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A Search for an α-Disulfoxide as an Intermediate in the Oxidation of an Aryl Thiolsulfinate[1]

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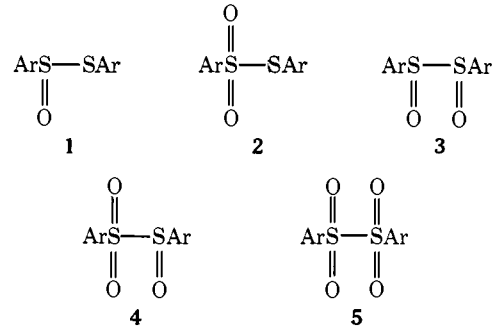
Abstract: The oxidation of *p*-fluorophenyl *p*-fluorobenzenethiolsulfinate (**1a**), ArS(O)SAr, to the corresponding thiolsulfonate, $ArSO_2SAr$ (**2a**), by peracetic acid, and other peracids, at −20 °C in chloroform has been studied by ^{19}F NMR. These studies show that the disulfide ArSSAr is *not* formed in detectable amounts during the course of the oxidation, thereby ruling out a mechanism for the oxidation of aryl thiolsulfinates by peracids proposed by Barnard and Percy (ref 8). Study of the oxidation of *p*-fluorophenyl benzenethiolsulfinate (**1b**), PhS(O)SAr, by the same reagent shows that the three different thiolsulfonates, $ArSO_2SAr$, $ArSO_2SPh$, and $PhSO_2SAr$, are all formed and in relative amounts consistent with *at least* 73% of the oxidation going via a pathway involving an α-disulfoxide, ArS(O)S(O)Ph, as an intermediate. The fact that α-disulfoxide ArS(O)S(O)Ar does not build up as an intermediate to a detectable level during the oxidation of **1a** means that it must be so thermally unstable that it has a half-life of less than 60 s at −20 °C. Since this suggests that $\Delta H^{\ddagger}$ for the decomposition of the α-disulfoxide is less than 20 kcal/mol, the S–S bond in an α-disulfoxide is apparently an extremely weak bond, much weaker than the S–S bonds in any of the other possible oxidized derivatives of disulfides.

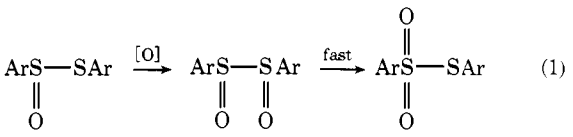
Structures of **1–5** represent the various possible oxidized forms of an aryl disulfide that still retain the S–S bond. Compounds having all of these structures,[2–5] *except* **3**, *the* α*-disulfoxide*, are known, although some, such as the sulfinyl sulfones,[4b] **4**, are not very stable thermally.

Several attempts[6,7] to prepare an aryl α-disulfoxide have been made, but each has failed, and the product isolated has been the corresponding thiolsulfonate, **2**. Thus, Barnard[6] found that treating benzenesulfinyl chloride with zinc gave phenyl benzenethiolsulfonate (**2**, Ar = C_6H_5), rather than the α-disulfoxide. Similarly, although several groups[7,8] have felt that an α-disulfoxide was an initial oxidation product of the oxi-



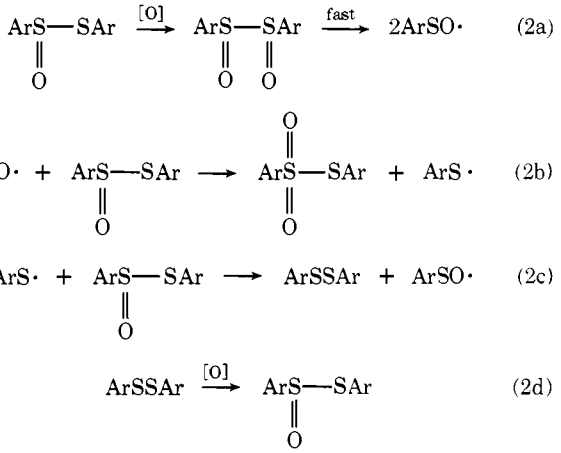
dation of a thiolsulfinate (**1**) by such oxidizing agents as peracids, the final product isolated in each instance was the thiolsulfonate. The previous evidence thus points toward the conclusion that α-disulfoxides are quite unstable compounds, but just how unstable was not clear.

Furthermore, there is disagreement as to just what role an α-disulfoxide plays as an unstable intermediate in the oxidation of a thiolsulfinate. Marangelli, Modena, and Todesco[7] and Modena and Todesco[9] believed that the α-disulfoxide, once formed, underwent rapid isomerization to the thiolsulfonate:



(1)

Barnard and Percy,[8] on the other hand, believed that the role of the α-disulfoxide was to serve as an initiator for an ArSO· initiated disproportionation of the thiolsulfinate to thiolsulfonate and disulfide, with the disulfide then being oxidized back to the thiolsulfinate by some of the remaining oxidizing agent (eq 2a-d). As evidence in favor of this mechanism they



(2a)

(2b)

(2c)

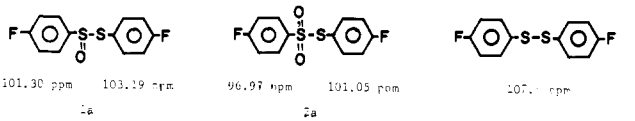
(2d)

claimed that the disulfide could be detected as a transient intermediate during the oxidation of PhS(O)SPh by hydrogen peroxide in acetic acid in amounts up to 30% of the original concentration of the thiolsulfinate. Modena and Todesco,[9] however, claimed that no disulfide could be detected as an intermediate in the oxidation of **1** by perbenzoic acid in dioxane, a situation that, given the comparable rates of oxidation of disulfides and **1** by peracid,[7] would preclude a mechanism of the type proposed by Barnard and Percy.

