

Mechanisms of Substitution Reactions at Sulfinyl Sulfur. Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid-Water¹

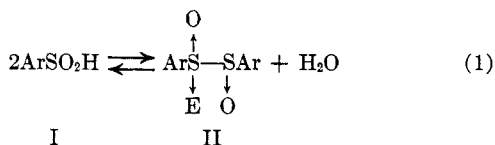
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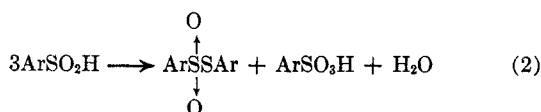
The effect of aryl group structure on the rate and equilibrium constants associated with the equilibrium (eq 1) between an aromatic sulfinic acid (I) and the corresponding sulfinyl sulfone (II) has been investigated. Briefly, the significant findings are as follows. (1) The equilibrium constant for formation of II is increased by electron-donating substituents in the aryl group. (2) The rate of acid-catalyzed solvolysis of II is *decreased* by electron-donating substituents in the aromatic ring attached to the *sulfonyl* group, but it is *increased* by the presence of the same substituents in the ring attached to the *sulfinyl* sulfur. This is particularly marked for the *p*-anisyl compound (II_d) which undergoes acid-catalyzed solvolysis much faster than any of the other sulfinyl sulfones. The mechanistic implications of these and other results are considered, and it is concluded that as the aryl group becomes better able to stabilize any electron deficiency on the sulfinyl sulfur the mechanism for the acid-catalyzed solvolysis of II goes from A₂ to A₁ in type. A suitable mechanism for acid-catalyzed solvolysis of II_b and *c* is accordingly thought to be eq 5 while the *p*-anisyl compound (II_d) is believed to undergo the same solvolysis *via* a mechanism (eq 6) not involving nucleophilic attack of solvent on the sulfinyl sulfur in the rate-determining step. The solvolysis of II_d would appear to be the first example of a substitution at sulfinyl sulfur in which there is no attack of the nucleophile on the sulfinyl group either prior to or during the rate-determining step.

In the preceding paper² we have seen that in acetic acid one can determine both the rate and equilibrium constants associated with the equilibrium (eq 1) be-



Ia and IIa, Ar = *p*-CH₃C₆H₄
 Ib and IIb, Ar = C₆H₅
 Ic and IIc, Ar = *p*-ClC₆H₄
 Id and II_d, Ar = *p*-CH₃OC₆H₄

tween an aromatic sulfinic acid (I) and the corresponding sulfinyl sulfone (II). In that paper our studies were confined to the equilibrium involving Ia and IIa, and principal discussion centered around the significance of the results for the detailed mechanism of the disproportionation of aromatic sulfinic acids (eq 2). In the present communication we will consider



the specific mechanism of the forward and reverse steps of the I-II equilibrium in acetic acid solvent.

The hydrolysis of II to two molecules of sulfinic acid (reverse step of eq 1) represents, of course, a substitution at a sulfinyl sulfur. Recent reports³⁻⁷ attest to current interest in the mechanisms of reactions involving substitution at sulfinyl and other tri-substituted sulfur atoms. Because the hydrolysis of II would seem to be significantly different in at least

several respects from the reactions investigated in ref 3-7, one might hope that information about its mechanism could contribute toward better understanding of the general principles governing reactions of this type.

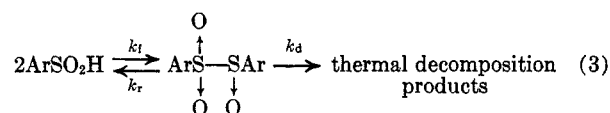
Results

In discussing the mechanism of the forward and reverse steps of the I-II equilibrium in acetic acid solvent we will make use of the data on the behavior of the Ia-IIa system given in Tables II and III of ref 2. To this data we will add the results outlined in the remainder of this section.

Rate and Equilibrium Constants for I-II Equilibria.—

The rate and equilibrium constants associated with the equilibria between Ib-d and the corresponding sulfinyl sulfones can be investigated by the same spectrophotometric procedure described² for the Ia-IIa system. We might note, however, that the wavelength at which the sulfinyl sulfone absorption maximum occurs varies slightly with the nature of the aryl group, as does also the magnitude of the extinction coefficient (see the Experimental Section).

