

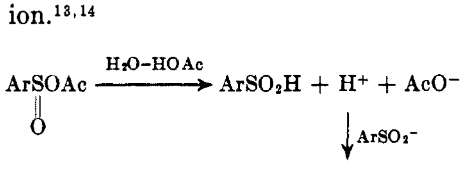
[12] J. L. Kice and G. Guaraldi. *J. Am. Chem. Soc.*, **89**, 4113 (1967).

and indicates that the acetate ion catalyzed reaction involves the same kind of rate-determining step as the other Nu-catalyzed hydrolyses of II, *i.e.*



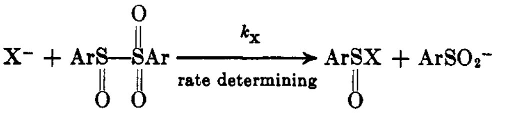
$$\mathrm{AcO^- + Ar\underset{O}{S}\!-\!\overset{O}{\underset{O}{S}}Ar \xrightarrow[\text{rate determining}]{k_{OAc}} Ar\underset{O}{S}OAc + ArSO_2^-} \qquad (7)$$

Subsequent steps (eq 8) then convert both ArS(O)OAc and $ArSO_2^-$ into sulfinic acid and also regenerate acetate ion.[13,14]

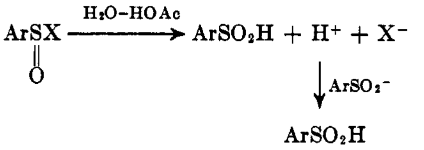


$$\begin{array}{ll} \mathrm{Ar\underset{O}{S}OAc \xrightarrow{H_2O-HOAc} ArSO_2H + H^+ + AcO^-} & (8) \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \mathrm{ArSO_2^-} & \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{ArSO_2H} & \end{array}$$

Effect of Solvent on the Reactivity of Nucleophiles toward II*a*.—In the halide ion catalyzed solvolyses the rate-determining step is known[3,12] to involve nucleophilic attack of X^- on II (eq 9). The values of k_X in Table II are therefore equal to the rate constants k_{Nu} for eq 6 in AcOH–15% H_2O for the cases where Nu^- equals Cl^- or Br^-, just as k_{OAc} is equal to the same quantity for the case where Nu^- equals AcO^-.



$$\mathrm{X^- + Ar\underset{O}{S}\!-\!\overset{O}{\underset{O}{S}}Ar \xrightarrow[\text{rate determining}]{k_X} Ar\underset{O}{S}X + ArSO_2^-} \qquad (9)$$



$$\begin{array}{ll} \mathrm{Ar\underset{O}{S}X \xrightarrow{H_2O-HOAc} ArSO_2H + H^+ + X^-} & (10) \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \mathrm{ArSO_2^-} & \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{ArSO_2H} & \end{array}$$

Our particular interest here is to compare the nucleophilic reactivity toward IIa of the three nucleophiles AcO^-, Cl^-, and Br^- with their reactivity toward the same sulfinyl sulfone in 60% dioxane.[3,12] This is done in Table III. From this table we see that the change from 60% dioxane to AcOH–15% H_2O produces quite a significant change in the relative reactivity of the three nucleophiles. Thus, relative to chloride ion, acetate ion is a considerably weaker nucleophile in acetic acid–15% water than it was in 60% dioxane and bromide ion is a considerably stronger one. These changes come about because, while k_{Nu} for Cl^- is roughly the same, k_{Nu} for AcO^- is notably smaller in AcOH–15% H_2O than in 60% dioxane and k_{Nu} for bromide ion is about four times larger.