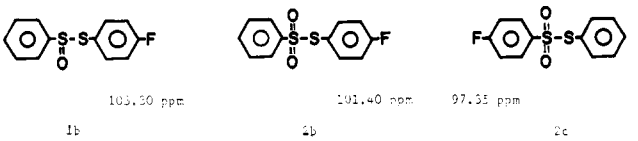
It seemed to us that it should be possible both to resolve this disagreement over the mechanism of oxidation of aryl thiolsulfinates by peracids and related compounds, and also to get some idea about the degree of instability of an aryl α-disulfoxide, by examining with time the ^{19}F NMR spectrum of a solution of an appropriate *p*-fluorophenyl thiolsulfinate plus peracid at relatively low temperatures (−20 to −30 °C) where the oxidation is not too rapid. The reason that this approach seemed likely to be productive is because the chemical shift of the ^{19}F of a *p*-fluorophenyl group varies significantly in a predictable fashion with the nature of the sulfur atom to which the *p*-FC_6H_4 group is attached. One can thus follow the disappearance of thiolsulfinate, appearance of thiolsulfonate, and detect the existence of any intermediates such as disulfide or α-disulfoxide that might build up to a significant concentration level at some point during the course of the oxidation. Our expectations have indeed been realized, and our results, and what they have to tell us about the course of the oxidation of aryl thiolsulfinates by peracids, form the subject of the present paper.

Results

p-Fluorophenyl *p*-fluorobenzenethiolsulfinate (**1a,** Ar = *p*-FC_6H_4-), *p*-fluorophenyl *p*-fluorobenzenethiolsulfonate (**2a,** Ar = *p*-FC_6H_4) and *p*-fluorophenyl disulfide, (*p*-$FC_6H_4S)_2$, were all prepared by standard routes and their ^{19}F NMR spectra determined in chloroform at −20 °C. The chemical shifts associated with the different fluorines in these molecules, expressed as ppm upfield from Freon 11, are summarized below:



The unsymmetrical thiolsulfinate, *p*-fluorophenyl benzenethiolsulfinate, $PhS(O)SC_6H_4F$-*p*, was also prepared. The chemical shift associated with the fluorine of its *p*-fluorophenyl group as well as those associated with the fluorines in the two unsymmetrical thiolsulfonates, $PhSO_2SC_6H_4F$-*p* and *p*-$FC_6H_4SO_2SPh$, are given below:



Changes in the ^{19}F NMR Spectrum During the Oxidation of 1a by Peracetic Acid at −20 °C. A solution of *p*-fluorophenyl *p*-fluorobenzenethiolsulfinate (**1a**) in chloroform was mixed with somewhat less than 1 equiv of peracetic acid in an NMR tube at −78 °C, and the changes in the ^{19}F NMR spectrum of the solution were then monitored with time at −20 °C. The signals at Φ = 103.19 and 101.30 ppm due to the fluorines of **1a** were observed to decrease in intensity. Concurrent with this decrease was the appearance of signals centered at 96.97 and 101.05 ppm due to the fluorines in **2a.** These particular changes are the only changes that can be detected during the course of the oxidation. In particular, there is *no sign of any peak in the 107–108 ppm region,* such as would be expected if a significant amount of $(FC_6H_4S)_2$ were present at any time during the course of the oxidation. We estimate that if the disulfide were to have built up during the oxidation to a concentration equal to 5% of the original concentration of **1a** its presence would have been clearly detectable. We can only conclude that under our reaction conditions, contrary to the suggestion of Barnard and Percy,[8] the disulfide is not produced in detectable amounts during the course of the oxidation of **1a** to **2a.**

As noted above, we used somewhat less than one mole of peracid per mole of **1a** in most of these experiments. According to the claims of Barnard and Percy,[8] this should still have been sufficient peracid to have resulted in the disappearance of *all* the thiolsulfinate. On the other hand, according to the ideas of Modena and Todesco[9] regarding the course of the reaction, it should not be, and there should still be thiolsulfinate left after all the peracid has been consumed. We indeed find that this is the case.

If the concentration of α-disulfoxide **3a** (Ar = *p*-FC_6H_4), or of any other possible intermediate, were to build up during the oxidation as an intermediate to a significant level (≧ 3% of the original concentration of **1a**), one would expect to be able to see this manifested by the appearance of appropriate ^{19}F resonance signals. Although no new resonances, except those due to thiolsulfonate **2a,** were observed (vide supra), it is conceivable that the chemical shift for the fluorines in **3a** (or other possible intermediate) might be ~101 ppm. If so, their presence, and the presence of **3a** in detectable concentration as an intermediate, might be masked by the signals due to the

resonances of $FC_6H_4S(O)$ in **1a** and FC_6H_4 in **2a**. One can check this possibility by determining the integrated intensities of the three signals at 96.97, 101.0–101.5, and 103.19 ppm at various times during the course of the oxidation. If the oxidation of **1a** produces only **2a** as a product, and if there is no significant build up of **3a** at any time during the oxidation, the sum of the integrals for the resonances at 96.97 ($FC_6H_4SO_2$ in **2a**) and 103.19 ppm (FC_6H_4S in **1a**) will be equal to the integral of the signals in the ~101 ppm region ($FC_6H_4S(O)$ in **1a** plus FC_6H_4S in **2a**) at *all* stages of the oxidation. On the other hand, if the chemical shift for the fluorines of **3a** should be ~101 ppm, and if the concentration of **3a** reaches a significant level during the course of the oxidation, then the integral of the signal in the 101 ppm region will be larger during that portion of the oxidation than the sum of the integrals at 96.97 and 103.19 ppm, although, at the end of the reaction, when all the **3a** has disappeared, the integrals should be equal.

