Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). 4. Acid- and Sulfide-Catalyzed Decomposition of *tert*-Butyl Benzenethiolsulfinate

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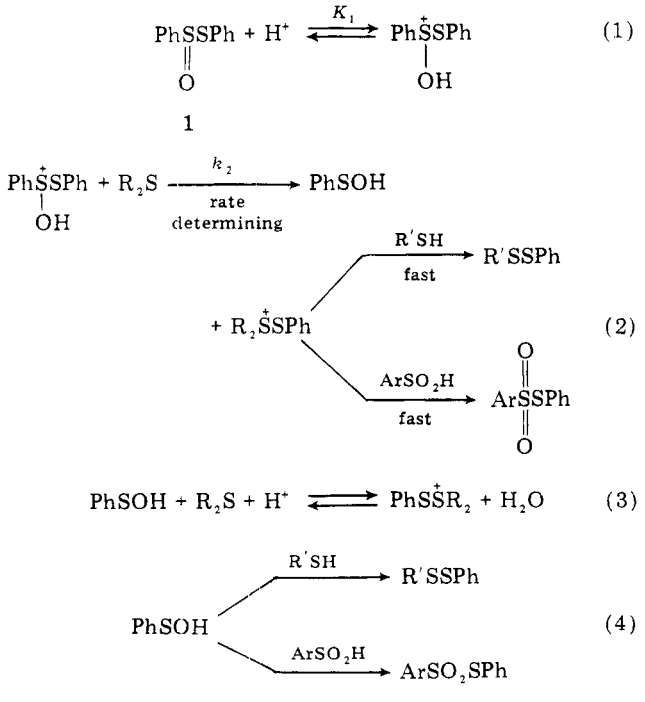
tert-Butyl benzenethiolsulfinate, PhS(O)SBu-*t* (**2**), undergoes acid- and sulfide-catalyzed decomposition in acetic acid–1% water to afford five products (yields in mmol/mmol of **2**): $PhSO_2SPh$ (0.27); PhSSBu-*t* (0.26); isobutylene (≥0.15); *t*-BuSSSBu-*t* (0.13); and $PhSO_2SSBu$-*t* (0.09). Kinetic studies, combined with the nature of the products, show that, despite the high steric hindrance to nucleophilic attack on the dicoordinate sulfur in **2**, the rate-determining step of the decomposition involves attack of the catalyzing alkyl sulfide on this sulfur in protonated **2**, $PhS^+(OH)SBu$-*t*, to give PhSOH and R_2S^+SBu-*t* (**3**). The benzenesulfenic acid is then rapidly converted to $PhSS^+R_2$, and a sequence of reactions (eqs 11–13) initiated by the reaction of this intermediate with **2** leads to the formation of PhSSBu-*t* and $PhSO_2SPh$. Intermediate **3** is thought to break down into a *tert*-butyl cation, which is the precursor of the isobutylene formed, and the thiosulfoxide $R_2S{=}S$. Thiosulfoxides are known[10] to decompose very rapidly into alkyl sulfide and sulfur. It is suggested that this sulfur will be liberated initially in a highly reactive form that could react readily with **2** to give PhS(O)SSBu-*t* (**8**). Alternatively the thiosulfoxide could react directly with **2** to give **8**. Compound **8** then undergoes a rapid acid- and sulfide-catalyzed breakdown to PhSOH and R_2S^+SSBu-*t* (**6**). Reaction of **6** with **2** is thought to initiate a sequence of reactions (eq 15–17) leading to *t*-BuSSSBu-*t* and $PhSO_2SSBu$-*t*.

In acid solution the reaction of phenyl benzenethiolsulfinate (**1**) with either sulfinic acids[1a] or thiols[1b] can be dramatically catalyzed by the addition of small amounts of alkyl sulfides. The mechanism for these sulfide-catalyzed reactions of **1** is shown in Scheme I. It involves a rate-determining nucleophilic attack by the alkyl sulfide on protonated **1** (step k_2) that leads to intermediates ($PhSS^+R_2$ and PhSOH) that are rapidly trapped by either $ArSO_2H$ or thiol. There is a marked dependence of rate on sulfide structure. The greater the electron density on the sulfur of R_2S, the more reactive the sulfide; *n*-Bu_2S is about eight times better a catalyst than $(PhCH_2)_2S$, for example.