In the present work data were obtained for the various I-II equilibria at 21° in acetic acid solvent containing known amounts of water (1-5%) and sulfuric acid (0.00-1.00 M). The results are shown in Table I. They are expressed in terms of three constants: K_e , k_f , and k_r . These are defined as in the previous paper.²



$K_e = \frac{k_f}{k_r + k_d}$, $k_r \gg k_d$ for all reaction conditions in present study

Solvolysis Rate for *p*-Chlorobenzenesulfinyl *p*-Tolyl Sulfone (III).—To provide further understanding of the reactivity pattern exhibited by sulfinyl sulfones IIa-d, we prepared the unsymmetrical compound, *p*-chlorobenzenesulfinyl *p*-tolyl sulfone, and measured its rate of solvolysis, k_r , under several reaction conditions. The results are shown in Table II.

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

(3) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, *ibid.*, **36**, 1452 (1964).

(4) C. R. Johnson, *ibid.*, **35**, 1020 (1963); C. R. Johnson and W. R. Phillips, *Tetrahedron Letters*, 2101 (1965).

(5) (a) D. Landini, F. Montanari, H. Hogeveen, and C. Maccagnani, *ibid.*, 2691 (1964); (b) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966); (c) S. Allenmark, *Acta Chem. Scand.*, **19**, 1 (1965).

(6) S. Oae, T. Kitao, Y. Kitaoka, and S. Kawamura, *Bull. Chem. Soc. Japan*, **38**, 546 (1965).

(7) J. Day and D. J. Cram, *J. Am. Chem. Soc.*, **87**, 4398 (1965).

TABLE I
RATE AND EQUILIBRIUM CONSTANTS FOR I-II EQUILIBRIA IN
ACETIC ACID AT 21°

Ar (eq 1)	C H ₂ O, M ^a	CH ₃ SO ₃ H, M	K _e , M ⁻¹	k _r × 10 ⁴ , sec ⁻¹	k _r × 10 ⁴ , M ⁻¹ sec ⁻¹
C ₆ H ₅	0.56	1.00	0.0455	2.6	1.2
		0.80	0.0415	1.7	0.71
		0.60	0.0313	1.1	0.35
		0.40	0.0246	0.71	0.177
		0.20	0.0170	0.30	0.053
		0.10	0.0133	0.18	0.025
		0.00	...	0.10 ^b	...
2.80	1.00	1.00	0.0040	2.3	0.092
		0.00	...	1.3 ^b	...
		0.00
p-ClC ₆ H ₄	0.56	1.00	0.0153	4.5	0.69
		0.80	...	3.3 ^b	...
		0.60	0.0100	2.3	0.23
		0.40	0.0077	1.5	0.115
		0.20	0.0055	0.73	0.041
		0.10	0.0044	0.52	0.024
		0.00	...	0.4 ^b	...
2.80	1.00	1.00	0.0014	10	0.14
		0.00	...	8.2 ^b	...
		0.00
p-CH ₃ OC ₆ H ₄	0.56	1.00	0.362	c	...
		0.60	0.264	c	...
		0.40	0.198	20	40
		0.20	0.145	5.5	8.0
		0.10	0.114	2.2	2.5
		0.05	...	0.95	...
		0.00	...	0.13 ^b	...
2.80	1.00	1.00	0.040	27	11
		0.80	0.034	18	6.1
		0.60	0.027	7.5	2.0
		0.40	0.022	3.1	0.68
		0.00	...	0.44 ^b	...

^a The stoichiometric concentration of water. ^b Too fast to measure. ^c Measured by following the solvolysis of compound II directly.

TABLE II
RATE CONSTANTS FOR SOLVOLYSIS OF
p-CHLOROBENZENESULFINYL p-TOLYL SULFONE IN ACETIC ACID
AT 21°

CH ₂ O, M ^a	CH ₃ SO ₃ H, M	k _r × 10 ⁴ , sec ⁻¹
0.56	1.00	1.6
	0.80	1.17
	0.60	0.83
	0.40	0.59

^a Stoichiometric concentration of water.

