CONCOMITANT ELECTROPHILIC AND NUCLEOPHILIC CATALYSIS

OF SULFUR-SULFUR BOND CLEAVAGE IN ARYL THIOLSULFINATES

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A RECENT study (1) demonstrated that at least some electrophilically-
catalyzed scissions of a disulfide bond also involve attack by a nucleophile
in the rate-determining step (eq. 1), rather than a unimolecular heterolysis
of $R-\overset{+}{\underset{E}{S}}-S-R$, as had normally been assumed in the past. This suggested the
important hypothesis that similar nucleophilic assistance might be a rather

$$R-S-S-R \;+\; E^+ \;\rightleftharpoons\; R-S-\overset{+}{\underset{E}{S}}-R$$

$$Nu: \;+\; R-S-\overset{+}{\underset{E}{S}}-R \;\xrightarrow[\text{determining}]{\text{rate}}\; R-S-Nu^+ \;+\; R-S-E$$

$$(1)$$

general phenomenon in the electrophilically-catalyzed cleavage of various
sulfur-sulfur bonds.

We have found that in acetic acid containing small amounts of water
and sulfuric acid phenyl benzenethiolsulfinate (I) reacts much more
readily with aromatic sulfinic acids ($ArSO_2H$) than it undergoes dispropor-
tionation (2), equation 2. In the presence of a sufficient excess of

$$2\ PhS(O)SPh \;\longrightarrow\; PhSO_2SPh \;+\; PhSSPh \qquad (2)$$

$$I$$

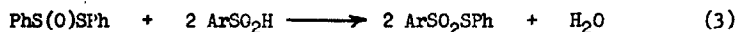sulfinic acid the stoichiometry of this reaction approaches that shown
in equation 3.[1] Kinetic study[2] of the reaction under conditions where

$$PhS(O)SPh \quad + \quad 2\ ArSO_2H \longrightarrow 2\ ArSO_2SPh \quad + \quad H_2O \qquad (3)$$

the sulfinic acid is in considerable stoichiometric excess (Table I) shows
that the reaction is first order in both sulfinic acid and thiolsulfinate,
subject to what appears to be general acid catalysis by added sulfuric
acid, and little affected by a change in the stoichiometric concentration
of water. The larger the pK_a of an aromatic sulfinic acid (3), the slower
it reacts under a given set of conditions.

Addition of a small amount of an alkyl or aryl sulfide (Table II)
brings about not only a substantial increase in the rate of the reaction
but also a profound change in the dependence of the rate on the various

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[1]
Product studies with a variety of thiolsulfinates and sulfinic acids
indicate that the reaction occurs in two steps, the first being

$$I \quad + \quad ArSO_2H \longrightarrow ArSO_2SPh \quad + \quad PhSOH$$

In the presence of sufficient excess sulfinic acid the sulfenic acid
PhSOH produced in the first step is consumed almost exclusively by
further reaction with $ArSO_2H$

$$PhSOH \quad + \quad ArSO_2H \longrightarrow ArSO_2SPh \quad + \quad H_2O$$

However, when the ratio $(ArSO_2H)/(PhSOPh)$ is smaller a significant
fraction of the sulfenic acid reacts with thiolsulfinate, rather
than sulfinic acid, according to the over-all equation shown below.

$$PhSOH \quad + \quad PhS(O)SPh \longrightarrow PhSO_2H \quad + \quad PhSSPh$$
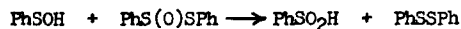
[2]
The rate of disappearance of I was followed spectrophotometrically
in the range 296 to 305 mμ. All runs were carried out with the
sulfinic acid present in considerable stoichiometric excess. Under
such conditions the disappearance of I follows good first-order kinetics.