The integrated intensities of the signals at 96.97, 101.0–101.5, and 103.19 ppm were determined throughout the course of the oxidation. Within experimental error the sum of the integrals for the 96.97 and 103.19 ppm resonances was equal throughout a run to the intensity of the integral of the signal in the 101 ppm region. From this we conclude that the concentration of **3a** *at no time* during the oxidation exceeds 2% of the initial concentration of **1a.**

We also used the change in the ratio of the intensity of the integral for the resonance at 103.19 ppm to the sum of the integrals for the resonances at 96.97 and 103.19 ppm to measure $[\mathbf{1a}]/[\mathbf{1a}]_0$ vs. time for the disappearance of the thiolsulfinate. If the disappearance of **1a** obeys the kinetic expression:

$$-d[\mathbf{1a}]/dt = k_{ox}[\mathbf{1a}][AcOOH]$$

and the stoichiometry:

$$\mathbf{1a} + AcOOH \xrightarrow{k_{ox}} \mathbf{2a} + AcOH \qquad (3)$$

then, given that **1a** was present initially in slight excess over AcOOH, one should find[10] that:

$$\ln\left\{\frac{[\mathbf{1a}]}{[\mathbf{1a}]_0} \times \left(\frac{1 - \dfrac{[\mathbf{1a}]_\infty}{[\mathbf{1a}]_0}}{\dfrac{[\mathbf{1a}]}{[\mathbf{1a}]_0} - \dfrac{[\mathbf{1a}]_\infty}{[\mathbf{1a}]_0}}\right)\right\} = k_{ox}[\mathbf{1a}]_\infty t \qquad (4)$$

with a plot of the logarithmic function vs. time being linear, with a slope equal to $k_{ox}[\mathbf{1a}]_\infty$. We found that a plot of the data for each run according to eq 4 was satisfactorily linear. From the slopes of these plots, divided by $[\mathbf{1a}]_\infty$, k_{ox} was found to be $2.4 \pm 0.3 \times 10^{-4}$ M^{-1} s^{-1} at −20 °C.

Changes in the ^{19}F NMR Spectrum During the Oxidation of 1b by Peracetic Acid. We also investigated the changes that occur in the ^{19}F NMR spectrum when a solution of the unsymmetrical thiolsulfinate, *p*-fluorophenyl benzenethiolsulfinate (**1b**), is oxidized with peracetic acid in chloroform solution. We were particularly interested in determining whether the oxidation of this unsymmetrical thiolsulfinate led to only unsymmetrical thiolsulfonate **2b,** or, alternatively, to a mixture of **2b, 2c, 2a,** and (presumably) $PhSO_2SPh$, and, if to such a mixture, what were the proportions of the different thiolsulfonates.

When **1b** was treated with 1 mol of peracetic acid at −20 °C the signal at 103.30 ppm due to the fluorine of **1b** diminished in intensity, and *four* new peaks appeared in the ^{19}F NMR spectrum of the solution at 96.97, 97.35, 101.05, and 101.40 ppm. The first and third of these, of course, are due to the two different fluorines in **2a.** The resonance at 97.35 ppm is due to the fluorine in **2c;** that at 101.40 to the fluorine in **2b.** Although **2a, 2b,** and **2c** are all formed in the oxidation of **1b,** they are not formed in equal amounts. Instead, there is about 2.5 times more **2b** than of either of the other two thiolsulfonates, both of which are formed in essentially equal amounts. There was no indication that the ratio of the three thiolsulfonates changed at all significantly during the course of the oxidation.

Because of the closeness of the chemical shifts for the pair of $FC_6H_4O_2$ fluorines in **2a** and **2c** and also for the pair of FC_6H_4S fluorines in **2a** and **2b** one cannot measure highly accurate integrals for each of the four peaks individually. One can, however, measure very accurately the sum of the two peaks in the 97-ppm region and the sum of the two peaks in the 101-ppm region. The ratio of these two integrals is equal to $([\mathbf{2a}] + [\mathbf{2c}])/([\mathbf{2a}] + [\mathbf{2b}])$ and was found to have a value of 0.574.

Oxidation of 1a by Other Oxidizing Agents. Oxidation of **1a** in chloroform with either perbenzoic or *m*-chloroperbenzoic acids led to exactly the same type of changes in the ^{19}F NMR spectrum of the solution as those observed with peracetic acid as the oxidizing agent. However, neither of these two peracids was sufficiently soluble at −20 °C in chloroform to permit use of the initial concentration levels of **1a** and peracid desirable for the NMR experiments, if one were to require, as seemed important, that all of the peracid be in solution at the start of the experiment.

As can be seen from eq 3, acetic acid is one of the products of the oxidation of **1a** by peracetic acid. In separate experiments we showed that the presence of acetic acid at concentration levels considerably in excess of what would be present in the oxidation experiments led to no change in the ^{19}F NMR spectra of either **1a** or **2a** and also did not lead to acid-catalyzed disproportionation[2b,d] of **1a** into **2a** and $(FC_6H_4S)_2$ at a measurable rate at −20 °C.