Dependence of Solvolysis Rate on Acidity.—Although the rates of solvolysis (k_r) of all the sulfinyl sulfones increase with increasing acidity of the medium they do not do so in the same way. This is perhaps most simply seen by reference to Figure 1, which shows plots of $\log k_r$ for IIa-d and III vs. $-H_0$ for the various acetic acid-0.56 M water-sulfuric acid solutions employed.⁸ Except for the *p*-anisyl compound (II d) such plots are curved. One can at least formally approximate these curved plots by assuming that k_r is composed of the sum of an acid-independent and an acid-dependent term (see eq 4). The percentage

$$k_r = k + k'h_0^a \quad (4)$$

$a = 0.8$ to 1.0 depending on sulfinyl sulfone; see text

contribution of the acid-independent term (k) to k_r at a given acidity seems to depend on the nature

(8) The H_0 values for these solutions used are those of Rocek, *Collection Czech Chem. Commun.*, **22**, 1 (1957).

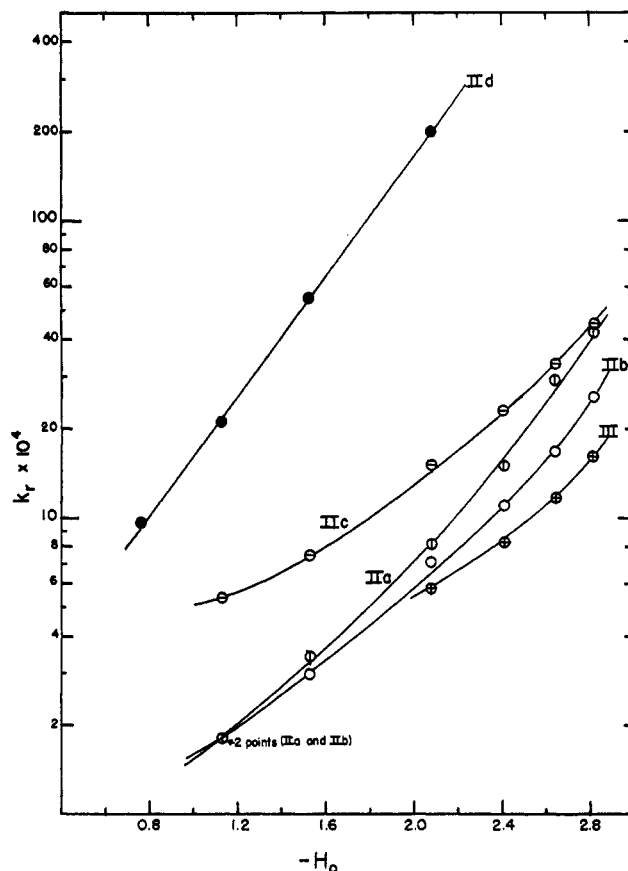


Figure 1.—Dependence of solvolysis rate (k_r) of sulfinyl sulfones on acidity ($-H_0$) in acetic acid-0.56 M water: \odot , IIa; \circ , IIb; \ominus , IIc; \bullet , II d; \oplus , III.

of the aryl group attached to the *sulfinyl* group of the sulfinyl sulfone. Thus for the *p*-anisyl compound k is so much smaller than $k'h_0$, even at 0.10 M sulfuric acid, that it contributes effectively nothing to the observed rate. As a result a plot of $\log k_r$ vs. $-H_0$ is linear, in contrast to the other cases. With both sulfinyl sulfones (IIc, III) having a *p*-chlorophenyl group attached to the sulfinyl sulfur the acid-independent term is responsible for about 25% of the total rate at $H_0 = -2.08$, while for the phenyl (IIb) and *p*-tolyl (IIa) compounds it is responsible for about 18 and 10%, respectively, of k_r at the same acidity. At higher acidities the per cent contribution of the acid-independent term becomes in each case progressively less.

The nature of the aryl group attached to the sulfinyl sulfur also seems to have some influence on the way in which the acid-dependent term responds to changes in h_0 . Thus a in eq 4 is 1.0 for II d, about 0.95 for IIa, 0.87 for IIb, and around 0.82 for IIc and III.