Scheme I. Mechanism of the Acid- and Sulfide-Catalyzed Reaction of Phenyl Benzenethiolsulfinate with Sulfinic Acids and Thiols



(1) (2) (3) (4)

The disproportionation of **1** (eq 5) in acid solution is also subject to marked catalysis by alkyl sulfides.[2] Although the formal kinetics of the sulfide-catalyzed disproportionation are the same as those for the sulfide-catalyzed reactions of **1** with thiols and sulfinic acids, i.e., all three reactions show the same dependence on acidity, sulfide concentration, etc., the sulfide-catalyzed disproportionation exhibits a very different dependence of rate on sulfide structure. In the sulfide-catalyzed disproportionation, *n*-Bu_2S and $(PhCH_2)_2S$ are of equal reactivity, rather than the butyl compound being eight times more reactive.

$$\underset{\mathbf{1}}{2PhS(O)SPh} \rightarrow PhSSPh + PhSO_2SPh \qquad (5)$$

The mechanism shown in Scheme II has been established[2] for the sulfide-catalyzed disproportionation of **1**. Detailed analysis[2] of the kinetics expected for Scheme II has indicated that the reason for the difference in the reactivity pattern observed for *n*-Bu_2S and $(PhCH_2)_2S$ as catalysts in the disproportionation from the pattern found in the other sulfide-catalyzed reactions of **1** is because in the disproportionation attack of sulfide on protonated **1** (step k_2) is no longer rate determining; instead, the rate-determining step is now reaction of R_2S^+SPh with **1** (step k_6 of Scheme II).[3]

Attack of nucleophiles on a dicoordinate sulfur is known[5] to be profoundly retarded if a *tert*-butyl group is attached to that sulfur. Since nucleophilic attack on a dicoordinate sulfur is involved in both the forward and reverse steps of eq 2, it seemed of interest to determine if *tert*-butyl benzenethiolsulfinate (**2**), PhS(O)SBu-*t*, would undergo acid- and sulfide-catalyzed decomposition under the same conditions used for **1** and, if it did, to ascertain to what extent both the rate and the course of the reaction might be significantly altered from the behavior found with **1**. The present paper describes the results of this investigation. As we will see, **2** does undergo acid- and sulfide-catalyzed decomposition, but at a considerably slower rate than **1**. This slow decomposition of **2** exhibits a dependence of rate on sulfide structure quite different from that found for the disproportionation of **1**. The products of the sulfide-catalyzed decomposition of **2** are also quite

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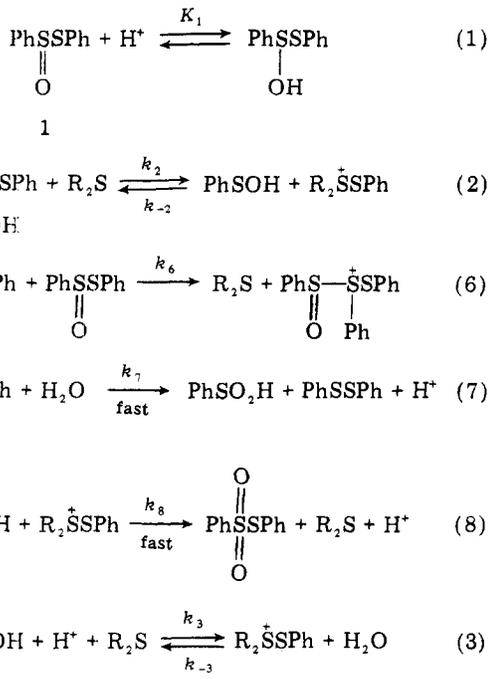
Scheme II. Mechanism of the Acid- and Sulfide-Catalyzed Disproportionation of Phenyl Benzenethiolsulfinate[a]



[a] For R_2S = *n*-Bu_2S or $(PhCH_2)_2S$: $k_6[1] < k_{-2}[PhSOH]$; $k_6[1] > k_{-3}[H_2O]$ in AcOH–1% H_2O.

different than what would be expected for a simple disproportionation of **2**.

Results and Discussion

Kinetics of the Decomposition of 2. In acetic acid–1% H_2O as solvent, **2** undergoes an acid- and sulfide-catalyzed decomposition that can be followed spectrophotometrically by monitoring the decrease in absorbance with time at 270–275 nm. The disappearance of **2** follows good first-order kinetics, and Table I shows the dependence of the experimental first-order rate constant (k_1) on various reaction variables. That the sulfide-catalyzed reaction is first order in sulfide is shown by the fact that for a given sulfide at a constant acidity, k_1 increases linearly with $[R_2S]$. The last column of Table I gives values of $k_d = k_1/[R_2S]$, the second-order rate constant for the sulfide-catalyzed decomposition of **2**. These are seen to increase with increasing acidity, and a plot of log k_d for either sulfide vs. the Hammett acidity function, $-H_0$, for the solutions[6] is linear with essentially unit slope. This is the same dependence on acidity found for the various acid- and sulfide-catalyzed reactions of **1**.[1,2]

Although the dependence of k_d on acidity for the sulfide-catalyzed decomposition of **2** is the same as for the sulfide-catalyzed disproportionation of **1** (eq 5), the dependence of k_d on sulfide structure is quite different. In the sulfide-catalyzed disproportionation of **1**, *n*-Bu_2S and $(PhCH_2)_2S$ are of almost exactly equal reactivity as catalysts;[2] in the decomposition of **2**, *n*-Bu_2S is 7.3 times more reactive as a catalyst than $(PhCH_2)_2S$. This type of difference in the reactivity of *n*-butyl and benzyl sulfides is virtually the same as that observed for the acid- and sulfide-catalyzed reactions of **1** with sulfinic acids[1a] or thiols,[1b] however.

