To determine the sulfur balance, a mixture of 1 (4.52 g, 20 mmoles), pyridine (3.16 g, 40 mmoles), and thiophenol (8.80 g, 80 mmoles) in carbon tetrachloride (50 ml) was allowed to react as before. The reaction mixture, washed with water and acid, was dried and evaporated to 13.0 g of oil. Analysis of the residue showed the sulfur content to be 34.86% or 4.53 g, showing the total recovery of sulfur (original amount, 4.49 g) as organic sulfur compounds to be 101%.

B. **Synthesis of Authentic *t*-Butyl Phenyl Disulfide.**—*t*-Butylsulfenyl chloride was prepared by allowing 7.5 g (106 mmoles) of chlorine to distil into a stirred solution of *t*-butyl disulfide (18.9 g, 107 mmoles) in *n*-pentane (200 ml) during 0.5 hr at 25–28°.[16] The mixture was stirred for 0.5 hr and then was added dropwise (1 hr) to a stirred solution of thiophenol (23.3 g, 212 mmoles) and dry pyridine (16.8 g, 212 mmoles) in *n*-pentane (250 ml) at 0°. The reaction mixture was stirred for 0.25 hr after the addition of the sulfenyl chloride was completed and then was washed with water, acid, aqueous alkali, and again with water until neutral. Drying, concentration, and distillation using a 20-cm spinning-band column gave 23.0 g (55%) of *t*-butyl phenyl disulfide, bp 87° (1 mm), $n^{25}\text{D}$ 1.5710; the infrared spectrum was identical with that of material isolated earlier.[5]

Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11; S, 32.33. Found: C, 60.65; H, 7.09; S, 32.04.

In a study of the disproportionation (eq 6) of *t*-butyl phenyl disulfide, a solution of 0.4968 and 0.3355 g of durene was prepared in sufficient 95% ethanol to give 25.0 ml. One milliliter of this solution was placed in each of 20 ampoules, which then were sealed. Half of the ampoules were shielded against light, and all were heated in boiling water. Samples were withdrawn at times up to 336 hr, at which point glpc analysis showed that the ratio of the area of the disulfide peak to that of the durene peak remained constant at 1.42 ± 10%, with no appreciable difference between shielded and unshielded samples. Furthermore, no trace of *t*-butyl disulfide could be detected. The extent of disproportionation of *t*-butyl phenyl disulfide after 336 hr therefore was less than 10% (estimated range of experimental error).

C. **With Diethyl Malonate.**—Sodium metal (2.30 g, 100 mg-atoms) was dissolved in absolute ethanol (100 ml). Diethyl malonate (8.00 g, 50 mmoles) and 1 (11.30 g, 50 mmoles) were added and the mixture was heated at reflux for 3 hr. Water was added, the mixture was neutralized with acid, and a methylene chloride extract was washed, dried, and concentrated to 12.10 g of oil. Glpc analysis (column temperature, 150°; flow rate, 60 ml/min) indicated a complex mixture of diethyl malonate (19%), *t*-butyl disulfide (15%), *t*-butyl trisulfide (34%), and an unknown component (32%) thought to be diethyl (*t*-butylthio)malonate. Two distillations (of the oil) using a 20-cm spinning-band column afforded 0.44 g of material with bp 79–80° (0.05 mm), $n^{25}\text{D}$ 1.4837; glpc analysis showed this to consist of 88% of presumed diethyl (*t*-butylthio)malonate. The infrared spectrum was consistent (ester and *t*-butyl groups). The nmr spectrum also was consistent. It showed a CH_3 multiplet centered at τ 8.68 (diethylmalonate, 8.73), the CH_2 quartet of the ethyl groups centered at 5.80 (diethyl malonate, τ 5.78), and a singlet at 5.96 (the multiplet for the methinyl hydrogen of diethyl methylmalonate is centered at τ 6.65 and the methylene singlet of diethyl malonate occurs at 6.63). Thus the nmr spectrum indicated the major component of the mixture to be a monosubstituted diethyl malonate in which the methinyl hydrogen was significantly deshielded by the *t*-butylthio substituent.

It is concluded that thioalkylation occurs with diethyl sodiomalonate just as with thiophenol and that a major product of this reaction is diethyl (*t*-butylthio)malonate. Unfortunately, other components in the mixture had too nearly the same boiling point to permit a facile separation, and the reaction clearly has negligible preparative value in its present form.

D. **Saponification.**—Methanolic potassium hydroxide (25.0 ml, 0.82 *N*) was heated with 0.7982 g (3.53 mmoles) of 1 under reflux for 0.25 hr. Neutralized formaldehyde solution (5 ml of 37% solution) was added to the cooled mixture, which then was titrated with acid. The saponification equivalent was 216 (a second experiment gave 235) (mol wt of 1, 226). Extraction with pentane and glpc analysis showed that the products consisted of *t*-butyl trisulfide (61%) and *t*-butyl disulfide (39%).

Acknowledgement.—We thank Professors D. L. Tuleen and N. Kharasch for helpful conversations.

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[16] W. A. Schulze, G. H. Short, and W. W. Crouch, *Ind. Eng. Chem.*, **42**, 916 (1950).

The Mechanism of the Disproportionation of Sulfinic Acids. Rate and Equilibrium Constants for the Sulfinic Acid–Sulfinyl Sulfone (Sulfinic Anhydride) Equilibrium[1]

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Using spectrophotometric techniques it has been possible to measure in acetic acid–water solvent both the rate and equilibrium constants associated with the equilibrium between *p*-toluenesulfinic acid (Ia) and *p*-toluenesulfinyl *p*-tolyl sulfone (IIa). Such data are of interest because of the role of the sulfinyl sulfone as an intermediate in the disproportionation of Ia. While the present results unequivocally confirm the mechanism proposed earlier for the disproportionation reaction, they also reveal several important and previously unrealized complexities associated with it. Specifically, the rate of hydrolysis of IIa to sulfinic acid is found to be much more closely comparable with the rate of thermal decomposition of IIa than had previously been imagined, particularly at high temperatures and low acidities. This means that thermal decomposition of IIa is not always the rate-determining step in the disproportionation reaction. One also finds that at low acidities extremely small concentrations (10^{-4} *M*) of added potassium chloride can rather dramatically accelerate the rate of attainment of equilibrium between Ia and IIa. Since chloride ion is very likely a common impurity in inadequately purified samples of sulfinic acid, this introduces further potential complications into interpretation of kinetic data for the disproportionation reaction.