We originally hoped to be able to use peroxytrifluoroacetic acid as the oxidant for **1a** in the NMR studies. It would, of course, give trifluoroacetic acid as a reaction product. Unfortunately we found that the presence of trifluoroacetic acid in the solution alters the chemical shifts of the various fluorines in **1a** and **2a,** the magnitude of the effect varying with the concentration of trifluoroacetic acid present and the particular fluorine. While the size of the shift approaches a limit at high enough concentrations of trifluoroacetic acid, at those concentrations acid-catalyzed disproportionation[2b,d] of **1a** becomes a significant problem. For these reasons any thought of the use of peroxytrifluoroacetic acid was abandoned in favor of use of peracetic acid, where such problems did not exist.

We also explored the behavior of *tert*-butyl hypochlorite with **1a** in chloroform. At low temperatures (−20 °C) reaction between these reagents was extremely slow. At room temperature, rather than a simple oxidation of **1a** to **2a,** one seemed to get considerable disproportionation of **1a** to disulfide and **2a** accompanying any oxidation, akin to what Barnard and Percy[8] reported finding with hydrogen peroxide in acetic acid as the oxidizing agent. Because of the fact that the reaction was not a clean oxidation, it was not explored in any detail.

Discussion

Barnard and Percy[8] have claimed that the oxidation of aryl thiolsulfinates (**1**) to thiolsulfonates (**2**) occurs by the mechanism shown in eq 2 and that a sizable amount of the corresponding disulfide can be detected as an intermediate in the course of the oxidation. Modena and Todesco,[9] on the other hand, have felt this is not correct and that there is no significant formation of disulfide as an intermediate during the oxidation. In the present ^{19}F NMR study of the course of the oxidation of *p*-fluorophenyl *p*-fluorobenzenethiolsulfinate (**1a**) by peracids at −20 °C we can find no indication of the build up of even a small amount of *p*-fluorophenyl disulfide as an intermediate, even though its presence would be readily detectable

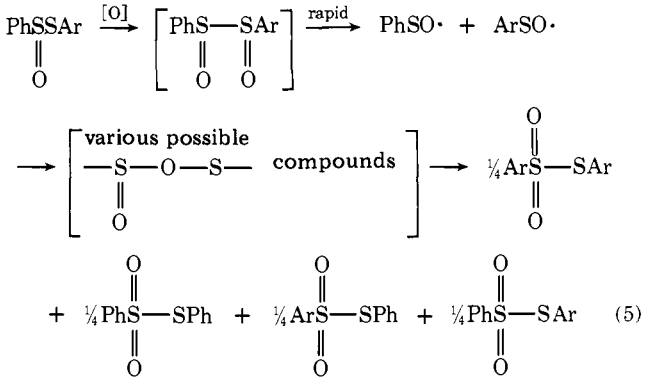
by ^{19}F NMR. Our results thus support the views of Modena and Todesco[9] and argue strongly against the mechanism proposed by Barnard and Percy,[8] at least where the oxidizing agent is a peracid.[12]

From our ^{19}F NMR study of the oxidation of **1a** we can also say that α-disulfoxide **3a** does not build up to any significant concentration as an intermediate during the oxidation, since the only ^{19}F NMR resonances that can be seen during the reaction are those due to **1a** and **2a.**

The failure to observe **3a** as an intermediate in the NMR during the oxidation can be due to either of two causes. The first possibility is that α-disulfoxide **3a** is formed as an intermediate but is very unstable and decomposes so rapidly that its concentration never exceeds more than 1 or 2% of the initial concentration of **1a.** The alternate possibility is that the oxidation of **1a** to **2a** by peracids does not actually involve **3a** as an intermediate. The simplest way that this could happen would be if the oxidation occurred by a direct oxidation of the S(O) group in **1a** to an SO_2 group. Since oxidation of the -S- in Ph_2S by perbenzoic acid in dioxane occurs only six times faster than oxidation of the S(O) group in $Ph_2S{=}O$ by the same reagent,[7,13] the possibility of peracetic acid reacting with **1a** at the sulfinyl group rather than the sulfenyl sulfur does have to be considered seriously. Fortunately, study of the oxidation of the unsymmetrical thiolsulfinate **1b** can provide the information necessary to decide this matter.

If the oxidation were to occur exclusively by a direct oxidation of the S(O) group in the thiolsulfinate to an SO_2 group, then the oxidation of an unsymmetrical thiolsulfinate PhS(O)SAr, like **1b,** should give the unsymmetrical thiolsulfonate $PhSO_2SAr$ (**2b**) as the only product, with no $ArSO_2SPh$, $ArSO_2SAr$, or $PhSO_2SPh$ being formed. The ^{19}F NMR spectrum of the oxidation of **1b** by peracetic acid shows clearly that sizable amounts of both **2c** ($ArSO_2SPh$) and **2a** ($ArSO_2SAr$) are formed along with **2b** in the oxidation reaction. This clearly demonstrates that the oxidation of **1b** cannot occur exclusively by the direct oxidation of the S(O) group to an SO_2 group. The same would also be true for the oxidation of **1a.**[16]