Table III

Nucleophilic Reactivity toward IIa

Nucleophile	k_{Nu} for eq 6: AcOH–15% H_2O	k_{Nu} for eq 6: 60% dioxane	(k_{Nu}/k_{Cl}): AcOH–15% H_2O	(k_{Nu}/k_{Cl}): 60% dioxane
AcO^-	3.7	9.0	0.19	0.75
Cl^-	19	12	(1.0)	(1.0)
Br^-	2.7×10^2	65	14	5.4

Acetic acid–15% water has a significantly lower dielectric constant ($D = 15$)[8] than that of 60% dioxane ($D = 27$).[15] Such a decrease in solvent dielectric constant, *per se*, will increase k_{Nu}.[16–18] Although an exact estimate of the magnitude of the effect is not possible, the available data[16–18] for analogous SN2 substitutions involving sp^3 carbon suggest that it will not be particularly large. More important, the increase in k_{Nu} due to this factor, while about the same for all three nucleophiles, should, if anything, be larger for acetate than for chloride, and larger for chloride than for bromide. The change in dielectric constant therefore cannot be responsible for either the decrease in (k_{OAc}/k_{Cl}) or the increase in (k_{Br}/k_{Cl}) which is observed on going from 60% dioxane to AcOH–15% H_2O.

As previously mentioned, the rate constants for SN2 reactions of the type given in eq 11 are usually

$$Nu^- + RX \rightarrow RNu + X^- \qquad (11)$$

orders of magnitude smaller in protic solvents than they are in aprotic ones of comparable dielectric constant.[4,5a] Parker and his coworkers have shown[5a,7a] that this occurs because the anion Nu^- is stabilized in the protic solvent by hydrogen-bonding interactions with the solvent to a greater degree than is the transition state for eq 11 ($Nu^{\delta-}$---R---$X^{\delta-}$). The effect is most pronounced when Nu^- is a small, nonpolarizable anion, since this kind of anion experiences the largest gain in solvation energy from this sort of solvation. Because of this, rate constants for reactions involving small, nonpolarizable Nu^- usually show a much larger decrease on going from an aprotic to a protic solvent than do reactions involving more polarizable Nu^-.[5a] The difference between the behavior of the various types of nucleophiles is large enough that the relative reactivity of a series of Nu^-

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(13) Actually, in the solutions containing little or no added sulfuric acid, the sulfinate ion $ArSO_2^-$ will not be completely protonated. Given the pK_a's of $ArSO_2H$[14] and acetic acid and the concentration of acetic acid in the present solutions, we estimate that the relation between the sulfinate ion concentration and the total concentration of sulfinic acid species would be

$$[ArSO_2^-] = C_{ArSO_2H}\left(\frac{1}{1 + \frac{3.6 \times 10^{-3}}{[AcO^-]}}\right); \quad C_{ArSO_2H} = [ArSO_2^-] + [ArSO_2H]$$

Because of the low concentrations of II used ($\sim 1.5 \times 10^{-4}$ *M*), this does not lead, however, even in the worst case, to more than a 10% decrease in the acetate ion concentration of the solution during the course of any run (due to protonation of AcO^- rather than $ArSO_2^-$ by part of the H^+ released in eq 8). For those solutions that contain a significant amount of initially added strong acid, and therefore a low acetate ion concentration, the fraction of $ArSO_2^-$ remaining unprotonated is, of course, much smaller, so that the percentage change in acetate ion concentration during these runs is also very small. The good first-order kinetics exhibited by all runs and the excellent fit of the data in Figure 1 to eq 4 demonstrate that not only is the change in acetate ion concentration during any run effectively negligible but also the $ArSO_2^-$ concentration at all times remains small enough so that the reverse of reaction 7, *i.e.*

$$ArSO_2^- + ArS(O)OAc \rightarrow II + OAc^-$$

does not compete to any extent with the hydrolysis of ArS(O)OAc to $ArSO_2H$. Based on previous experience with acetate ion in 60% dioxane,[3] this is what would be expected for the sulfinate ion concentrations involved in the present experiments.

(14) C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Am. Chem. Soc.*, **83**, 4602 (1961).

(15) Landolt-Bornstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," Vol. II, Part 6, 6th ed, Springer Verlag, Berlin, Gottingen, 1959, p 753.