Previous studies[2-4] of the disproportionation of aromatic sulfinic acids (eq 1) have suggested that the mechanism of the reaction is as outlined in Chart I.

$$3ArSO_2H \longrightarrow ArSO_2SAr + ArSO_3H + H_2O \qquad (1)$$

This involves an initial equilibrium (eq 2) between the sulfinic acid and an unstable sulfinyl sulfone (II), followed by unimolecular thermal decomposition of II (eq 3). The latter reaction is apparently[3] a homolytic dissociation of the sulfur–sulfur bond in II, with subsequent head-to-tail recombination of the radical fragments giving the sulfenyl sulfonate III. Reaction of III with an additional molecule of sulfinic acid (eq 4) yields the final products.

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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.

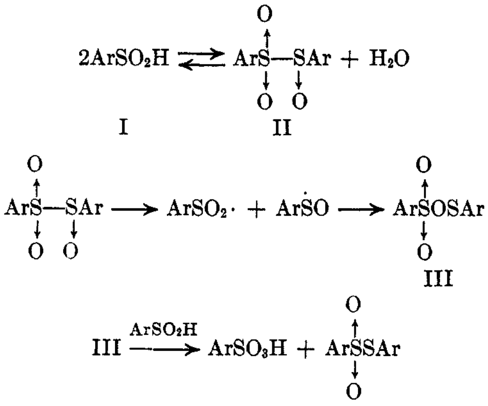
[2] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

[3] (a) J. L. Kice and N. E. Pawlowski, *ibid.*, **86**, 4898 (1964); (b) *J. Org. Chem.*, **28**, 1162 (1963).

[4] J. L. Kice, D. C. Hampton, and A. Fitzgerald, *ibid.*, **30**, 882 (1965).

CHART I

MECHANISM OF SULFINIC ACID DISPROPORTIONATION



$$\underset{\text{I}}{2\text{ArSO}_2\text{H}} \rightleftarrows \underset{\text{II}}{\text{Ar}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{—}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{Ar}} + \text{H}_2\text{O} \qquad (2)$$

$$\text{Ar}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{—}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{Ar} \longrightarrow \text{ArSO}_2\cdot + \text{Ar}\dot{\text{S}}\text{O} \longrightarrow \underset{\text{III}}{\text{Ar}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{OSAr}} \qquad (3)$$

$$\text{III} \xrightarrow{\text{ArSO}_2\text{H}} \text{ArSO}_3\text{H} + \text{Ar}\overset{\overset{\text{O}}{\uparrow}}{\underset{\underset{\text{O}}{\downarrow}}{\text{S}}}\text{SAr} \qquad (4)$$

Despite the fact that the sulfinyl sulfone is normally present at equilibrium in only very low concentration, we have now been able to measure directly, in the same media used for earlier studies[2] of the disproportionation reaction, both the equilibrium concentration of the sulfinyl sulfone and the individual rate constants for its formation and hydrolysis. When such data are combined with data on both the rate of unimolecular thermal decomposition of II[3] (eq 3) and the rate of disproportionation of I[2] (eq 1) they allow one to delineate the detailed mechanism of the disproportionation reaction with greatly increased precision. As we shall see, this leads to the discovery of several important previously unrealized complexities in that mechanism.

Results

The disproportionation of *p*-toluenesulfinic acid[2,4] (Ia, Ar = *p*-$CH_3C_6H_4$) and the thermal decomposition of its sulfinyl sulfone[3] (IIa) have been more thoroughly studied than those of other aryl sulfinic acids. The most extensive kinetic data on the disproportionation of Ia were obtained[2] in acetic acid solvent containing known amounts of water (0.5–5.0%) and sulfuric acid (0.0–1.3 *M*). For this reason, the equilibrium between Ia and IIa in this particular solvent medium was the system chosen for study in the present work.

Estimation of Sulfinyl Sulfone Concentration.—*p*-Toluenesulfinyl *p*-tolyl sulfone (IIa) has a strong ultraviolet maximum at 300 mμ (ε 8000), a wavelength at which in acetic acid solvent the corresponding sulfinic acid is effectively transparent. This makes it possible to detect very small concentrations of IIa (10^{-4}–10^{-5} *M*) in the presence of much larger concentrations of the sulfinic acid (0.01–0.08 *M*).

When a sample of Ia is dissolved at room temperature in acetic acid–water containing some sulfuric acid, the optical density of the solution at 300 mμ initially rises quite rapidly and after a time levels off at an equilibrium value. That this absorbance at 300 mμ is due to the small amount of IIa in equilibrium with the sulfinic acid is demonstrated by the fact that its equilibrium value under a given set of conditions is *proportional to the square of the concentration of Ia.* Table I shows some representative data illustrating this point.