Discussion

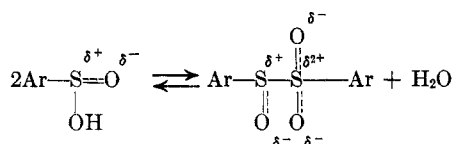
Effect of Structure on K_e .—The influence of the acidity and water content of the solvent on K_e for a I-II equilibrium seems to be effectively independent of the nature of the aryl group. This means that it makes no difference which acetic acid-water-sulfuric acid medium we use for comparing the K_e values of the various I-II equilibria. We have chosen acetic acid-0.56 M water-0.6 M sulfuric acid; the appropriate data are shown in Table III. From these it is evident that the nature of the aryl group has a sizeable effect

TABLE III
EFFECT OF STRUCTURE ON THE EQUILIBRIUM CONSTANT FOR THE
SULFINIC ACID-SULFINYL SULFONE EQUILIBRIUM

Aryl group	$K_e \times 10^3$ (AcOH-0.56 M H ₂ O-0.6 M H ₂ SO ₄)
<i>p</i> -CH ₃ OC ₆ H ₄	26.4
<i>p</i> -CH ₃ C ₆ H ₄	8.2
C ₆ H ₅	3.13
<i>p</i> -ClC ₆ H ₄	1.0

on K_e , electron-donating substituents promoting formation of the sulfinyl sulfone from the sulfinic acid and electron-withdrawing substituents hindering it.

The general effect which the various substituents have on K_e is easily understood. In the sulfinyl sulfone one has a repulsion between two adjacent, somewhat electron-deficient sulfurs that is not present in the sulfinic



acid. By decreasing the magnitude of the electron deficiency at the two sulfurs, electron-releasing substituents (such as *p*-MeO or *p*-Me) can make the equilibrium constant for sulfinyl sulfone formation more favorable. Electron-withdrawing substituents (such as *p*-Cl) make it less favorable by increasing the electron deficiency of the sulfurs and thereby increasing the repulsion between them.

Effect of Sulfinyl Sulfone Structure on Rate of Acid-Catalyzed Solvolysis.—We have seen (eq 4) that in the present solvent system the rate of solvolysis of a sulfinyl sulfone, k_r , can be expressed as the sum of an acid-independent and an acid-dependent term. At high acidities the acid-independent term accounts in all cases for only a small fraction of the over-all rate. For this reason we can use the variation of k_r with structure under such conditions (acetic acid-0.56 M water-1.0 M sulfuric acid) as a valid measure of the effect of changes in structure on the rate of acid-catalyzed solvolysis. Such data are presented in Table IV.

TABLE IV
EFFECT OF STRUCTURE ON THE RATE OF ACID-CATALYZED
SOLVOLYSIS OF SULFINYL SULFONES

Sulfinyl sulfone	Y in Y--S	X in X--SO ₂	$k_r \times 10^3, \text{sec}^{-1}$ (AcOH-0.56 M H ₂ O-1.0 M H ₂ SO ₄) ^a
IIId	CH ₃ O	CH ₃ O	110 ^b
IIa	CH ₃	CH ₃	4.2
III	Cl	CH ₃	1.6
IIc	Cl	Cl	4.5
IIb	H	H	2.6

^a See data at 21°. ^b Extrapolated from data at lower acidities.

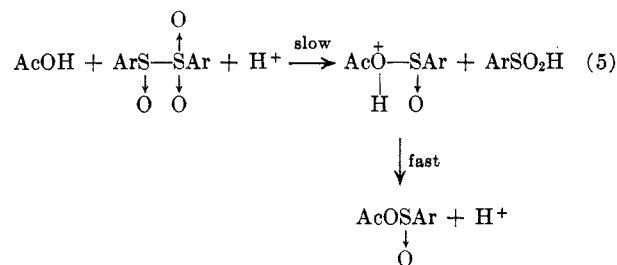
The most striking feature of these data is the fact that the rate of acid-catalyzed solvolysis of the *p*-anisyl compound (IIId) is about 25 times greater than that of any of the other sulfinyl sulfones. Another point worth noting is that the k_r values of IIc and III show that replacement of an electron-withdrawing substituent (*p*-Cl) by an electron-donating one (*p*-Me) in the aromatic ring attached to the *sulfonyl* group leads to a significant decrease in rate. This means that it is

the *p*-anisyl group attached to the *sulfinyl* sulfur in IIId which is *solely* responsible for the fast rate of solvolysis of this compound, and it implies that electron-donating substituents in the ring attached to the sulfinyl group accelerate the rate of acid-catalyzed solvolysis. The same conclusion is also suggested by the relative magnitude of the k_r values of IIa and III, the *p*-toluenesulfinyl compound (IIa) undergoing acid-catalyzed solvolysis about three times faster than the *p*-chlorobenzene-sulfinyl one.