In the acid- and sulfide-catalyzed reactions of **1** with sulfinic acids or thiols the rate-determining step (k_2 in Scheme I) is nucleophilic attack of the sulfide on protonated **1**, while in the sulfide-catalyzed disproportionation of **1** it is reaction of R_2S^+SPh with **1** (step k_6 of Scheme II). The kinetic behavior of the sulfide-catalyzed decomposition of **2** suggests that in this reaction, in contrast to the situation in the sulfide-catalyzed disproportionation of **1**, the rate-determining step is presumably attack of the sulfide on the protonated thiolsulfinate. From the products of the sulfide-catalyzed decomposition of **2** one can distinguish whether this still involves attack at the dicoordinate sulfur or whether, alternatively, because of the steric hindrance to attack at this position provided by the *tert*-butyl group, attack now occurs preferentially at the other sulfur.

Table I. Kinetics of the Sulfide-Catalyzed Decomposition of *tert*-Butyl Benzenethiolsulfinate[a]

$[2]_0 \times 10^4$, M	C_{H_2O}, M	$C_{H_2SO_4}$, M	$[R_2S] \times 10^3$, M	$k_1 \times 10^3$, s^{-1}	$k_d = k_1/[R_2S]$, $M^{-1}\ s^{-1}$
			n-butyl sulfide		
3.22	0.56	0.20	1.92	0.56	0.29
			4.29	1.31	0.31
			7.97	2.34	0.29
		0.10	7.78	0.78	0.10
		0.30	2.42	1.52	0.63
	1.13	0.20	7.63	1.14	0.15
6.44	0.56	0.20	7.96	2.28	0.29
			benzyl sulfide		
3.00	0.56	0.10	8.08	0.115	0.0143
		0.20	7.99	0.33	0.042
			12.1	0.48	0.040
		0.30	8.03	0.69	0.086

[a] All runs are at 40 °C in acetic acid containing the stoichiometric amounts of water and sulfuric acid indicated.

After outlining the results of examination of the products of the decomposition of **2**, we will return to consideration of the mechanism of the reaction and of some further aspects of its kinetics.

Products of the Sulfide-Catalyzed Decomposition of 2. In the absence of added alkyl sulfide, **2** (0.1 M) undergoes no significant decomposition in acetic acid–1% H_2O containing 0.1 M H_2SO_4 during 8 h at 40 °C. In the presence of 0.01 M added *n*-butyl sulfide, decomposition of **2** was complete under otherwise identical reaction conditions. The various products formed by the acid- and sulfide-catalyzed decomposition under these conditions and their isolated yields are given in Table II. Changing the concentration of *n*-Bu_2S to 0.05 M gave no change in products or product yields.

One of the main products is phenyl *tert*-butyl disulfide, PhSSBu-*t*. That this is formed directly in the decomposition of **2** and does *not* result from disproportionation of an initially formed mixture of *t*-BuSSBu-*t* and PhSSPh was shown by the fact that heating *t*-BuSSBu-*t* (0.1 M) and PhSSPh (0.1 M) in acetic acid–1% H_2O containing 0.1 M H_2SO_4 and 0.01 M *n*-Bu_2S for 8 h at 40 °C did not lead to the formation of a detectable amount of PhSSBu-*t*. Furthermore, neither *t*-BuSSBu-*t* nor PhSSPh could be detected as products of the sulfide-catalyzed decomposition of **2**.

Table II. Products of the Sulfide-Catalyzed Decomposition of *tert*-Butyl Benzenethiolsulfinate[a]

Product	Registry No.	Yield, mmol/mmol of **2**
PhSSBu-*t*	2943-20-6	0.26 ± 0.02
$PhSO_2SPh$	1212-08-4	0.27 ± 0.02
t-BuSSSBu-*t*	4253-90-1	0.13 ± 0.01
$PhSO_2SSBu$-*t*	68510-84-9	0.09 ± 0.01
$CH_2{=}C(CH_3)_2$	115-11-7	≥0.15[b]

[a] Reaction conditions: 0.1 M **2** and 0.01 M *n*-Bu_2S in acetic acid–1% H_2O containing 0.10 M H_2SO_4 at 40 °C for 8 h. [b] Minimum yield for this product. Actual yield could be considerably larger (see text).