Equilibrium Concentration of Sulfinyl Sulfone.—The results in Table I indicate that one can determine the equilibrium concentration of IIa by measuring the equilibrium optical density of the solution at 300 mμ. We can then define an equilibrium constant (K_e) relating the equilibrium concentration of sulfinyl sulfone to the stoichiometric concentration of sulfinic acid.

$$K_e = \frac{[\text{IIa}]}{C^2_{\text{ArSO}_2\text{H}}} \qquad (5)$$

TABLE I

EQUILIBRIUM ABSORBANCE AT 300 mμ AS A FUNCTION OF SULFINIC ACID CONCENTRATION

Solvent	Temp, °C	$C_{\text{ArSO}_2\text{H}} \times 10^2$, M^a	A_{equil} at 300 mμ	$A_{\text{eq}} \times 10^{-2}/C^2_{\text{ArSO}_2\text{H}}$
HOAc–1% H_2O containing 0.2 *M* H_2SO_4	30	5.52	1.26	4.1
		4.09	0.66	4.0
		2.77	0.33	4.3
HOAc–5% H_2O containing 1.0 *M* H_2SO_4	30	7.55	0.565	1.0
		4.03	0.178	1.1

[a] $C_{\text{ArSO}_2\text{H}}$ equals the stoichiometric concentration of sulfinic acid.

The data in Table II show how K_e depends on each of the following variables in acetic acid–water–sulfuric acid medium: (1) stoichiometric concentration of water; (2) concentration of sulfuric acid; (3) temperature. The following points are worth noting. (1) Increasing the stoichiometric concentration of water under otherwise constant conditions leads to a sharp drop in K_e. (2) Increasing the concentration of sulfuric acid at a fixed stoichiometric water concentration results in an increase in K_e, but the increase is a fairly modest and gradual one. This is perhaps best seen from Figure 1, which shows K_e for acetic acid–0.56 *M* water solutions plotted against sulfuric acid concentration. (3) K_e is only very slightly de-

TABLE II

EQUILIBRIUM CONSTANTS FOR SULFINYL SULFONE FORMATION IN ACETIC ACID

Temp, °C	C_{H_2O}, M^a	$C_{H_2SO_4}$, *M*	K_e, M^{-1}
21.0	0.56	1.00	0.121
		0.80	0.098
		0.60	0.086
		0.40	0.065
		0.20	0.048
		0.10	0.041
		0.00	0.035[b]
	2.80	1.00	0.0118
30.0	0.56	1.00	0.125
		0.60	0.086
		0.40	0.062
		0.20	0.050
		0.10	0.040
		0.00	0.039[b]
	2.80	1.00	0.0131
		0.80	0.0115
		0.60	0.0099
		0.40	0.0084
39.2	0.56	0.60	0.090
		0.40	0.069
		0.20	0.055
		0.10	0.042
	2.80	1.00	0.0134
48.2	0.56	0.40	0.072
		0.20	0.056
		0.10	0.046

[a] Stoichiometric concentration of water. [b] Attainment of equilibrium catalyzed by addition of 10^{-4} *M* KCl.

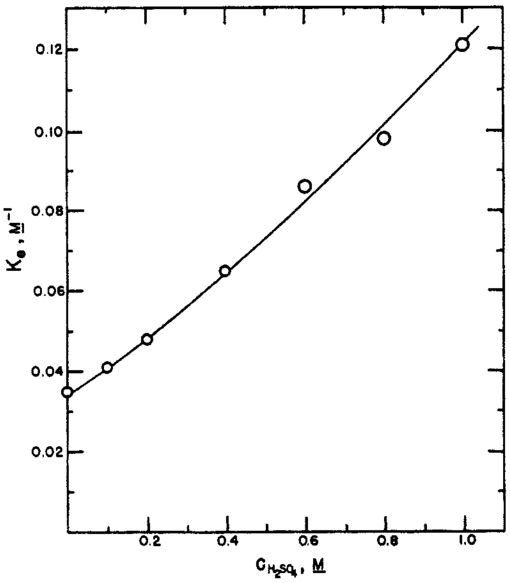


Figure 1.—Equilibrium constant for sulfinyl sulfone formation as a function of sulfuric acid concentration: acetic acid–0.56 *M* water as solvent; temperature 21°.

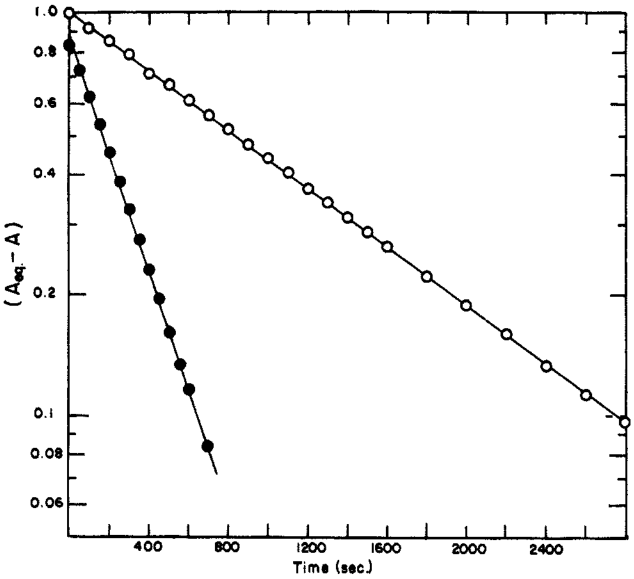


Figure 2.—Rate of attainment of equilibrium concentration of IIa in acetic acid–0.56 *M* water at 30°. Data for two representative runs plotted according to eq 8: ○, (H_2SO_4), 0.20 *M* (Ia, 0.0598 *M*); ●, (H_2SO_4), 0.60 *M* (Ia, 0.0398 *M*).

pendent on temperature, being but a few per cent larger at 48° than it is at 21°.

Rate of Attainment of Equilibrium.—As noted earlier, the equilibrium absorbance at 300 mμ is not achieved immediately. Rather the concentration of IIa builds toward its equilibrium value at a rate which, while sometimes very rapid, is still slow enough to be measurable under most of the reaction conditions shown in Table II. The rate of attainment of equilibrium is, of course, determined by the rates of the reactions responsible for the formation and disappearance of IIa.