(16) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 349.

(17) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, Inc., New York, N. Y., 1966, pp 31–57. W. J. Broach and E. S. Amis, *J. Chem. Phys.*, **22**, 39 (1954).

(18) (a) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd ed, Clarendon Press, Oxford, 1947, pp 120 ff; (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, New York, N. Y., 1961, pp 147–150.

in eq 11 is quite different in a protic solvent than in an aprotic one.[5a]

In the present case we are dealing with a change from one protic solvent (60% dioxane) to another (AcOH–15% H_2O) which, because of the greater strength of acetic acid as a hydrogen bond donor, should be even better at stabilizing anions by hydrogen-bonding interactions. Of the trio of nucleophiles in Table III, AcO^-, being the least polarizable,[19,20] should experience the greatest increase in solvation energy from such an increase in the ability of the solvent to act as a hydrogen bond donor, while Br^-, being the most polarizable, should experience the least increase in solvation energy. Since the change from 60% dioxane to AcOH–15% H_2O will increase the solvation energy of AcO^- more than that of Cl^-, it will decrease the free energy of AcO^- relative to Cl^- and will cause (k_{OAc}/k_{Cl}) to be appreciably smaller in AcOH–15% H_2O than it is in 60% dioxane. Since the same change in solvent will increase the solvation energy of Br^- less than that of chloride ion, (k_{Br}/k_{Cl}) should be larger in AcOH–15% H_2O than in 60% dioxane, again in agreement with what is found.

In the cases Parker investigated[5a,7a] the gain in solvation energy due to hydrogen-bonding interactions experienced on going from the aprotic to the protic solvent was always greater for the anion Nu^- than for the transition state $(Nu^{\delta-}{-}{-}{-}R{-}{-}{-}X^{\delta-})$, so that rate constants for eq 11 were always lower in the protic solvent. On this basis, one might think that for each nucleophile in the present system k_{Nu} would be smaller in AcOH–15% H_2O than it is in 60% dioxane. While this is true for the case of AcO^-, it is not so in the case of Cl^-, or, particularly, in the case of Br^-.

We believe this behavior can be quite easily explained as follows. Parker has also shown[7a] that, for a given Nu^-, hydrogen-bonding solvation of the transition state $(Nu^{\delta-}{-}{-}{-}R{-}{-}{-}X^{\delta-})$ is significantly stronger when X = Cl than when X = I, with the result that the rate decrease is always much smaller for transfer of a reaction of RCl to the protic solvent than for the corresponding reaction of RI. Thus, when the *leaving group* X is one which, as X^-, is susceptible to strong hydrogen-bonding solvation, hydrogen-bonding solvation of the transition state of an SN2 displacement can be quite significant. In the present case the leaving group is $ArSO_2$ and, since $ArSO_2^-$ should certainly be strongly stabilized by hydrogen-bonding interactions with a protic solvent, we would expect that the transition state for eq 6 should be quite strongly stabilized by hydrogen-bonding interactions with protic solvents. In particular, its solvation energy due to this phenomena might well be closely comparable with the solvation energy for a polarizable anion like Br^-. If so, transfer of the reaction of Br^- with IIa from 60% dioxane to AcOH–15% H_2O would increase the hydrogen-bonding solvation energy of Br^- and the transition state by essentially the same amount; in that event, one can see how the previously mentioned rate enhancement, which would be expected as the result of the lower dielectric constant of AcOH–15% H_2O, could easily be greater than any retardation caused by that solvent being a better hydrogen bond donor, so that k_{Nu} would actually be quite a bit larger in AcOH–15% H_2O, just as is observed.

The present results suggest that it might be quite interesting to determine the effect of a change in solvent from aqueous dioxane to acetic acid on the rates of a variety of displacements of the type shown in eq 11 and that such studies might contribute to increased knowledge of the effect of solvation phenomena on SN2 reactions.