Although no *tert*-butyl disulfide is formed in the decomposition of **2**, a significant amount of *tert*-butyl *trisulfide*, *t*-BuSSSBu-*t*, is formed. The identity of this initially unexpected product was confirmed by comparison of all of its spectral properties with those of an authentic sample of the trisulfide[7] prepared from *t*-BuSH and sulfur dichloride using the procedure of Schöberl and Wagner.[8]

Another major product of the decomposition is phenyl benzenethiolsulfonate, $PhSO_2SPh$, isolated in a yield of 0.27 mol/mol of **2**, and thus accounting for over 50% of the phenyl groups originally present in thiolsulfinate **2**. This was the only thiolsulfonate formed; neither $PhSO_2SBu$-*t* nor *t*-BuSO_2SBu-*t* was detected.

Instead of $PhSO_2SBu$-*t* we did find a significant amount of a related compound possessing an extra sulfur, $PhSO_2SSBu$-*t* (2-methylpropane-2-sulfenic benzenesulfonic thioanhydride or, alternatively, 1-phenyl 3-*tert*-butyl trisulfide 1,1-dioxide). That the compound did indeed possess this additional sulfur, and was *not* $PhSO_2SBu$-*t*, was shown unequivocally by both elemental and mass spectral analyses.

Isobutylene is also an important product of the acid- and sulfide-catalyzed decomposition of **2**. This was established by sweeping this olefin out of the reaction solution, trapping it in a trap cooled in liquid nitrogen, and then titrating it with bromine. The procedure used probably did not result in trapping all of the isobutylene actually produced in the decomposition of **2**. For this reason, the yield of 0.15 mol/mol of **2** listed in Table II is definitely a lower limit. It is also important to stress that since, as noted earlier, **2** undergoes no detectable decomposition in acetic acid–1% H_2O containing 0.10 M H_2SO_4 in the absence of added *n*-Bu_2S, the isobutylene detected is formed as a result of the sulfide-catalyzed decomposition of the thiolsulfinate and *not* as a result of any solvolytic side reaction involving only **2**.

The various products listed in Table II account collectively for 89% of the phenyl groups, and at least 76% of the *tert*-butyl groups, originally present in **2**.

Mechanism of the Sulfide-Catalyzed Decomposition of 2. The kinetics indicate that the rate-determining step of the reaction is attack of the catalyzing sulfide on protonated **2**. In principle this could occur either on the dicoordinate sulfur (eq 9) in a reaction analogous to step k_2 in the decomposition of **1**, but with a much slower rate because of the steric hindrance to attack at this sulfur provided by the *tert*-butyl group, or, alternatively, on the tricoordinate sulfur (eq 10) to give $R_2S^+S(O)Ph$ (**4**) and *t*-BuSH. Under the present reaction conditions, intermediate **4** should then rapidly hydrolyze to R_2S and $PhSO_2H$.[9] Further reaction of *t*-BuSH with protonated **2** would be expected[1b] to lead to the formation of a significant amount of *tert*-butyl disulfide, a product not found in detectable yield. The absence of any *tert*-butyl disulfide and the fact that the actual products can be accounted for by a mechanism that will be elaborated in succeeding paragraphs, in which further reactions starting from the PhSOH formed in eq 9 lead to the formation of PhSSBu-*t* and $PhSO_2SPh$ while reactions starting from **3** lead to the eventual formation of isobutylene, *t*-BuSSSBu-*t*, and $PhSO_2SSBu$-*t*, cause us to believe that the attack of R_2S on protonated **2** in the rate-determining step occurs in the manner shown in eq 9.

$$PhS^+(OH)SBu\text{-}t + R_2S \xrightarrow{k_9} \underset{\mathbf{3}}{PhSOH} + R_2S^+SBu\text{-}t \quad (9)$$

$$R_2S + PhS^+(OH)SBu\text{-}t \rightarrow R_2S^+S(O)Ph + t\text{-BuSH} \quad (10)$$
$$\mathbf{4}$$

In discussing the formation of the various final products from PhSOH and **3**, we will first outline the path by which PhSSBu-*t* and $PhSO_2SPh$ are formed from PhSOH. Subsequently we will outline the paths that we believe lead from **3** to isobutylene, *t*-BuSSSBu-*t*, and $PhSO_2SSBu$-*t*.