Table I

Kinetics of Reaction of Aromatic Sulfinic Acids with I

Sulfinic acid $(pK_a)^a$	$(ArSO_2H)$ x 10^2,M^b	(H_2SO_4), M	(H_2O), M^c	k_1 x 10^4, sec^{-1}	$\dfrac{k_1 \text{ x } 10^2}{(ArSO_2H)}$
p-toluene(1.24)	2.7	0.10	0.56	2.48	0.94
	5.6	0.10	0.56	5.10	0.91
	8.6	0.10	0.56	7.7	0.90
	2.7	0.20	0.56	4.55	1.74
	2.7	0.30	0.56	6.6	2.52
	2.7	0.40	0.56	8.9	3.4
	2.7	0.20	0.28	4.2	1.58
	2.7	0.20	1.16	4.6	1.76
benzene (1.21)	2.7	0.10	0.56	2.36	0.90
p-bromobenzene(1.09)	2.7	0.10	0.56	3.76	1.43
p-nitrobenzene(0.64)	2.7	0.10	0.56	8.4	3.2

^{a} Data of ref. 3. ^{b}Initial thiolsulfinate concentration, 3.8 x 10^{-3} $\underline{M}$, temperature, 39.3° in all runs. $(ArSO_2H)$ is the average sulfinic acid concentration during a run and corresponds to initial sulfinic acid concentrations of 3.0, 6.0 and 9.0 x 10^{-2} $\underline{M}$. ^{c}Stoichiometric concentration of water.

reaction variables; yet the presence of the sulfide does not change the nature of the products formed. Kinetically the sulfide-catalyzed portion of the rate is found to be first order in both thiolsulfinate and added sulfide and independent of sulfinic acid concentration. The rate constant for the sulfide-catalyzed reaction, k_c, exhibits an entirely different dependence on the concentration of added strong acid and water, a plot of log k_c vs. $-H_0$ (4) being linear with slope of 1.0. For the several sulfides used as catalysts a plot of log k_c vs. the logarithm of their

Table II

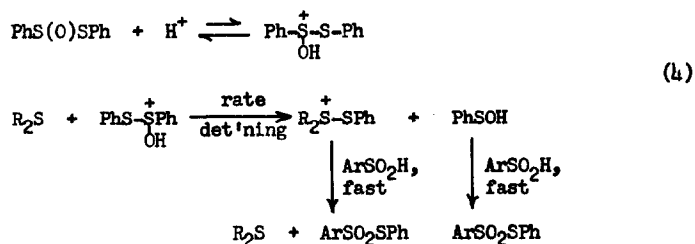Sulfide Catalysis of the Reaction of I with p-Toluenesulfinic Acid[a]

Sulfide	(sulfide) $\times 10^4$, M	(ArSO$_2$H) $\times 10^2$, M	(H$_2$SO$_4$), M	(H$_2$O), M	$k_1 \times 10^4$, sec^{-1}	$\dfrac{k_1 - k_1^o}{(\text{sulfide})} = k_c$[b]
n-butyl	0.10	2.7	0.10	0.56	18.2	158
	0.02	2.7	0.10	0.56	5.7	166
	0.02	5.6	0.10	0.56	8.4	167
benzyl	0.10	2.7	0.10	0.56	4.51	20.3
	0.20	2.7	0.10	0.56	6.4	19.8
	0.10	2.7	0.20	0.56	10.4	53.8
benzyl phenyl	5.0	2.7	0.10	0.56	4.47	0.40
	10.0	2.7	0.10	0.56	6.5	0.40
	15.0	2.7	0.10	0.56	8.3	0.39
	5.0	4.1	0.10	0.56	5.9	0.43
	5.0	5.6	0.10	0.56	7.1	0.40
	5.0	2.7	0.20	0.56	10.7	1.23
	5.0	2.7	0.30	0.56	19.2	2.52
phenyl	199	2.7	0.10	0.56	4.18	0.0085
	215	2.7	0.20	0.56	8.9	0.020
	195	2.7	0.30	0.56	16.2	0.049
	71	2.7	0.30	0.56	10.1	0.050
	97	2.7	0.40	0.56	15.6	0.069
	205	2.7	0.20	1.15	7.3	0.013

[a] All runs at 39.3° and an initial thiolsulfinate concentration of 3.8×10^{-3} M .
[b] k_1^o is the rate of disappearance of I in the absence of added sulfide (see Table 1). The sulfide-catalyzed portion of the rate is accordingly given by $k_1 - k_1^o$.

rate of oxidation by acidic hydrogen peroxide (5) is linear with a slope of 2.6. Since the latter reaction definitely involves nucleophilic attack by sulfur on the O-O bond, it seems almost certain that the sulfide also acts as a nucleophile in the sulfide-catalyzed reaction of I with sulfinic acids.