This acceleration of the acid-catalyzed solvolysis rate by electron-donating substituents in the ring attached to the sulfinyl group is not correlated by the Hammett equation, however. Thus, regardless of whether one takes σ or σ^+ constants for the substituents, the actual rate for IIId is much faster than would be predicted from the rates for III and IIa. This sort of behavior suggests that one has a change or, at the least, a significant gradation in mechanism on going from *p*-chlorobenzene-sulfinyl to *p*-toluenesulfinyl to *p*-methoxybenzenesulfinyl.

Mechanism of the Acid-Catalyzed Solvolysis.—Although the available data do not permit one to specify all details of the mechanism, several important points seem clearly established from a collective consideration of the present results and those⁹ on the closely related concomitant sulfide and acid-catalyzed solvolysis of II. First, a proton is transferred to the departing ArSO₂ group in the rate-determining step and this proton transfer is responsible for the acid catalysis of the solvolysis.¹⁰ Second, the solvolysis of the *p*-anisyl compound involves a significantly different mechanism than that of the *p*-chlorophenyl or phenyl compounds. Specifically it appears that a much greater electron deficiency develops on the sulfinyl sulfur in the acid-catalyzed solvolysis of IIId. The simplest way to explain this difference in behavior is to assume that there is much more extensive nucleophilic participation by solvent in the transition state for solvolysis of IIb and IIc than in the case of IIId.

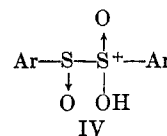
Thus a suggested acceptable mechanism for the solvolysis of IIb and IIc is the one shown in eq 5 in which



Mechanism for acid-catalyzed solvolysis of IIb and IIc

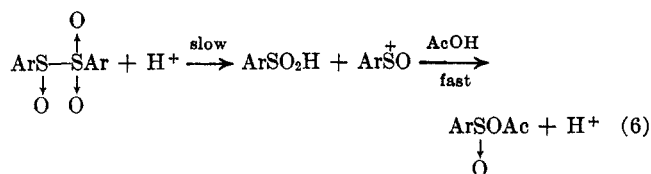
(9) (a) J. L. Kice and G. Guaraldi, *Tetrahedron Letters*, 501 (1966); (b) *J. Am. Chem. Soc.*, in press.

(10) Transfer of the proton to the sulfonyl group prior to the rate-determining step and the intervention of the sulfonyl-protonated sulfinyl sulfone IV as an intermediate has been convincingly ruled out for the concomitant



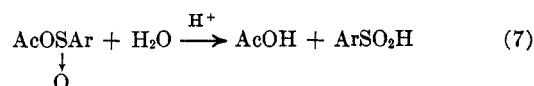
sulfide and acid-catalyzed reaction.⁹ The close similarities between that reaction and the simple acid-catalyzed solvolysis suggest that IV is also unlikely to be an intermediate here.

nucleophilic attack by solvent on sulfinyl sulfur accompanies transfer of the proton to the departing ArSO_2 group. On the other hand, the acid-catalyzed solvolysis of II_d does not require participation of the solvent as a nucleophile and can proceed by the mechanism shown in eq 6. The mixed acetic-sulfinic an-



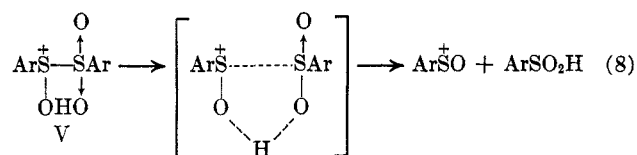
Mechanism for acid-catalyzed solvolysis of II_d

hydride formed in both eq 5 and 6 subsequently hydrolyzes rapidly (eq 7).



To our knowledge, the acid-catalyzed solvolysis of II_d in acetic acid is the first example of a substitution at sulfinyl sulfur which does not involve nucleophilic attack on sulfinyl sulfur either prior to or during the rate-determining step. It demonstrates that under suitable circumstances substitution at sulfinyl sulfur can occur by an $\text{S}_{\text{N}}1$ -type mechanism, a fact which is of significant interest.