The previous work[2] on the sulfide-catalyzed disproportionation of **1** indicates that PhSOH (benzenesulfenic acid) once formed by eq 9 would be readily transformed into R_2S^+SPh (see eq 3 in Scheme II). Nucleophilic attack of **2** on this intermediate (eq 11), in a reaction analogous to eq 6 in Scheme II, should occur readily since the dicoordinate sulfur in $PhSS^+R_2$, unlike the one in *t*-$BuSS^+R_2$, is not sterically hindered. Hydrolysis of intermediate **5** (eq 12) followed by reaction of the $PhSO_2H$ produced with another $PhSS^+R_2$ (eq 13) accounts for the formation of phenyl *tert*-butyl disulfide (PhSSBu-*t*) and phenyl benzenethiolsulfonate ($PhSO_2SPh$).

$$PhS(O)SBu\text{-}t + PhS^+SR_2 \rightarrow \underset{\mathbf{5}}{PhS\cdot(O)S^+(t\text{-Bu})SPh} + R_2S \quad (11)$$

$$PhS(O)S^+(t\text{-Bu})SPh + H_2O \rightarrow PhSO_2H + t\text{-BuSSPh} + H^+ \quad (12)$$

$$PhSO_2H + PhSS^+R_2 \rightarrow PhSO_2SPh + R_2S + H^+ \quad (13)$$

Because of the steric hindrance to attack on the dicoordinate sulfur, R_2S^+SBu-*t* (**3**) does not react under our reaction conditions with either $PhSO_2H$ or **2** at a rate that is kinetically important. Neither does it react with PhSOH to revert to protonated **2** and R_2S at a rate that is fast enough to be kinetically competitive with the conversion of PhSOH to products via eq 3 followed by eq 11 and 13. This is the reason that attack of the sulfide on protonated **2** is rate determining for the *tert*-butyl ester, whereas in the case of **1**, where reaction of PhSOH with the unhindered dicoordinate sulfur of $PhSS^+R_2$ is rapid, it is not.

What then is the fate of **3**? Although nucleophilic attack on the dicoordinate sulfur of **3** is severely hindered, **3**, because of the stability of a *tert*-butyl cation, could decompose as shown in eq 14. Loss of a proton from the carbonium ion accounts for the isobutylene formed in the decomposition.

$$R_2S^+SBu\text{-}t \rightarrow R_2S{=}S + (CH_3)_3C^+ \xrightarrow{-H^+} CH_2{=}C(CH_3)_2 \quad (14)$$

The remaining products of the decomposition, *t*-BuSSSBu-*t* and $PhSO_2SSBu$-*t*, can be easily accounted for if R_2S^+SSBu-*t* (**6**) can in some way be formed as an intermediate during the reaction, for **6**, with an unhindered dicoordinate sulfur adjacent to the sulfonium center, should react readily with both **2** and $PhSO_2H$ in a fashion analogous to $PhSS^+R_2$ to form *t*-BuSSSBu-*t* and $PhSO_2SSBu$-*t* (eq 15–17).

$$PhS(O)SBu\text{-}t + \underset{\mathbf{6}}{R_2S^+SSBu\text{-}t} \rightarrow PhS(O)S^+(t\text{-Bu})SSBu\text{-}t + R_2S \quad (15)$$

$$PhS(O)S^+(t\text{-Bu})SSBu\text{-}t + H_2O \rightarrow PhSO_2H + t\text{-BuSSSBu-}t + H^+ \quad (16)$$

$$PhSO_2H + R_2S^+SSBu\text{-}t \rightarrow PhSO_2SSBu\text{-}t + R_2S + H^+ \quad (17)$$

We believe that the most likely source of **6** is from the acid- and sulfide-catalyzed decomposition of the trisulfide monoxide PhS(O)SSBu-*t* (**7**). Protonated **7**, having an unhindered dicoordinate sulfur adjacent to the protonated sulfinyl group, would be cleaved very rapidly by R_2S as shown in eq 18b to give PhSOH and **6**. The sulfenic acid would then react further

(eq 3 and 11–13) as discussed earlier, while **6** would react according to eq 15–17.

$$\underset{\mathbf{7}}{\text{PhS(O)SSBu-}t} + H^+ \rightleftarrows \text{PhS}^+\text{(OH)SSBu-}t \quad (18a)$$

$$\text{PhS}^+\text{(OH)SSBu-}t + R_2S \rightarrow \text{PhSOH} + \underset{\mathbf{6}}{R_2S^+SSBu\text{-}t} \quad (18b)$$

Two plausible possibilities for the formation of **7** from **2** and the thiosulfoxide $R_2S{=}S$ formed in eq 14 come to mind. In the first, eq 19, the thiosulfoxide, which a recent report[10] indicates would be very unstable and reactive, "donates" a sulfur atom directly to the relatively weak S–S bond of the thiolsulfinate. In the second, sulfur, produced by the reportedly[10] very fast decomposition of the thiosulfoxide, inserts into the S–S bond of the thiolsulfinate (eq 20). Although the exact mechanism of the decomposition of $R_2S{=}S$ to R_2S and sulfur is not yet known, the extreme rapidity of the reaction suggests that the sulfur may be liberated initially in a highly reactive state, rather than S_8. If true, reaction of **2** with this reactive form of sulfur, possibly atomic sulfur, could conceivably occur readily and lead to **7**.