Since the rate of disproportionation of Ia (eq 1) under any of the present conditions is very much slower than its rate of equilibration with IIa, and since the equilibrium concentration of IIa is only a very small fraction of the concentration of Ia, the concentration of sulfinic acid remains constant during an experiment, and, as a result, so too does the rate of formation of IIa. If all reactions involving the disappearance of IIa are first order in sulfinyl sulfone the change of sulfinyl sulfone concentration with time will be given by

$$\frac{d[\mathrm{IIa}]}{dt} = k_0 - k_1[\mathrm{IIa}] \qquad (6)$$

k_0 = rate of formation of IIa from Ia

k_1 = experimental first-order rate constant for disappearance of IIa

Remembering that at equilibrium d[IIa]/dt is zero and, therefore, $[\mathrm{IIa}]_{\mathrm{equil}} = (k_0/k_1)$, we can integrate eq 6 and obtain

$$\ln([\mathrm{IIa}]_{\mathrm{equil}} - [\mathrm{IIa}]) = -k_1t + \text{constant} \qquad (7)$$

Since the absorbance at 300 mμ is proportional to the concentration of IIa, *i.e.*, $A = \epsilon_{\mathrm{IIa}}\,[\mathrm{IIa}]$, eq 7 can be written as

$$\ln[A_{\mathrm{equil}} - A] = -k_1t + \text{constant} \qquad (8)$$

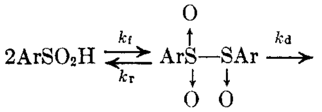
Figure 2 shows plots of the data according to eq 8 for several representative runs. Their excellent linearity demonstrates that eq 6 correctly expresses the rate of change of the concentration of IIa. The slope of such a plot is equal to k_1, the experimental first-order rate constant for the disappearance of the sulfinyl sulfone. The k_1 values observed for various reaction conditions and temperatures are given in Table III. (Experiments at different sulfinic acid concentrations showed that k_1 is not dependent on the concentration of sulfinic acid.)

Table III
Rate Constants for Forward and Reverse Steps of the Ia–IIa Equilibrium in Acetic Acid

Temp, °C	C_{H_2O}, M[a]	$C_{H_2SO_4}$, M	$k_1 \times 10^3$, sec^{-1}	$k_r \times 10^3$, sec^{-1}[b]	$k_f \times 10^4$, M^{-1} sec^{-1}[c]
21.0	0.56	1.00	4.2	4.2	5.1
		0.80	2.9	2.9	2.9
		0.60	1.5	1.5	1.3
		0.40	0.83	0.82	0.53
		0.20	0.35	0.34	0.17
		0.10	0.19	0.18	0.078
		0.00	0.083[d]	0.073	...
	2.80	1.00	2.2	2.2	0.26
30.0	0.56	0.80	5.9	5.9	6.3
		0.60	3.6	3.6	3.1
		0.40	1.9	1.9	1.3
		0.20	0.82	0.79	0.40
		0.10	0.43	0.40	0.18
	1.68	1.00	4.9	4.9	1.3
	2.80	1.00	3.9	3.9	0.51
		0.80	2.9	2.9	0.33
		0.60	2.1	2.1	0.21
		0.40	1.5	1.5	0.12
39.2	0.56	0.60	8.5	8.4	7.7
		0.40	4.3	4.2	3.1
		0.20	1.9	1.8	0.98
		0.10	1.0	0.91	0.45
	2.80	1.00	7.8	7.7	1.05
48.2	0.56	0.40	9.7	9.4	7.2
		0.20	4.0	3.7	2.3
		0.10	2.5	2.1	1.1

[a] Stoichiometric concentration of water. [b] $k_r = k_1 - k_d$. Values of $k_d \times 10^3$ (temperature): 0.35 (48.2); 0.10 (39.2); 0.03 (30.0); 0.01 (21.0). Data for k_d from ref 6. [c] k_f calculated from eq 10. [d] Measured by following solvolysis of IIa directly.

Without specifying any details about the mechanisms of the various steps we can write the following formal scheme for the reactions involved in both the equilibrium between Ia and IIa (eq 2) and the decomposition of the latter compound (eq 3).



$$2\mathrm{ArSO_2H} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{Ar}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}-\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\mathrm{Ar} \xrightarrow{k_d}$$

thermal decomposition products (9)

In terms of this scheme k_1 and k_0 of eq 6 are then

$$k_1 = k_r + k_d,\ k_0 = k_f C^2{}_{\mathrm{ArSO_2H}}$$

We will be particularly interested in k_f and k_r, the rate constants for the forward and reverse steps, respectively, of the Ia–IIa equilibrium.

$$k_f = K_e k_1 \qquad (10)$$

$$k_r = k_1 - k_d \qquad (11)$$

Values of k_f for the various reaction conditions can be calculated from eq 10, using the K_e values in Table II and the k_1 values in Table III.[5] They are shown in the last column of Table III.

For any of the reaction conditions in Table III k_d for IIa is much smaller than k_1.[6] However, since for certain runs k_d does amount to up to 10–15% of k_1, one is not justified in uniformly taking k_r as equal to k_1. Instead we have used eq 11 and the k_d values for IIa in acetic acid shown at the bottom of Table III to convert our k_1 values to values for k_r. These are shown in the fifth column of Table III.

Acid Catalysis.—In contrast to the behavior of the equilibrium constant K_e, which was not greatly influenced by changes in sulfuric acid concentration, the rate constants for the forward and reverse reactions of the equilibrium are very markedly accelerated by an increase in sulfuric acid concentration. In acetic acid–0.56 M water, for example, k_r increases more than tenfold on going from 0.20 to 1.00 M sulfuric acid. Since previous work[3] has indicated that k_d is not subject to acid catalysis, this means that the ratio k_d/k_r will be strongly dependent on the acidity of the medium. As we shall see in the Discussion this introduces previously unrealized complexities into the mechanism of the disproportionation reaction.