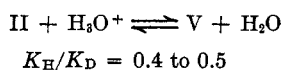
At present we cannot say whether the proton transferred to the departing ArSO_2 group in eq 6 comes from a general acid present in the solution or from a neighboring protonated sulfinyl group, as in eq 8. The same is



true for the proton transfer in eq 5. Unfortunately, for reasons outlined in detail elsewhere^{9b} the usual diagnostic tools for the timing of proton transfers (solvent isotope effect measurements¹¹ and rate-acidity dependence) do not provide a means of distinguishing between these two possibilities in the present system.

Effect of Sulfinyl Sulfone Structure on Rate of Uncatalyzed Solvolysis.—The acid-independent term (k) in eq 4 shows a rather different dependence on sulfinyl sulfone structure than does the acid-catalyzed rate. This becomes evident when one examines Table V, which summarizes solvolysis rates for II_a–d in the

(11) We have measured the solvent isotope effect for the H_3O^+ -catalyzed solvolysis of II_d in acetic acid–0.56 M H_2O –0.10 M H_2SO_4 and find $k_{\text{H}}/k_{\text{D}} = 0.72$. As Kresge and Preto¹² have shown this is a possible value for a general acid catalyzed reaction where H_3O^+ is the catalyzing acid, provided one assumes that the proton has been almost completely transferred to the substrate by the time the transition state is reached. Such a transition state for eq 6 seems perfectly reasonable. On the other hand, $K_{\text{H}}/K_{\text{D}}$ for the reversible protonation of II_d to V_d is probably about 0.4 to 0.5¹³ so that if eq 8 were



to have an isotope effect of $(k_{\text{H}}/k_{\text{D}}) = 1.4$ to 1.8 one would also get an over-all $k_{\text{H}}/k_{\text{D}}$ of 0.72 for this mechanism as well. Thus the solvent isotope effect is of no help in deciding the details of the proton transfer.

(12) A. J. Kresge and R. J. Preto, *J. Am. Chem. Soc.*, **87**, 4593 (1965).

(13) The solvent isotope effect for this equilibrium should be similar to those observed in aqueous solution.¹⁴

(14) (a) E. Hogfeldt and J. Bigeleisen, *J. Am. Chem. Soc.*, **82**, 15 (1960);

(b) J. G. Pritchard and F. A. Long, *ibid.*, **80**, 4162 (1958).

TABLE V

EFFECT OF STRUCTURE ON RATE OF UNCATALYZED SOLVOLYSIS OF SULFINYL SULFONES^a

Sulfinyl sulfone	Ar in ArSO_2SOAr	$k_r \times 10^3, \text{sec}^{-1}$	
		$\text{AcOH}-0.56 M$ H_2O	$\text{AcOH}-2.80 M$ H_2O
II _d	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	0.12	0.43
II _a	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	0.073	0.69
II _b	C_6H_5	0.09	1.3
II _c	<i>p</i> - ClC_6H_4	0.4	8.3

^a All data at 21°, $[\text{H}_2\text{SO}_4] = 0.00 M$.

absence of sulfuric acid, and compares the data there with those for the acid-catalyzed solvolysis given earlier in Table IV. Particularly noteworthy is the fact that the *p*-anisyl compound (II_d) no longer shows a markedly enhanced rate of solvolysis. Instead the reactivity pattern observed is comparable with the one found in the alkyl sulfide-catalyzed solvolysis of II.^{9b}

For all the sulfinyl sulfones the rate of uncatalyzed solvolysis is notably faster in acetic acid–2.80 M water than it is in acetic acid–0.56 M water, but the exact magnitude of the increase depends considerably on sulfinyl sulfone structure, varying from a factor of 3.5 for II_d to a factor of 19 for II_c. By way of contrast, the change in the rate of acid-catalyzed solvolysis, as evaluated by comparing values for the various sulfinyl sulfones of $(k_r - k)$ at $H_0 = -1.94$ in 0.56 and 2.80 M water, shows no such variation with structure, all sulfinyl sulfones showing about two to three times faster acid-catalyzed solvolysis rate in acetic acid–2.80 M water.