$$R_2S{=}S + \underset{\mathbf{7}}{\text{PhS(O)SBu-}t} \rightarrow R_2S + \underset{\mathbf{7}}{\text{PhS(O)SSBu-}t} \quad (19)$$

$$R_2S{=}S \xrightarrow[\text{fast}]{\text{very}} R_2S + S \quad (20a)$$

$$\underset{\mathbf{2}}{\text{PhS(O)SBu-}t} + S \rightarrow \underset{\mathbf{7}}{\text{PhS(O)SSBu-}t} \quad (20b)$$

We also considered the possibility that **6** might be formed by a nucleophilic displacement by $R_2S{=}S$ on **3** (eq 21). However, the severe steric hindrance to attack on a *t*-BuS sulfur experienced by other nucleophiles[5] and the presumably very short average lifetime of the thiosulfoxide[10] make us hesitant to suggest such a possibility.

$$R_2S{=}S + t\text{-BuSS}^+R_2 \rightarrow R_2S^+SSBu\text{-}t + R_2S \quad (21)$$

Although speculative, we feel that eq 19 or 20 is quite reasonable. We thus believe that the sequence of reactions of eq 14, followed by either eq 19 or 20, and then by eq 18 and 15–17 represents an attractive mechanistic proposal for the manner in which $R_2S^+SBu\text{-}t$ leads to the final products isobutylene, t-$BuS_3Bu\text{-}t$, and $PhSO_2SSBu\text{-}t$. It is also interesting that the collection of reactions proposed for the mechanism of the sulfide-catalyzed decomposition of **2** leads to a stoichiometry for the reaction close to that in eq 22.[11] In the case of the first four products, where accurate yields could be determined, this is very similar to what is observed.

$$\begin{aligned}\text{PhS(O)SBu-}t \rightarrow\ & 0.29\text{PhSSBu-}t + 0.29\text{PhSO}_2\text{SPh} \\ & + 0.14t\text{-BuSSSBu-}t + 0.14\text{PhSO}_2\text{SSBu-}t \\ & + 0.29\text{CH}_2{=}\text{C(CH}_3)_2 + 0.14\text{H}_2\text{O}\end{aligned} \quad (22)$$

One final point. Since eq 9 is believed to be rate determining for the sulfide-catalyzed decomposition of **2**, the rate constants for the reaction, k_d, given in Table I should be equal to $k_d = aK_1'k_9a_{H^+}$, where k_9 is the rate constant for eq 9, K_1' is the equilibrium constant for the protonation of **2** (eq 23), and a is the total number of molecules of **2** consumed for each occurrence of step k_9. Under product study conditions ($[\mathbf{2}]_0$ = 0.1 M) this is 3.5, but under kinetic conditions ($[\mathbf{2}]_0 = 3 \times 10^{-4}$ M) it could be as low as 1.5 if **2** is unable at this much lower concentration to "trap" all of the thiosulfoxide liberated by the decomposition of **3**.

$$\text{PhS(O)SBu-}t + H^+ \overset{K_1'}{\rightleftarrows} \text{PhS}^+\text{(OH)SBu-}t \quad (23)$$

The rate constant, k_s, for the sulfide-catalyzed reaction of **1** with either thiols or sulfinic acids under the same conditions is equal to $K_1k_2a_{H^+}$ (Scheme I). The steric hindrance to attack on the dicoordinate sulfur of protonated **2** should cause k_9 to be much smaller than k_2. Given this, one would expect k_d/k_s to be much less than 1, and this is indeed the case, k_d/k_s for both sulfides being $\sim 5 \times 10^{-4}$. Since *t*-BuS is inductively a somewhat weaker electron-withdrawing group than PhS, K_1' should be larger than K_1. This, plus the fact that a may be as large as 3.5, means that k_9/k_2 is undoubtedly significantly smaller than the $\sim 5 \times 10^{-4}$ value of k_d/k_s. This is not surprising since a rate ratio of 5×10^{-6} has been found[12] for nucleophilic attack of *n*-BuS$^-$ on these two thiolsulfinates.

Experimental Section

***tert*-Butyl Benzenethiolsulfinate (2).** This was prepared from benzenesulfinyl chloride and 2-methyl-2-propanethiol (Aldrich Chemical) using the same general procedure described by Chau and Kice[13] for the preparation of *p*-fluorophenyl benzenethiolsulfinate from *p*-fluorothiophenol and the same sulfinyl chloride. After removal of the ether solvent, the crude **2** was purified by recrystallization from chloroform–hexane: yield 40%; mp 51–52 °C (lit.[14] mp 51–52 °C).