The k_r values for the acetic acid–0.56 M water solutions can be approximated quite well by an equation of the form

$$k_r = k + k' h_0^{0.95} \qquad (12)$$

where $-\log h_0 = H_0$, the Hammett acidity function. (The h_0 values used were those of Rocek.[7]) The intercept of a plot of k_r *vs.* $h_0^{0.95}$ is k, which should be equal to k_r for 0.0 M H_2SO_4. The values of k_r at 0.00 M H_2SO_4 for acetic acid–0.56 M water solution estimated in this way are 0.8×10^{-4} sec^{-1} (21.0°); 2.1×10^{-4} sec^{-1} (30.0°); 5.0×10^{-4} sec^{-1} (39.2°). The value at 21.0° agrees well with one obtained by direct measurement of the rate of solvolysis of IIa in acetic acid–0.56 M water (see Table III). We accordingly believe that the 30 and 39.2° values are also reliable.

Temperature Dependence of k_f and k_r.—From plots of log k_f or log k_r *vs.* $1/T$ one can determine apparent activation energies for k_f and k_r for various reaction conditions. Sufficient data are available to do this for acetic acid–0.56 M water solutions containing 0.10 to 0.60 M sulfuric acid and for acetic acid–2.80 M water containing 1.0 M H_2SO_4.

The apparent activation energies for k_f and k_r in acetic acid–0.56 M water solution do not appear to be influenced appreciably by changes in sulfuric acid concentration. The average values are $k_f = 18.2$ kcal, $k_r = 16.6$ kcal. The apparent activation energies for both reactions are *ca.* 3.5 kcal lower in acetic acid–2.80 M H_2O–1.0 M H_2SO_4: $k_f = 14.6$ kcal, $k_r = 12.9$ kcal.

At this juncture it seems important to point out that in acetic acid the activation energy for the thermal decomposition of IIa (eq 3) is considerably higher (27 kcal). For this reason, even though k_r is much larger than k_d at room temperature under any of the reaction conditions in Table III, the rates of the two reactions will be more closely comparable at 70°, the temperature at which the most extensive kinetic study of the disproportionation of Ia was carried out.[2] The extent to which this complicates the mechanism of eq 1 will be pointed out in the Discussion.

Catalysis by Added Potassium Chloride.—The hydrolysis of IIa represents a substitution at sulfinyl sulfur. In several other cases[8,9] such reactions have been observed to be catalyzed by chloride ion, and, for this reason, it seemed of interest to determine the effect of added potassium chloride on k_r. Not surprisingly, it was found to have a catalytic effect. What was rather surprising, however, was the extremely low concentration ($\sim 10^{-4}$ M) of potassium chloride required, particularly at low sulfuric acid concentrations. Table IV summarizes our results. The last column in the table, which compares the observed rate with that obtained under identical conditions in the absence of chloride, shows just how much k_r can be increased by very small amounts of added potassium chloride. As above 0.1 M sulfuric acid the rate of the chloride-catalyzed reaction does not increase with increasing sulfuric acid concentration, a given amount

TABLE IV

EFFECT OF POTASSIUM CHLORIDE ON THE RATE OF CONVERSION OF IIA TO SULFINIC ACID

Temp, °C	C_{H_2O}, M^a	$C_{H_2SO_4}$, M	[KCl] × 10^4, M	$k_r \times 10^3$, sec^{-1}	$(k_r/k_r^0)^b$
21.0	0.56	0.40	1.37	2.0	2.4
		0.20	1.37	1.6	4.7
		0.10	1.37	1.5	8.3
			4.12	4.8	27
			6.86	7.5	42
		0.00	1.37	0.70	9.6
			0.69	0.49	6.7

[a] Stoichiometric concentration of water in the acetic acid solvent. [b] k_r^0 equals the rate constant in the absence of added chloride under otherwise identical conditions.

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(5) Before making these calculations for the acetic acid–0.56 M water solutions the K_e values for each temperature were plotted *vs.* $C_{H_2SO_4}$ as in Figure 1, and a smooth curve was put through the data for each temperature. The values of K_e used in eq 10 were taken from these smooth curves. This procedure helps to reduce the extent to which random experimental errors in K_e are carried over into k_f.

(6) Rate constants for the thermal decomposition of IIa in acetic acid have been determined at several temperatures by N. E. Pawlowski in this laboratory.

(7) J. Rocek, *Collection Czech Chem. Commun.*, **22**, 1 (1957).

(8) K. Mislow, T. Simmons, J. T. Mellilo, and A. J. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

(9) H. F. Herbrandson and R. T. Dickerson, *ibid.*, **81**, 4102 (1959).

of chloride produces the greatest percentage increase in k_r in the 0.00–0.10 M sulfuric acid solutions.

The incomplete ionization of HCl in acetic acid solvent[10] and the low degree of dissociation of H^+Cl^- ion pairs in this medium[10] both suggest that any attempt to draw specific conclusions regarding the mechanism of the chloride-catalyzed reaction from the data in Table IV would be presumptuous and risky. Other solvent systems seem much better suited for detailed investigation of this reaction, and, indeed, such studies are currently in progress. However, the fact that one cannot at present specify the mechanism of the chloride-catalyzed reaction should not obscure its potential as a complicating factor in studies of the mechanism of sulfinic acid disproportionation. In particular, it seems very likely that the usual methods of preparation (reduction of $ArSO_2Cl$) and initial purification (precipitation with concentrated HCl) of aryl sulfinic acids often lead to the presence of small amounts of chloride ion(or substances yielding chloride on solvolysis) as an impurity in the sulfinic acid. This means that in solutions of low sulfuric acid content rate constants k_r and k_f could vary rather widely from sample to sample because of variations in the trace amounts of chloride present as an impurity.