Mechanism of the Uncatalyzed Solvolysis of II in Acetic Acid–Water.—Since the rate constants for the halide ion catalyzed hydrolysis of II in aqueous dioxane[12] have both an acid-independent and an acid-dependent term, *i.e.*

$$k_X = k_X^\circ + k_x'[H^+]$$

one may wonder whether the uncatalyzed (or spontaneous) solvolysis of II in acetic acid–water (k_u in eq 4) could possibly represent a reaction catalyzed by *both* acetate and hydrogen ion, rather than being simply an uncomplicated solvolysis of II. The following considerations, however, indicate that this is not the case. Studies in 60% dioxane[3,12] with the halide ions and other similar nucleophilic catalysts for the hydrolysis of II show that k_X°/k_X' is not very dependent on X^- and that k_X' is usually no more than 2–3 times larger than k_X°, so that the acid-dependent term contributes little except at high acidities. In the present system the data in Table II show that an acid-dependent term cannot be detected as a contributor to either k_{Cl} or k_{Br} at the acidities used in the present work; if a term of the form $k_x'[H^+][X^-]$ makes no contribution to the halide ion catalyzed solvolysis under these conditions, it seems quite impossible that one of the form $k_{OAc}'[H^+][OAc^-]$ could be responsible for a term as large as k_u.

We therefore feel quite certain that the spontaneous solvolysis of II in acetic acid–water does, in fact, represent merely a solvolysis of II by the solvent. Table IV indicates how the rate of spontaneous solvolysis of II (k_u) depends on the percentage of water in the solvent. It also provides a comparison between the rates of spontaneous solvolysis in aqueous acetic acid and those[12] in aqueous dioxane solutions of roughly comparable water content. From Table IV we see that in aqueous acetic acid k_u increases markedly with increasing water content of the medium. We also see that for a given water content in the 20–40% region k_u is about tenfold larger in aqueous acetic acid than it is in aqueous dioxane.

TABLE IV

RATE OF SPONTANEOUS HYDROLYSIS OF II IN ACETIC ACID–WATER

	AcOH–H_2O, wt % H_2O[b]				Dioxane–water, % H_2O (v/v)[a]	
	5%	15%	20%	40%	20%	40%
$k_u^{IIa} \times 10^3$, sec^{-1}	0.3	1.1	2.5	24	0.26	2.0
$k_u^{IIb} \times 10^3$, sec^{-1}	0.5	2.5	6.0	...	0.62	4.6

[a] Data from ref 12. [b] Percentage of H_2O refers to grams of water per 100 ml of solution.

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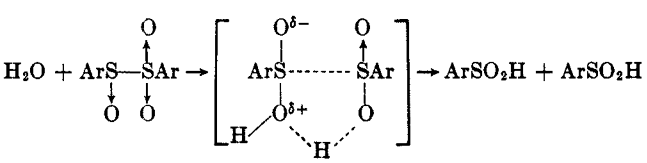
(19) Edwards' E_n values[20] presumably provide a good indicator of relative polarizability.

(20) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1965, p 54.

Our previous studies[12] of the spontaneous hydrolysis of II in aqueous dioxane have led us to suggest the mechanism shown in eq 12 for the reaction. This



$$H_2O + ArS(\rightarrow O)-S(\rightarrow O)_2Ar \rightarrow [\text{transition state}] \rightarrow ArSO_2H + ArSO_2H$$

transition state (12)

involves a nucleophilic attack of water on the sulfinyl group which is concerted with the cleavage of S–S bond in II and the transfer of one of the protons of the attacking water molecule to the departing $ArSO_2$ group. Since k_u drops off just about as sharply with decreasing water content in aqueous acetic acid as it does in aqueous dioxane, it seems likely that it is a water molecule which performs the nucleophilic attack on the sulfinyl group in both solvents. In view of the presumably much greater nucleophilicity of water, compared with that of acetic acid, this is perfectly reasonable. We believe that the mechanism for the spontaneous solvolysis of II in aqueous acetic acid is essentially the same as that in aqueous dioxane, namely, the one shown in eq 12.