***tert*-Butyl phenyl disulfide** was prepared by refluxing 2-methyl-2-propanethiol (9.0 g, 0.1 mol) and *N*-phenylthiophthalimide (25.5 g, 0.1 mol) together in 400 mL of benzene for 96 h using the general procedure for the synthesis of unsymmetrical disulfides developed by Harpp and co-workers.[15] After filtration to remove phthalimide, followed by removal of the benzene solvent under reduced pressure, the residue was subjected to vacuum distillation, giving 15.8 g (80%) of *tert*-butyl phenyl disulfide: bp 60–62 °C (0.05 mm) [lit.[16] bp 48 °C (0.03 mm)]; NMR ($CDCl_3$) δ 1.32 (s, 9 H), 7.2–7.8 (m, 5 H); mass spectrum (25 °C and 20 eV), *m/e* (intensity) 198 (M^+, 81), 142 (100), 109 (52), 78 (95), 57 (100).

Di-*tert*-butyl Trisulfide. Purified sulfur dichloride (1.1 g, 0.01 mol) and 1.88 g (0.02 mol) of 2-methyl-2-propanethiol were allowed to react in anhydrous ether following the procedure for the preparation of trisulfides outlined by Schöberl and Wagner.[8] The ether was then removed under reduced pressure, and the residue was subjected to vacuum distillation to afford 1.76 g (84%) of di-*tert*-butyl trisulfide: bp 46 °C (0.3 mm) [lit.[7] bp 86 °C (4 mm)]; NMR ($CDCl_3$) δ 1.39 (s); mass spectrum, *m/e* 210 (M^+), 154 ($M^+ - C_4H_8$), 89 (C_4H_9S).

Purification of Other Reagents. Commercial glacial acetic acid, *n*-butyl sulfide, and benzyl sulfide were purified as described earlier.[2]

Procedure for Kinetic Runs. The preparation of the reaction solutions for the kinetic runs followed the same procedure as used[2] in studying the kinetics of the sulfide-catalyzed disproportionation of **1**. A portion of the reaction solution was placed in a 1-cm cell in the thermostatted cell compartment of an ultraviolet spectrophotometer, and the reaction was followed directly in the spectrophotometer at 270–275 nm by monitoring the change in the optical density as a function of time.

Products of the Sulfide-Catalyzed Decomposition of 2. To a solution of 2.15 g (10 mmol) of **2** in 20 mL of acetic acid–1% H_2O was added 0.16 g (1.1 mmol) of *n*-butyl sulfide in 20 mL of the same solvent followed by 60 mL of 0.17 M H_2SO_4 in acetic acid–1% H_2O. The reaction solution was allowed to stand at 40 °C for 8 h. At the end of this time, the solution was poured into 1 L of water and the resulting suspension was extracted three times with 100-mL portions of ether. The ether extracts were combined and washed first with water and then with 5% sodium bicarbonate (until the pH of the washings remained basic). The ether extracts were then dried over magnesium sulfate, and the ether was removed under reduced pressure. The residue (1.87 g) was then chromatographed on silica gel using successively hexane, hexane–benzene, benzene, and benzene–ether as eluents.

Elution with 2:1 hexane–benzene gave a fraction which could be separated by GLC (5% SE-30, 5 ft × ⅛ in., 120 °C) into three separate components whose retention times were identical with those of *n*-butyl sulfide, di-*tert*-butyl trisulfide, and *tert*-butyl phenyl disulfide, respectively. There were no peaks at the retention times for either di-*tert*-butyl disulfide or diphenyl disulfide. The identity of the trisulfide was unequivocally established by its separation from the mixture by preparative gas chromatography and comparison of the mass spectrum and other spectral properties of the material so separated with those of an authentic sample of the trisulfide. The relative amounts of t-$BuS_3Bu\text{-}t$ and $PhSSBu\text{-}t$ in the fraction could be determined either from the areas of the GLC peaks or from the relative

integrated intensities of the singlets in the NMR for the methyl groups in t-BuS_3Bu-t (δ 1.39) and t-BuSSPh (δ 1.32). As would be expected, the ratio of the singlet at δ 1.32 to the aromatic multiplet at δ 7.2–7.8 was 9:5.

Elution with 1:1 hexane–benzene gave 0.170 g of an oil that crystallized on cooling in a freezer. It could be recrystallized at low temperature from 4:1 hexane–ethanol, but a melting point could not be determined because the compound melts below room temperature. The spectral properties of the compound were as follows: IR, strong absorption at 1320 and 1135 cm^{-1}, showing the presence of an SO_2 group; NMR ($CDCl_3$) δ 1.39 (s, 9 H), 7.6–8.2 (m, 5 H); mass spectrum (at 70 eV), m/e 262 (M^+), 206 ($M^+ - C_4H_8$), 182, 143, 142 ($PhSO_2H$), 141 ($PhSO_2$), 126, 125, 110, 109, 97, 78, 77, 58, and 57; UV (dioxane) λ_{max} 254 nm (ϵ 7900), 225 (1.34×10^4). On the basis of these results the compound was assigned the structure $PhSO_2SBu$-t. Anal. Calcd for $C_{10}H_{14}O_2S_3$: C, 45.80; H, 5.34; S, 36.64. Found: C, 45.82; H, 5.40; S, 36.75.