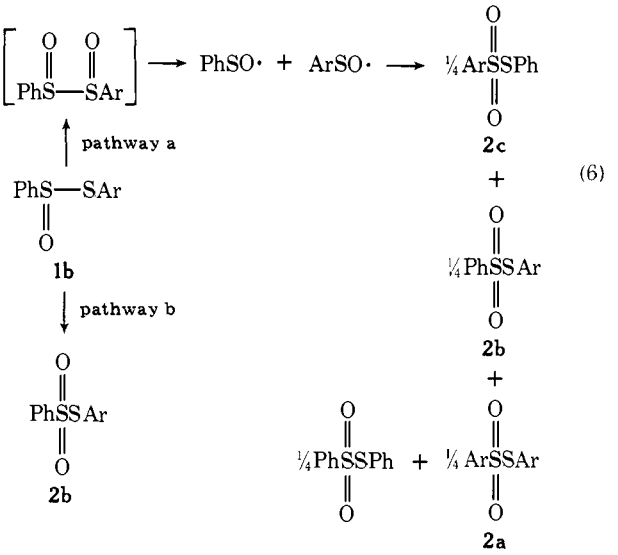
If the α-disulfoxide PhS(O)S(O)Ar is formed as an intermediate in the oxidation of **1b** and dissociates into ArSO· and PhSO· radicals that then recombine in a *random* manner to give the various possible sulfenyl sulfinates, -S(O)OS-, which themselves quickly rearrange to the corresponding thiolsulfonates (eq 5), then oxidation of **1b** by peracetic acid ought to



(5)

yield a mixture of equimolar amounts of all four possible thiolsulfonates, **2a, 2b, 2c,** and $PhSO_2SPh$. Experimentally one finds by ^{19}F NMR that, while **2a** and **2c** are formed in essentially equimolar amounts, the amount of **2b** formed is about 2.5 times larger than the amount of either **2a** or **2c.**

This could be explained in terms of the mechanism of eq 5 if one were to assume there was considerable cage recombination of initial ArSO·PhSO· radical pairs with such recombination for some unknown reason showing a strong preference to form ArSOS(O)Ph. However, given the relative rates of oxidation at Ph_2S and $Ph_2S{=}O$ by a peracid in an aprotic solvent noted earlier, we feel equally serious consideration has to be accorded to an explanation which assumes that oxidation of **1b** by peracetic acid takes place by two competing pathways: (a) the pathway shown in eq 5 involving the α-disulfoxide as an intermediate; and (b) a pathway involving the direct oxidation of the S(O) group of the thiolsulfinate (eq 6). One can



(6)

then ask what fraction of the oxidation would need to go by each pathway in eq 6 in order to accommodate our experimental results. The quantity that we can measure most accurately from the ^{19}F NMR integrals is the product ratio, ([**2a**] + [**2c**])/([**2a**] + [**2b**]); this has a value of 0.574. If we let α equal the fraction of the oxidation taking place by pathway a and $(1 - \alpha)$, that by pathway b, then:

$$0.574 = \frac{[\mathbf{2a}] + [\mathbf{2c}]}{[\mathbf{2a}] + [\mathbf{2b}]} = \frac{\frac{1}{4}\alpha + \frac{1}{4}\alpha}{\frac{1}{4}\alpha + (1 - \alpha) + \frac{1}{4}\alpha}$$

$$0.574 = \frac{0.5\alpha}{1 - 0.5\alpha}$$

$$\alpha = 0.73$$

Thus, even if part of the reaction is occurring by direct oxidation of the S(O) group to an SO_2 group, *at least* 73% of thiolsulfinate **1b** is oxidized via the pathway involving the α-disulfoxide as an intermediate. No more than about 25% of the reaction can be occurring via the alternate path involving direct oxidation of S(O) to SO_2.[18] Since most of the oxidation of **1a** or **1b** by a peracid therefore involves the route with the α-disulfoxide, and, since the concentration of the α-disulfoxide never builds up to a detectable level, this must mean that even at −20 °C the α-disulfoxide decomposes rapidly to give fragments which then recombine in such a fashion as to lead to all the different possible thiolsulfonates (eq 5).[19]

We can also use some of our results to estimate at least a *lower limit* for the rate of decomposition of α-disulfoxide **3a** under our reaction conditions. For a reaction scheme of the type:

$$A + B \xrightarrow{k_1} X \xrightarrow{k_2} P$$

Chien[21] has given expressions from which one can calculate $[X]/[A]_0$ as a function of $[A]/[A]_0$, where $[A]_0$ is the initial concentration of A, for different values of k_1/k_2. The shape of the curve and, in particular, $[X]_{max}/[A]_0$ depends markedly on $k_1[A]_0/k_2$. Since the concentration of **3a** does not build up to a detectable level in the ^{19}F NMR during the oxidation of **1a** by peracid, its maximum concentration must be less than

2% of the initial concentration of **1a**. A value of $[X]_{max}/[A]_0 \leqq 0.02$ requires that $k_1[A]_0/k_2 \leqq 0.025$. As described in the Results, we have measured the rate of disappearance of **1a** under our reaction conditions and know the second-order rate constant ($2.4 \pm 0.3 \times 10^{-4}$ M^{-1} s^{-1}) for its oxidation by peracetic acid at −20 °C. From this and the initial concentration of **1a** we can calculate $k_1[A]_0$ for our reaction conditions and from this and the relationship $k_1[A]_0/k_2 \leqq 0.025$ estimate a *lower limit* for the value of k_2. We conclude that for **3a** at −20 °C $k_2 \geqq 1 \times 10^{-2}$ s^{-1}, which means that the half-life for the α-disulfoxide at this temperature is less than 60 s. We should stress, however, that, since the maximum concentration of **3a** during a run could in actuality be much less than the 2% of $[\mathbf{1a}]_0$ estimated as the minimum concentration that would be detectable in our NMR experiments, the actual rate constant for the decomposition of the α-disulfoxide *could well be significantly larger* than the lower limit of 10^{-2} s^{-1} just calculated, and the half-life very short indeed.