The kinetics of the sulfide-catalyzed reaction requires that the rate-

determining transition state be composed of a proton, and a molecule each of
thiolsulfinate and sulfide, with the latter acting as a nucleophile. The
only reasonable role for the proton is as an electrophilic catalyst which
aids the cleavage of the S-S bond by converting PhS(O)- to the better
leaving group Ph-$\overset{+}{\underset{OH}{S}}$-. The mechanism shown in equation 4 thus seems indicated.

$$PhS(O)SPh \;+\; H^+ \;\rightleftharpoons\; Ph-\overset{+}{\underset{OH}{S}}-S-Ph$$

$$(4)$$

$$R_2S \;+\; PhS-\overset{+}{\underset{OH}{S}}Ph \;\xrightarrow[\text{det'ning}]{\text{rate}}\; R_2\overset{+}{S}-SPh \;+\; PhSOH$$

$$\qquad\qquad\qquad\qquad \downarrow \text{ArSO}_2\text{H,} \atop \text{fast} \qquad \downarrow \text{ArSO}_2\text{H,} \atop \text{fast}$$

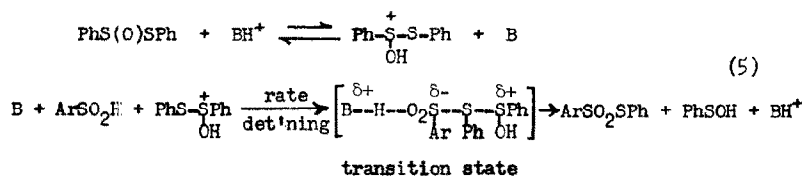$$\qquad\qquad\qquad R_2S \;+\; ArSO_2SPh \qquad ArSO_2SPh$$

Three important conclusions can be drawn from the present results:
(1) In accord with the suggested hypothesis, concomitant electrophilic
and nucleophilic catalysis can indeed be involved in the cleavage of
sulfur-sulfur bonds other than those in disulfides; (2) extremely low
concentrations of relatively weak nucleophiles can be strikingly effective
(witness the seven-fold acceleration by 10^{-5} M n-butyl sulfide in the present
system); (3) because of this, such catalysis would appear to have enormous
practical potential for effecting cleavage of sulfur-sulfur bonds in acid
media.

Although the mechanism of the uncatalyzed I-ArSO$_2$H reaction cannot at
present be specified as exactly, the effect of sulfinic acid structure on
rate argues that formation of the transition state involves an increase in
the electron-density on the sulfinic acid-sulfur. This and the dependence
on sulfuric acid concentration are consistent with a mechanism (eq. 5) which,

like the sulfide catalyzed reaction, also involves nucleophilic attack on the protonated thiolsulfinate in the rate-determining step.

$$PhS(O)SPh + BH^+ \rightleftharpoons Ph\underset{OH}{\overset{+}{-}S}\text{--}S\text{--}Ph + B \tag{5}$$

$$B + ArSO_2H + PhS\underset{OH}{\overset{+}{-}}SPh \xrightarrow[\text{det'ning}]{\text{rate}} \left[\underset{Ar}{\overset{\delta+}{B}}\text{--}H\text{--}\underset{Ph}{\overset{\delta-}{O_2S}}\text{--}S\text{--}\underset{OH}{\overset{\delta+}{SPh}} \right] \rightarrow ArSO_2SPh + PhSOH + BH^+$$

transition state

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