Elution with 1:2 hexane–benzene gave 0.76 g of a fraction that crystallized on standing. The infrared and NMR spectra of this material were identical with those of a known sample[1a] of phenyl benzenethiolsulfonate, $PhSO_2SPh$. Recrystallization from ethanol gave material with mp 43–45 °C (lit.[17] mp 43–44.5 °C).

The formation of isobutylene in the sulfide-catalyzed decomposition of **2** was investigated in a separate experiment. Thiolsulfinate **2** (0.214 g, 1.0 mmol) and n-butyl sulfide (0.017 g, 0.1 mmol) were dissolved in 10 mL of acetic acid–1% H_2O containing 0.10 M H_2SO_4, and the solution was heated at 50 °C for 5 h while a slow stream of nitrogen was passed through the solution. The solution was contained in a flask attached to a reflux condenser, and after exiting from the condenser the nitrogen flow was led through two traps, the first cooled in ice and the second in liquid nitrogen. At the end of the reaction period, the trap cooled in liquid nitrogen was removed and a few milliliters of chloroform was added to it. To the cold chloroform solution was then added 1.0 mL of a 0.527 N solution of bromine in acetic acid, and the mixture was allowed to warm to room temperature. At this point 10 mL of 10% potassium iodide solution was added, and the iodine that was liberated was titrated with standard sodium thiosulfate (1.53 mL of 0.156 N solution was required).

In an additional experiment we also checked to see if acetone was produced as a product of the decomposition of **2**. Thiolsulfinate **2** (5 mmol) was decomposed at 40 °C in acetic acid–1% H_2O in the presence of n-butyl sulfide and sulfuric acid in exactly the same way as in the earlier product study. At the end of the reaction, about half of the solvent was distilled under reduced pressure (120 mm) into a dry ice-cooled receiver. The contents of the receiver were then melted and an equal volume of water added. This was followed by 10 mL of a solution of 2,4-dinitrophenylhydrazine (1.2 g) dissolved in water (10 mL), concentrated H_2SO_4 (6 mL), and ethanol (32 mL). No precipitate of acetone 2,4-dinitrophenylhydrazone formed. A separate experiment in which 0.07 g (1.2 mmol) of acetone was deliberately added to the reaction solution prior to the distillation showed that any acetone present in the solution would have distilled over and led to the formation of a precipitate of acetone 2,4-dinitrophenylnitrophenylhydrazone upon addition of the 2,4-dinitrophenylhydrazine solution.

Behavior of a Mixture of Di-*tert*-butyl Disulfide and Diphenyl Disulfide Under Reaction Conditions. A mixture of 0.89 g (5 mmol) of di-*tert*-butyl disulfide, 1.09 g (5 mmol) of diphenyl disulfide, and 0.88 g (0.54 mmol) of n-butyl sulfide was dissolved in 50 mL of acetic acid–1% H_2O containing 0.1 M H_2SO_4, and the solution was kept at 40 °C for 8 hr. At the end of this time the solution was poured into 10 times its volume of water and worked up by ether extraction, etc., in the same way as in the product studies of the decomposition of **2**. The residue, after removal of the ether, was subjected to gas–liquid chromatography. The only compounds found were the starting materials: PhSSPh, t-BuSSBu-t, and n-Bu_2S. There was no peak corresponding to the retention time of $PhSSBu$-t.

Stability of 2 in the Absence of *n*-Butyl Sulfide. Thiolsulfinate **2** (1.07 g) was dissolved in 50 mL of acetic acid–1% H_2O containing 0.10 M H_2SO_4 and kept at 40 °C for 8 h. At the end of this time the solution was worked up by pouring it into water and extracting with ether in the same way as in the product studies. The residue, after removal of the ether (0.999 g), melted at 49–52 °C and had an infrared spectrum identical with that of a known sample of **2**. Chromatography on silica gel did not lead to detectable amounts of any of the products found in the sulfide-catalyzed decomposition of **2**.

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Registry No.—**2**, 63752-74-9; benzenesulfinyl chloride, 4972-29-6; 2-methyl-2-propanethiol, 75-66-1; N-phenylthiophthalimide, 14204-27-4; sulfur dichloride, 10545-99-0; n-butyl sulfide, 544-40-7; benzyl sulfide, 538-74-9.

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