Even though the value of 10^{-2} s^{-1} is strictly a *lower limit* for the rate of decomposition of the α-disulfoxide at −20 °C, it is still *many* orders of magnitude faster than the rate of thermal decomposition of any other oxidized aryl disulfide derivative (**1, 2, 4,** and **5**). For example, a typical aryl sulfinyl sulfone, the least stable thermally of the other compounds, would be predicted to have a rate of thermal decomposition of only 3×10^{-9} s^{-1} at −20 °C, or 3.3 *million* times slower than the lower limit for the rate of decomposition of the α-disulfoxide. Clearly an α-disulfoxide is an extremely unstable compound compared with any other oxidized derivative of a disulfide.

An estimate of the upper limit for $\Delta H^{\ddagger}$ for the decomposition of **3a** suggests just how weak the S–S bond in an α-disulfoxide must be. Values of $\Delta S^{\ddagger}$ for the decompositions of **1**[2c] (+12.6 eu), **4**[4b] (+11.2 eu), and **5**[5b] (+16.6 eu) suggest that $\Delta S^{\ddagger}$ for the decomposition of **3** is probably around +12 eu. Using that value and the lower limit for the rate constant for decomposition of **3a** at −20 °C calculated earlier, one estimates that the *maximum* value for $\Delta H^{\ddagger}$ for the decomposition of **3a** is only 20 kcal/mol. The S–S bond in an α-disulfoxide is therefore extremely weak. It is also striking to compare this *upper limit* of 20 kcal/mol for $\Delta H^{\ddagger}$ for the thermal decomposition of **3a** with the $\Delta H^{\ddagger}$'s observed for the thermal decompositions of other oxidized derivatives of disulfides: **1**[2c] (34.5 kcal/mol), **4**[4b] (27.6 kcal/mol), and **5**[5b] 40.9 kcal/mol).

The present studies suggest that an α-disulfoxide is apparently an extraordinarily unstable type of sulfur compound and that the only hope of ever being able to observe **3a** in significant concentration in solution would be to find some extremely potent oxidizing agent that would be able to effect the oxidation of **1a** rapidly even at very low temperatures.

Experimental Section

Preparation of *p*-Fluorophenyl *p*-Fluorobenzenethiolsulfinate (1a). Commercial (Aldrich Chemical Co.) *p*-fluorothiophenol (5.42 g, 42.3 mmol) was mixed with 50 ml of 10% aqueous sodium hydroxide solution and cooled to 0 °C. To this mixture 6 ml of 30% hydrogen peroxide solution was added slowly over the course of 5 min. After stirring for 30 min, the mixture was extracted three times with 20-ml aliquots of ether; the extracts were washed three times with 10% aqueous NaOH solution, twice with water, and then were dried over anhydrous sodium sulfate. Upon removal of the ether, *p*-fluorophenyl disulfide, $(p\text{-}FC_6H_4S)_2$, was obtained in 58% yield (3.2 g) as a yellow oil: ^{19}F NMR ($CHCl_3$, −20 °C) Φ 107.8 ppm. The disulfide was used in the next step without further purification.

Commercial (Aldrich Chemical Co.) 85% *m*-chloroperbenzoic acid (2.31 g, 11.4 mmol) was dissolved in 50 ml of chloroform and added over the course of about 1 h to a stirred solution of the disulfide (3.05 g, 12 mmol) in chloroform held at 0 °C. After the addition was complete, the mixture was allowed to stir for another hour at room temperature, then extracted four times with 30-ml portions of 5% aqueous sodium bicarbonate, twice with water, and finally dried over anhydrous sodium sulfate. Upon removal of the chloroform a yellow, oily residue remained which was crystallized from a mixture of pentane and chloroform in 75% yield (2.4 g): mp 75.5–76.5 °C; ir ($CHCl_3$) 1585 (s), 1483 (s), 1149 (s), 1081 (s), and 1060 cm^{-1} (s); ^{19}F NMR ($CHCl_3$, −20 °C) Φ 101.30 ($FC_6H_4S(O)SC_6H_4F$) and 103.19 ppm ($FC_6H_4S(O)SC_6H_4F$); mass spectral peaks at 50 °C, 20 eV (intensity): *m/e* 386 (1.4, $M^+ + 16$), 270 (10.9, M^+), 254 (57.3, $M^+ - 16$), 222 (18, $M^+ - SO$), 159 (3.1, $FC_6H_4SO_2$), 143 (100, FC_6H_4SO), 128 (10.3, FC_6H_4SH), 127 (97.4, FC_6H_4S). Anal. Calcd for $C_{12}H_8F_2OS_2$: C, 53.32; H, 2.98; S, 23.72. Found: C, 53.09; H, 2.89; S, 23.97.