In the present work we have taken certain steps (see the Experimental Section) in the purification of the sulfinic acid which are intended to lead to as chloride free a sample as possible. We have tested each batch of sulfinic acid used to see that it gave proper values of k_r and k_f at low sulfuric acid concentration and have discarded or further purified any which gave significantly faster rates than normal. We have also checked our other reagents to make sure that by the usual tests they were chloride free. Nonetheless, the concentration level at which chloride can exert a significant effect is so small that, despite these precautions, a part of the measured rates in Table III for k_r and k_f at *low* sulfuric acid concentrations may be due to a chloride impurity catalyzed reaction, although we are quite confident that its contribution is at best a very small one.

Reinvestigation of the Rate of Disproportionation of Ia in Acetic Acid–0.56 *M* Water.—At the time the original kinetic studies[2] on the disproportionation of Ia were carried out the effect of traces of chloride ion on k_r and k_f was unknown and no special precautions were taken to keep such contamination to a minimum. Of course, if k_r were much larger than k_d under all conditions, the amount of chloride present would not affect the rate of disproportionation, since k_d would be truly rate determining and chloride, being a catalyst, naturally does not alter k_f/k_r. Unfortunately, however, at elevated temperatures and *low* sulfuric acid concentrations k_d and k_r (in the absence of chloride) are closely comparable in magnitude (see Discussion) and traces of chloride can influence the rate of disproportion under such conditions. For this reason it seemed desirable to redetermine the rate of disproportionation of Ia in acetic acid–0.56 M water using the same sulfinic acid samples employed in the study of the Ia–IIa equilibrium.

These studies showed that for runs at 70° in the presence of 0.20 M or more sulfuric acid the rates were the same within the experimental error as those previously determined.[2] For 0.10 M sulfuric acid the rate ($k_2 = 0.75 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$) was slightly lower than the earlier[2] experimental value of $0.82 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$. For 0.00 M sulfuric acid the second-order rate constant (0.46×10^{-3}) was very definitely lower than the previously reported[2] value (0.60×10^{-3}). We believe the higher rates are probably due to some chloride impurity in the samples of sulfinic acid used in the earlier work.

Discussion

Comparison of Calculated and Experimental Rates of Disproportionation.—If the mechanism in Chart I is correct, k_2, the experimental second-order rate constant for the disproportionation of Ia, should be related to the rate constants k_f, k_r, and k_d of eq 9 as follows.

$$k_2 = 3k_f\left(\frac{k_d}{k_r + k_d}\right) \tag{13}$$

From plots of log k *vs.* $1/T$ one can estimate k_r and k_f at 70° for a variety of reaction conditions for which k_2 values for Ia have been determined experimentally. These values of k_r and k_f are given in Table V. A similar plot of log k_d *vs.* $1/T$ gives k_d for IIa at 70° in acetic acid as $5.3 \times 10^{-3}\ \text{sec}^{-1}$. Previous studies[3] have indicated that k_d is not very solvent dependent, and it should therefore have essentially this same value in the various acetic acid–water solutions used for kinetic study of the disproportionation. If this is true and the mechanism in Chart I is correct, values of k_2 calculated from eq 13 using this value of k_d and the k_r and k_f values in Table V should correspond closely to those actually observed experimentally under the same reaction conditions. The last two columns in Table V show that this is indeed the case. The agreement between calculated and experimental values is amazingly good, particularly in view of the fact that our assumption that k_d shows *no* variation with the water and sulfuric acid content of the medium is almost certainly not quite strictly true. The mechanism in Chart I for the disproportionation of sulfinic acids in acetic acid medium would now seem to have been put to its severest test and to have been completely validated.

TABLE V

RATE CONSTANTS FOR IA–IIA EQUILIBRIUM AND FOR THE DISPROPORTIONATION OF IA AT 70° IN ACETIC ACID

C_{H_2O}, M	$C_{H_2SO_4}$, M	$k_f \times 10^3$, $M^{-1}\ \text{sec}^{-1}$	$k_r \times 10^3$, sec^{-1}	$k_2 \times 10^3$, $M^{-1}\ \text{sec}^{-1}$ Calcd[a]	Exptl[b]
2.80	1.00	0.88	50	0.25	0.24
0.56	0.60	9.7	93	1.57	1.53
	0.40	4.4	50	1.27	1.25
	0.20	1.4	19	0.90	0.94
	0.10	0.70	10	0.72	0.75
	0.00	(0.32)[c]	(5.5)[c]	(0.47)[c]	0.46

[a] Calculated from eq 13 using k_r and k_f in this table and k_d equal to $5.3 \times 10^{-3}\ \text{sec}^{-1}$. [b] Data for 0.0, 0.1, and 0.2 M H_2SO_4 solutions are from present work; data for other solutions are from ref 2, corrected in several cases for fact present solutions are 0.56 rather than 0.53 M in water. [c] Less accurate than other values since some k_r values at lower temperatures not obtained directly by experiment (see section on acid catalysis).

The Nature of the Rate-Determining Step.—In all previous considerations[2,4] of the mechanism in

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[10] S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 1 (1956).