We know from earlier work² that chloride ion in very low concentrations ($\sim 10^{-4} M$) is very effective at accelerating the solvolysis of II_a. Acetate ion in comparable concentrations might well be about equally effective at accelerating the solvolysis. The possibility therefore exists that all or part of the acid-independent term in eq 4 is actually due not to an uncatalyzed solvolysis of the sulfinyl sulfone but rather to an *acid-catalyzed* reaction of II with acetate ion, the conjugate base of the solvent.¹⁵ Because of this potential complication to a meaningful interpretation of the data in Table V, we shall not indulge in any speculation regarding the mechanism of the uncatalyzed solvolysis at the present time. Hopefully studies of the solvolysis in other media which are currently in progress will shed further light on this subject.

Experimental Section

Preparation and Purification of Materials. Sulfinic Acids.—*p*-Chlorobenzenesulfinic, *p*-methoxybenzenesulfinic, and benzenesulfinic acids were all prepared and purified by previously described¹⁷ procedures. Sulfuric acid was employed rather than hydrochloric for any precipitations of sulfinic acid by acidification of an aqueous solution.

Sulfinyl Sulfones.—Compounds II_b and II_c were prepared and purified as outlined by Kice and Pawlowski.¹⁸

***p*-Methoxybenzenesulfinyl *p*-Anisyl Sulfone (II_d).**—Fifteen grams of sodium *p*-methoxybenzenesulfinate (dried under vacuum at 175°) was mixed with 150 ml of hexane, and, while the mixture

(15) Wiberg and Evans¹⁶ estimate the concentration of acetate ion in acetic acid–2.80 M water as $2 \times 10^{-4} M$.

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

(17) J. L. Kice, D. C. Hampton, and A. Fitzgerald, *J. Org. Chem.*, **30**, 882 (1965).

(18) J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964).

was stirred, thionyl chloride was added slowly in small portions until gas was no longer evolved from the mixture upon addition of a fresh increment of the reagent. The mixture was then filtered, and the hexane was removed from the filtrate under reduced pressure at room temperature. After the hexane had been removed, the residue of *p*-methoxybenzenesulfinyl chloride was subjected to a vacuum of 0.1 mm at 50° for 0.5 hr to remove any excess thionyl chloride. It was then used immediately in the subsequent step.

The sulfinyl chloride prepared above was dissolved in 30 ml of anhydrous ether and 15 g of dry sodium *p*-methoxybenzenesulfinate was added in portions to this solution. The mixture was stirred for 30 min at 0°. The crude sulfinyl sulfone was then removed by filtration. It was freed of sodium chloride by an extensive series of triturations with small amounts of ice-water. Any organic impurities were removed by several triturations with small amounts of ice-cold ether. The purified sulfinyl sulfone was then dried under high vacuum and stored in a desiccator at -20° until used, mp 100-101°.

Anal. Calcd for $C_{14}H_{14}O_6S_2$: C, 51.19; H, 4.32. Found: C, 51.10; H, 4.24.

***p*-Chlorobenzenesulfinyl *p*-Tolyl Sulfone (III).**—*p*-Chlorobenzenesulfinyl chloride, prepared in the same manner as for the preparation of IIc,¹⁸ was treated with sodium *p*-toluenesulfinate using the same general procedure described for the preparation of IIId. Work-up of the reaction and purification of the sulfinyl sulfone were also analogous. *p*-Chlorobenzenesulfinyl *p*-tolyl sulfone, mp 88°, exhibits infrared and ultraviolet spectral properties consistent with those expected from the spectra of the other sulfinyl sulfones.

Anal. Calcd for $C_{13}H_{11}ClO_3S_2$: C, 49.60; H, 3.52. Found: C, 50.30; H, 3.70.

Solvents.—The purification of acetic acid and the preparation of the various acetic acid-water and acetic acid-water-sulfuric

acid solutions were carried out as described in the preceding paper.²

Acetic Acid-*d*.—Deuterium oxide (2.25 moles) was slowly added with stirring to freshly fractionally distilled (20 plate column) acetic anhydride (2.31 moles). The two-phase mixture was stirred and *gradually* heated to reflux. (Miscibility of the two phases appeared complete at 80-90°.) The solution was heated at reflux for 1 hr and was then fractionally distilled through a 25-cm silvered, vacuum-jacketed Vigreux column using a reflux ratio of 10:1. After discarding a small forerun (16 g, bp 114-117°) there was obtained 254 g of acetic acid-*d*, bp 117-117.5°.