Preparation of *p*-Fluorophenyl Benzenethiolsulfinate (1b). Benzenesulfinyl chloride was prepared by the method of Pawlowski,[22] and *p*-fluorophenyl benzenethiolsulfinate was then prepared from this and *p*-fluorothiophenol by a modification of the procedure of Kice and Cleveland.[23] Pyridine (1.6 g) was mixed with *p*-fluorothiophenol (2.6 g, 20 mmol) in 40 ml of anhydrous ether, and this mixture was added slowly over 2 h to a stirred solution of freshly prepared benzenesulfinyl chloride (3.25 g, 20 mmol) in 40 ml of dry ether at room temperature. After the addition was complete, the precipitate of pyridine hydrochloride was filtered off, and the filtrate was extracted once with 1 N sulfuric acid, washed twice with 5% sodium bicarbonate, then twice with water, and finally dried (Na_2SO_4). Removal of the ether left a yellow residue which was purified by chromatography on silica gel (150 g) using 1% acetic acid in benzene as eluent. The first yellow fraction collected (1.5 g) was identified by ^{19}F NMR to be a mixture of bis(*p*-fluorophenyl) disulfide and phenyl *p*-fluorophenyl disulfide. The second yellow fraction was the desired thiolsulfinate, **1b.** It was crystallized from a mixture of hexane and chloroform in 54% yield (2.7 g): mp 62–63 °C; ir ($CHCl_3$) 1592 (s), 1488 (s); 1149 (s), 1080 (s), and 1051 cm^{-1} (m); ^{19}F NMR ($CHCl_3$, −20 °C) Φ 103.30 ppm; mass spectral peaks at 40 °C and 20 eV (intensity): *m/e* 252 (43.3, M^+), 236 (51.7, $M^+ - 16$), 218 (10.3), 204 (84.9), 186 (19.5), 143 (51.7), 127 (83.4), 125 (100, C_6H_5SO), 109 (19.3, C_6H_5S), 97 (33.9, C_6H_5F), and 77 (12.0, C_6H_5). Anal. Calcd for $C_{12}H_9FOS_2$: C, 57.12; H, 3.60; S, 25.41. Found: C, 57.33; H, 3.67; S, 25.20.

Preparation of *p*-Fluorophenyl *p*-Fluorobenzenethiolsulfonate (2a). This was prepared from *p*-fluorophenyl disulfide by oxidation with 2 equiv of *m*-chloroperbenzoic acid using a procedure patterned after that of Marangelli, Modena, and Todesco.[7] After recrystallization from ethanol **2a** melted at 70–71 °C. ^{19}F NMR ($CHCl_3$, −20 °C) Φ 96.97 ($FC_6H_4SO_2SC_6H_4F$) and 101.05 ppm ($FC_6H_4SO_2SC_6H_4F$). Anal. Calcd for $C_{12}H_8F_2O_2S_2$: C, 50.34; H, 2.82. Found: C, 50.56; H, 2.97.

Oxidation of 1a by Peracetic Acid. Peracetic acid was prepared from 90% hydrogen peroxide and acetic anhydride following the procedure of Emmons.[24] In order to remove the small amount of sulfuric acid used as a catalyst in that procedure so that it could not cause any problems, such as inducing the acid-catalyzed disproportionation[2d] of **1a**, the final chloroform solution from the reaction was stirred with anhydrous sodium acetate for 5 min. The excess sodium acetate was then removed by filtration, and the peracetic acid titer of the chloroform solution was determined iodimetrically. Chloroform was then added to dilute the concentration of peracetic acid to desired value.

In a typical run about 0.5 mmol of thiolsulfinate **1a** was dissolved in 0.1 ml of chloroform in an NMR tube and cooled to −78 °C. A chloroform solution (0.25 ml) of peracetic acid (~1.8 M) was added, the two solutions thoroughly mixed, and the resulting solution was thermostated at −20 °C in the NMR probe of a Varian XL-100 NMR spectrometer. The ^{19}F NMR spectrum of the solution (a small amount of Freon 11 was present in the solution as an internal standard) was recorded at selected time intervals thereafter. The two resonances at Φ equal 101.30 and 103.19 ppm due to the fluorines in **1a** were observed to decrease in intensity as the reaction proceeded, while resonances at Φ equal 96.97 and 101.05 ppm due to the fluorines of **2a** first appeared and then grew in intensity. Integrals of the various peaks in the spectrum were also measured as a function of time. At no time during the oxidation was there any evidence of the appearance of a detectable signal at 107.8 ppm, where $(p\text{-}FC_6H_4S)_2$ would be expected to have its ^{19}F resonance. Neither was any signal detected which could be ascribed to the presence of any significant amount of *p*-fluorophenyl α-disulfoxide, **3a**, as an intermediate in the oxidation.

Similar spectral changes were observed when either perbenzoic or

m-chloroperbenzoic acids were used as the oxidizing agent instead of peracetic acid.

Oxidation of 1b by Peracetic Acid. Unsymmetrical thiolsulfinate **1b** (0.12 g, 0.48 mmol) was dissolved in 0.1 ml of chloroform and cooled to −20 °C. It was then mixed at −20 °C in an NMR tube with 0.26 ml of a chloroform solution of peracetic acid (~1.8 M) and the ^{19}F NMR spectrum of the resulting solution was then examined as a function of time while the solution was allowed to warm gradually from −20 °C to room temperature. As the oxidation occurred the signal at Φ 103.30 ppm, due to the fluorine in **1b**, decreased in intensity and four new signals, centered at 96.97, 97.35, 101.05, and 101.40 ppm, appeared and increased in intensity. The first and third of these peaks are, of course, due to the two different fluorines in **2a**; the peak at 97.35 is due to the fluorine of **2c**, that at 101.40 ppm to the fluorine in **2b**. The four signals were not of equal intensity, that at 101.40 being about 2.5 times stronger than the other three, which were of essentially equal intensity. A carefully measured integral taken at the end of the oxidation after essentially all the thiolsulfinate had been consumed indicated that the integral for the two peaks in the 101 ppm region was 1.74 times larger than the integral of the sum of the two closely spaced resonances in the 97-ppm region. No other signals were evident in any other portion of the spectrum.