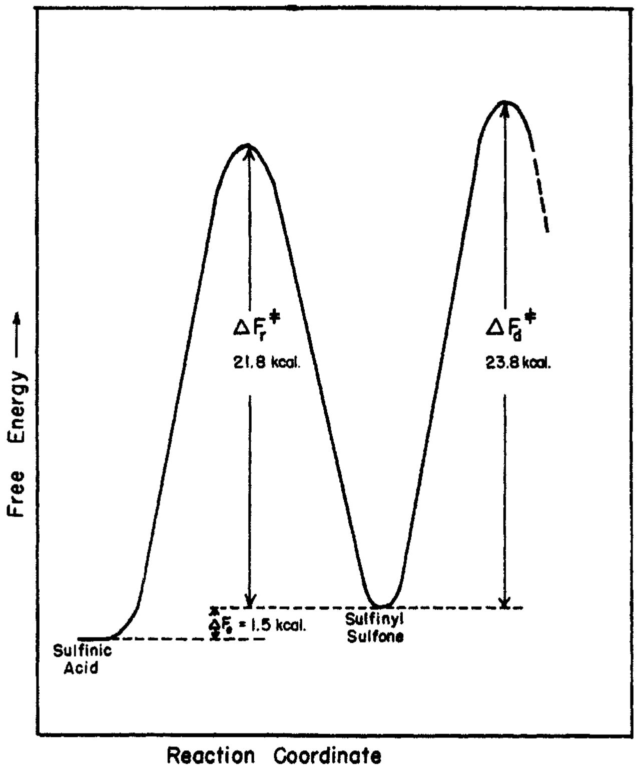

Figure 3.—Free-energy profile for disproportionation of Ia in acetic acid–0.56 *M* water–0.60 *M* H_2SO_4 at 70°. Various ΔF values are defined as follows: $\Delta F_e = -RT \ln K_e$; $\Delta F_r^* = RT(\ln kT/h - \ln k_r)$; $\Delta F_d^* = RT(\ln kT/h - \ln k_d)$.

Chart I it was generally assumed that equilibrium between the sulfinic acid and the sulfinyl sulfone was established rapidly and that the thermal decomposition of IIa (eq 3) was truly rate determining. This is equivalent to saying that $k_d << k_r$ for all reaction conditions. The data in Table V, however, show that this is not uniformly the case and that solvolysis and thermal decomposition of IIa are clearly much more closely comparable in rate at 70° than had been thought previously. Furthermore, because of the ~10-kcal difference in their activation energies (see Results), k_d will compete even more favorably with k_r at higher temperatures. Thus for acetic acid–1% water–0.10 *M* sulfuric acid one calculates that a change from 70 to 90° will change k_r/k_d from 1.9 to 0.9.

Because of the comparable magnitude of k_r and k_d and the dependence of k_d/k_r on temperature and acidity, what reaction constitutes the rate-determining step of the disproportionation will depend on the exact reaction conditions. At lower temperatures and higher sulfuric acid concentrations, k_d is truly rate determining, but at higher temperatures and low sulfuric acid concentration k_d can become enough faster than k_r so that formation of the sulfinyl sulfone (k_f) becomes effectively rate determining. This introduces a most important, and previously unrealized, complexity into the mechanism of Chart I. This is particularly so since k_f exhibits an entirely different dependence on acidity and stoichiometric water concentration than does the ratio k_dk_f/k_r, which is, of course, the rate ratio governing the disproportionation rate when k_d is rate determining.

The entire picture is further complicated by the powerful catalytic effect which traces of chloride ion can have on both k_r and k_f at low sulfuric acid concentrations. At higher temperatures and low acid concentration the presence of relatively small amounts of chloride as an impurity could easily accelerate k_r and k_f sufficiently so that k_d would replace k_f as the rate-determining step.

Free-Energy Profile for Disproportionation of Ia.—Even for those reaction conditions where k_d is rate determining the free-energy profile for the disproportionation of Ia in acetic acid–0.56 *M* water is a most unusual and interesting one. This can be seen from Figure 3, which shows the relationship between the free energies of Ia, IIa, and the transition states for k_r and k_d at 70° for a solution containing 0.6 *M* sulfuric acid. The sulfinyl sulfone, the key intermediate in the reaction, lies in a rather deep free-energy well, whose bottom is only 1–2 kcal above the free energy of the sulfinic acid, and whose two walls are almost equal in height. This latter equality arises from the fact that ΔS^* for k_r is much more negative than for k_d, a fact which largely compensates for the ~10-kcal lower activation energy associated with k_r.

Equilibrium Concentration of Sulfinyl Sulfone.—The K_e values in Table II show that the concentration of IIa which will be present at equilibrium in many of the acetic acid–water solutions, while small, is still substantial. Thus at 30° in acetic acid–0.56 *M* water–0.6 *M* sulfuric acid about 1.5% of the Ia in a 0.1 *M* solution will be converted to the sulfinyl sulfone at equilibrium. Even in the least favorable case in Table II (acetic acid–2.80 *M* water–0.4 *M* sulfuric acid) the equilibrium concentration of IIa is still 0.08% that of Ia. The results confirm the previous tentative hypothesis[4] that in media of low water activity the fraction of the sulfinic acid present as the sulfinyl sulfone at equilibrium can quite easily be as much as several per cent. This fact and the very facile thermal decomposition of the sulfinyl sulfone suggest that sulfinyl sulfones may in general play a more important role as intermediates in various reactions of sulfinic acids than has been realized in the past.

Mechanism of the Sulfinic Acid–Sulfinyl Sulfone Equilibrium.—The mechanism of the forward and reverse steps of the Ia–IIa equilibrium remains to be considered. We have elected to treat this subject in a separate paper,[11] which accompanies this one. In it various additional experimental data, particularly with respect to the effect of variations in aryl group structure on the rate and equilibrium constants for the I–II equilibrium, are presented. These additional data allow one to conduct a more meaningful discussion of the various possible mechanistic alternatives.