For aqueous dioxane we suggested[12] that the proton transfer depicted in eq 12 probably took place *via* a chain of intervening water molecules (a so-called Grotthus chain). In aqueous acetic acid, in contrast to aqueous dioxane, both types of solvent molecules can participate in such a chain. This could mean that the amount of solvent reorganization (and loss of entropy) involved in the formation of the chain will be less in aqueous acetic acid than in aqueous dioxane and could be responsible for the fact that k_u is larger in aqueous acetic acid than in aqueous dioxane of similar water content.

Another factor which might also be responsible for the larger k_u in aqueous acetic acid is the following. The transition state for the spontaneous hydrolysis of II presumably has some dipolar character, as shown in eq 12. While water should do a better job than acetic acid of solvating the partial positive charge on oxygen, acetic acid should be better than water in solvating the partial negative charge on the other oxygen. Thus a mixed acetic acid–water solvent might be able to do a better job of solvating the dipolar transition state than one like aqueous dioxane, in which water was the sole protic component of the solvent. Of course, to some extent this would presumably be counterbalanced by the unfavorable effect of the lower dielectric constant of acetic acid–water solutions of a given water content.

The fact that k_u is quite a bit larger in acetic acid–water than in dioxane–water solutions of roughly similar water content can thus be accommodated perfectly well with the mechanism for the spontaneous hydrolysis in eq 12.

Experimental Section

Preparation and Purification of Materials.—The preparation and purification of the two sulfinyl sulfones has been described in earlier papers[2,21] as has the purification of potassium chloride[21] and acetic acid.[21] Potassium bromide (reagent grade) was recrystallized twice from water. The concentrated sulfuric acid (Baker and Adamson reagent grade) used is certified by the manufacturer to contain less than $2 \times 10^{-5}\%$ chloride.

Procedure for Kinetic Runs.—The apparatus used has already been described.[21] The exact procedure employed depended on the water content of the solvent being used. For the runs in acetic acid–5% water a weighed amount of II was placed in chamber A of the apparatus and the proper volume of acetic acid–5% water solvent containing the desired concentration of sulfuric acid was placed in chamber B. The solution in B was then brought to temperature in the constant-temperature bath. The sulfinyl sulfone was then dissolved as quickly as possible in the solution in B and once solution was effected the final solution was allowed to flow into spectrophotometer cell C. The apparatus was immediately placed in a previously described[21] thermostated cell holder inside a Cary Model 15 spectrophotometer and the disappearance of the sulfinyl sulfone was followed by recording the decrease in the optical density with time at 300–306 mμ, the exact wavelength used depending on the sulfinyl sulfone.[2,21]

In more aqueous acetic acid the solid sulfinyl sulfone dissolves too slowly for the above procedure to be used, particularly since the rates of hydrolysis of II are faster in such solvents. For the runs in these more aqueous media the procedure was modified as follows. A weighed amount of II was dissolved in a known volume of glacial acetic acid and a small measured volume of this solution was pipetted into chamber A. Because the sulfinyl sulfones solvolyze only very slowly in glacial acetic acid, this does not lead to any significant amount of solvolysis of II during the time necessary to prepare this solution, place it in chamber A, and bring it to temperature. At that point it was then mixed with a solution which had been previously placed in chamber B and which consisted of the remaining required acetic acid, the necessary amount of water, and any other additives—sulfuric acid, potassium chloride or bromide—that were to be used in that run. The final solution was then poured into cell C and the kinetics of the hydrolysis were followed as before. With this procedure one could begin accurate rate measurements within a few seconds after mixing, so that quite rapid rates of hydrolysis could be followed.

Registry No.—IIa, 13737-19-4; IIb, 788-86-3; acetic acid, 64-19-7; water, 7732-18-5.

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(21) J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966).