References and Notes

(1) This research supported by the National Science Foundation, Grant MPS75 19408.

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(7) U. Marangelli, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90,** 681 (1960).

(8) D. Barnard and E. J. Percy, *Chem. Ind.*, 1332 (1960).

(9) G. Modena and P. E. Todesco, *Ric. Sci.*, **30,** 1788 (1960).

(10) The expression in eq 3 may be derived from the expression given by Frost and Pearson[11] for a second-order equation where the reactants are not present in equivalent amounts by making use of the relationships that $[1a]_\infty = [1a]_0 - [AcOOH]_0$ and $[AcOOH] = [AcOOH]_0 - ([1a]_0 - [1a])$.

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed, Wiley, New York, N.Y., 1961, pp. 15–17.

(12) One possible explanation for the divergence between our (and the Italian workers[9]) results and those of Barnard and Percy[8] is the difference in the nature of the oxidizing agent employed. We and the Italian workers have used organic peracids, while Barnard and Percy used hydrogen peroxide in acetic acid. Since we have found that treatment of **1a** with *tert*-butyl hypochlorite, rather than peracid, as the oxidizing agent leads to a considerable amount of disproportionation of **1a** to disulfide plus **2a** along with oxidation, it is possible that the oxidizing agent employed by Barnard and Percy is also one that, like *t*-BuOCl, leads to much disproportionation of **1** accompanying the oxidation, whereas peracids do not.

(13) The difference in the rates of oxidation of sulfide and sulfoxide by peracids is much larger in either aqueous dioxane,[7] water,[14] or acetic acid,[15] k_S/k_{SO} being anywhere from 300 to 1000, rather than the small value of 6 found in anhydrous dioxane.[7] However, since the solvent used for the present work, chloroform is, like dioxane, an aprotic solvent, it is certainly within reason that the rate of attack of peracetic acid on the S(O) group of **1a** could be comparable with its rate of attack on the sulfenyl sulfur of the same compound.

(14) G. Kresze, W. Schramm, and G. Cleve, *Chem. Ber.*, **94,** 2060 (1960).

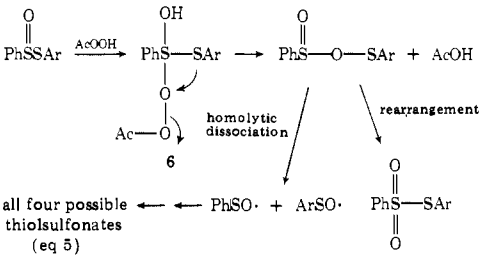
(15) M. J. Böeseken and E. Arias, *Recl. Trav. Chim.*, **54,** 711 (1935).

(16) A factor influencing the ease of oxidation of either of the sulfurs of an aryl thiolsulfinate by a peracid will, of course, be the electron-withdrawing or electron-releasing character of the aryl group attached to the sulfur in question.[7] However, since *p*-F has almost the same σ value ($\sigma = +0.06$, $\sigma_+ = -0.07$)[17] as *p*-H, the presence of a *p*-F in only one of the rings of **1b** will not cause this thiolsulfinate to behave significantly differently than **1a** in terms of the relative ease of oxidation of the two different sulfurs by peracid.

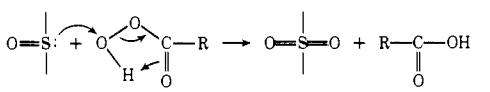
(17) (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23,** 420 (1958); (b) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79,** 1913 (1957); **80,** 4979 (1958).

(18) To the extent that there is any tendency for termination of radical pairs in eq 5 to lead to greater than the statistically expected amount of PhS(O)OSAr based on random combination of radicals, the actual percentage of the oxidation going via the α-disulfoxide pathway will be even higher than 75%.

(19) Professor J. C. Martin (private communication) has suggested that the product distribution for the oxidation of **1b** could also be explained by a mechanism in which one had initial addition of peracid across the sulfinyl group, followed by a rearrangement of the adduct **6** to sulfenyl sulfinate PhS(O)OSAr, with the latter reactive intermediate then in part rearranging directly to $ArSO_2SPh$ and in part dissociating directly to ArSO· and PhSO· radicals. These radicals would then recombine in random fashion to give equimolar amounts of all four possible thiolsulfonates.



While this explanation is an intellectually ingenious one, and cannot be completely dismissed, we think it less likely than a scheme involving the initial intermediacy of the α-disulfoxide for the following reasons. In other cases[20] involving the reaction of peracids with sulfinyl compounds in media in which the peracid is not significantly dissociated, addition of the peracid across the sulfinyl group is not competitive with nucleophilic attack of the unshared pair on sulfur on oxygen:



Addition of the peracid to the sulfinyl group is only observed[20] to be competitive in those situations where a significant fraction of the peracid is present at equilibrium as the anion RCO_3^-. Based on this behavior we feel that in our reaction medium, where CH_3CO_3H is not at all dissociated, formation of **6** would be unlikely to be able to be competitive with other reactions involving **1b** and the peracid.

(20) R. Curci, A. Giovine, and G. Modena, *Tetrahedron*, **22,** 1235 (1966), and references cited therein.

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(24) W. D. Emmons, *J. Am. Chem. Soc.*, **79,** 5528 (1957).