Experimental Section

Purification of Materials. ***p*-Toluenesulfinic Acid.**—Sodium *p*-toluenesulfinate (Aldrich Chemical) was dissolved in water and *p*-toluenesulfinic acid was precipitated by the addition of the calculated amount of 6 *N* sulfuric acid to this solution. (In earlier work[2,4] 6 *N* hydrochloric acid was used for this precipitation, but in view of the catalytic effect of traces of chloride on the rates of the forward and reverse steps of the Ia–IIa equilibrium this should definitely be avoided.) The precipitated acid was filtered off and washed rapidly several times with ice-cold distilled water. (Although some *p*-toluenesulfinic acid is lost by this washing, it also seems necessary to get the purest product pos-

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

sible.) The acid was then thoroughly dried under vacuum, after which it was recrystallized several times from ether–hexane in the manner described earlier.[2]

p-Toluenesulfinyl p-Tolyl Sulfone.—This was prepared and purified as outlined by Bredereck, *et al.*[12]

Solvents.—Acetic acid was purified as described in an earlier paper.[2] Tests with silver nitrate indicated it was chloride free. The same was true of the distilled water used to prepare the various acetic acid–water solutions. These were made up in the manner outlined previously,[13] as were the stock solutions of sulfuric acid in acetic acid–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 Rate and Equilibrium Studies.—The reaction cell was of the same basic design as that shown in Figure 2 of ref 3a. The only modification was that, in order to accommodate the apparatus to the cell compartment of a Cary Model 15 spectrophotometer, the 1-cm cell, C, was attached to a different side of chamber B.

To make a run a weighed amount of Ia was placed in chamber A and 5 ml of the appropriate acetic acid–water–sulfuric acid solution was placed in B. The apparatus was then attached to the vacuum line through D, the contents were frozen, and stopcock E was then opened. After the apparatus had been evacuated, dry, prepurified nitrogen was admitted to the apparatus and the contents of B were melted. This modified degassing procedure was repeated several times. After the final time stopcock E was closed and the apparatus was removed from the line. The solution in B was then brought to the temperature at which the run was to be carried out. At this point the Ia in A was quickly dissolved in the solution in B and, once solution was effected, the final solution was allowed to flow into cell C. The apparatus was then placed in the cell compartment of a Cary Model 15 spectrophotometer which was equipped to permit thermostating of the 1-cm cell, and the optical density of the solution at 300 mμ was recorded as a function of time.

After a run was complete the apparatus was removed and the solution in it was replaced by an equivalent amount of the same acetic acid–water–sulfuric acid solution, but lacking the sulfinic acid. The optical density of this was determined, and this small absorbance owing to solvent was deducted from all readings made during the run.

In determining the equilibrium absorbance at 300 mμ owing to IIa there is one further small correction that must be made in certain runs. Because one of the products of the disproportionation of Ia, namely, the aryl thiolsulfonate, does have, unlike Ia, some absorbance at 300 mμ, the occurrence of any disproportionation of Ia leads to an increase in the optical density at 300 mμ. To the extent that it occurs one will observe a slow, steady upward drift in the absorbance at 300 mμ which persists after the concentration of IIa has reached its equilibrium value. For many of the present reaction conditions the disproportionation rate is slow enough compared to the rate of establishment of equilibrium that no such drift is detectable and equilibrium optical densities owing to IIa can be evaluated directly. However, at higher temperatures and lower acid concentrations the steady final drift, while never large, does become significant. In those runs we have measured the rate of this drift, after waiting sufficient time to ensure that equilibrium between Ia and IIa was completely established. Using this steady final rate of drift we then corrected all optical densities obtained during the run by subtracting from them an amount equal to the time multiplied by the rate of increase in $A_{300\ m\mu}$ due to disproportionation. The largest correction, required by the runs at 48.2° with 0.1 M sulfuric acid, was such that the true equilibrium absorbance due to IIa at 300 mμ was found to be about 10% lower than the measured absorbance of the solution after 10 half-lives for k_1. This shows that even in the worst case the correction is a rather small one.

Extinction Coefficient for IIa at 300 mμ in Acetic Acid–Water.—Although not needed for determination of k_1, the extinction coefficient of IIa must be known before one can calculate K_e from the corrected equilibrium absorbance at 300 mμ. To obtain this in acetic acid–water medium we proceeded as follows. At 21° and 0.1 or 0.2 M sulfuric acid the rate of hydrolysis of IIa in acetic acid–0.56 M water is slow enough (half-life, 0.5–1.0 hr) so that one can determine the extinction coefficient for IIa simply by dissolving it quickly in the acetic acid–water solution and measuring the optical density of the solution at 300 mμ. This was done both for solutions 0.1 and 0.2 M in sulfuric acid and at several IIa concentrations. The extinction coefficient did not appear to change significantly with sulfuric acid concentration. The average value was 8000. This value was used in calculating the K_e values in Table II.

In these experiments, along with measuring the initial optical density of the solutions, one can also follow the slow decrease in absorbance with time due to hydrolysis of IIa to sulfinic acid. From such measurements one can determine rate constants for the disappearance of IIa which can be compared with the k_1 values in Table III for the same reaction conditions, and which should have the same value. The agreement was found to be excellent. This method was used in preference to the normal kinetic procedure for determining k_1 for IIa in solutions containing no added sulfuric acid.

Besides determining the extinction coefficient at 300 mμ we have examined the general character of the ultraviolet absorption spectrum of IIa in the region 270–360 mμ both in acetic acid–water and dioxane. Besides the maximum at 300 there is a minimum at about 280 mμ. The shapes of our spectra agree with that reported by Beck[14] for IIa.

Experiments with Added Potassium Chloride.—These were carried out in the same general way as the equilibrations without added chloride. A dilute stock solution of potassium chloride in acetic acid–0.56 M water was made up and suitable amounts of this were used in making up the 5 ml of solution initially placed in chamber B of the apparatus.

The potassium chloride used was a sample of unusually high purity donated by Professor W. J. Fredricks of this department. It was originally purified for use in solid-state studies on KCl crystals.

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[12] H. Bredereck, A. Wagner, H. Beck, and R. J. Klein, *Ber.*, **93**, 2736 (1960).

[13] J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **85**, 3472 (1963).

[14] E. H. Beck, Dissertation, Technische Hochschule, Stuttgart, 1958. We are grateful to Dr. Beck for sending us a copy of this dissertation.