Sulfuric acid-*d*₂ was purchased from Calbiochem. Its sulfuric acid content was determined by titration with standard base. The remainder of the material was assumed to be deuterium oxide.

Procedure for Rate and Equilibrium Studies.—The same apparatus and procedures described in the preceding paper² were used. Most of the rate data were obtained by starting with the sulfinic acid and following the build-up of the sulfinyl sulfone to its equilibrium concentration. However, a number of runs were also made starting with the sulfinyl sulfone and following its disappearance. In all cases investigated agreement between *k_t* values obtained by the two methods was excellent.

Extinction coefficients and absorption maxima for IIb-d were determined by the same method used for IIa in the earlier paper.² They are IIb, 300 mμ (ε 7000); IIc, 306 mμ (ε 8000); IIId, 306 mμ (ε 13,000). In the *p*-anisyl system, unlike the other I-II equilibria studied, the sulfinic acid itself has a large enough extinction coefficient at 306 mμ so that it contributes something to the absorbance of the solution at this wavelength. As a result, to obtain the absorbance of a Id-IIId solution owing to IIId alone one must correct the measured absorbance using the following equation: $A_{IIId} = A_{soIn} - 11C_{ArSO_2H}$.

Sulfolene¹-Sulfur Dichloride Adducts. Stereochemical Considerations²

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The reaction of sulfolene with sulfur dichloride in methylene chloride gave two isomeric adducts, characterized as *dl*- and *meso-trans*-4,4'-dichloro-3,3'-disulfolanyl sulfides. Oxidation was accomplished with retention of geometrical integrity. Dehydrochlorination of each isomeric pair gave, in turn, a common product related by oxidation. Partial resolution of the *dl* adduct was effected simply by stereoselective dehydrochlorination with *l*-brucine. Despite their structural similarity to "mustard gas," the adducts solvolyzed very slowly in aqueous acetone. Considerable ion-pair return during solvolysis was suggested by scrambling of recovered adduct and confirmed by the polarimetric rate of rearrangement of optically active material.

The addition of sulfenyl halides to olefinic unsaturation has been extensively investigated in recent years and considerable evidence has accumulated supporting its *trans* nature.³⁻⁷ Although the stereochemistry of sulfur dichloride addition to double bonds has received less attention, by analogy, *trans* addition might also have been anticipated. The reaction of sulfur dichloride with excess sulfolene therefore was expected to yield novel *trans*-2-chloroalkyl sulfides, of possible interest in a variety of applications because of their "mustard gas"^{8,9} character.

(1) Butadiene sulfone or 2,5-dihydrothiophene 1,1-dioxide.

(2) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(3) N. Kharasch and co-workers, *J. Am. Chem. Soc.*, **69**, 1612 (1947); **75**, 3734 (1953); **75**, 6030 (1953); **75**, 6035 (1953); **78**, 1207 (1956).

(4) D. J. Cram, *ibid.*, **71**, 3883 (1949).

(5) H. L. Goering, D. I. Relyea, and K. L. Howe, *ibid.*, **79**, 2502 (1957).

(6) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956); **80**, 887 (1958).

(7) For a recent review of sulfenyl halide addition to olefins and the nature of the products, see K. D. Gunderman, *Angew. Chem. Intern. Ed. Engl.*, **2**, 674 (1963).

(8) R. C. Fuson and co-workers, *J. Org. Chem.*, **11**, 469 (1946), and following papers.

(9) P. D. Barlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).

Results

The reaction of sulfur dichloride with 2 equiv of sulfolene proceeded at a moderate rate in methylene chloride at ambient temperatures, unaccelerated appreciably by either Lewis acid or ultraviolet radiation. Approximately equal quantities of two isomeric solids, I and II, analyzing correctly for 2:1 sulfolene-sulfur dichloride adducts, were isolated as the major reaction products in 60-90% yield; no other characterizable products were obtained, but their presence was not excluded.

In the presence of weak base, both I and II readily dehydrochlorinated in high yield to a common disaturated sulfide III. When this dehydrochlorination was performed in dimethyl sulfoxide with less than a stoichiometric equivalent of *l*-brucine, partially resolved I* (shown as $[\alpha]^{25D} - 8.6^\circ$) was recovered under conditions identical with those from which recovered II had no rotation.

Rapid oxidation of the isomeric adducts I and II with hydrogen peroxide in hot acetic acid gave cleanly,