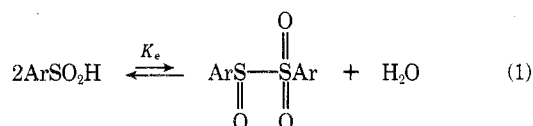


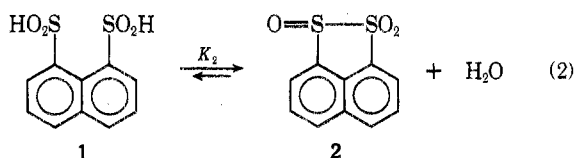
The Naphthalene-1,8-disulfinic Acid-Naphtho[1,8-*cd*]-1,2-dithiole 1,1,2-Trioxide Equilibrium. A Sulfinic Acid-Sulfinyl Sulfone Equilibrium Where the Sulfinyl Sulfone is Strongly Favored Even in Aqueous Solution

Summary: In aqueous dioxane the equilibrium between the cyclic sulfinyl sulfone, naphtho[1,8-*cd*]-1,2-dithiole 1,1,2-trioxide, and naphthalene-1,8-disulfinic acid strongly favors the sulfinyl sulfone; this is in dramatic contrast to the usual situation in aqueous media, where no detectable amount of sulfinyl sulfone can be found in equilibrium with the corresponding sulfinic acid.

Sir: Aryl sulfinyl sulfones, $\text{ArS(O)SO}_2\text{Ar}$, are the anhydrides of aromatic sulfinic acids.¹ The equilibrium constant for their formation (eq 1) is normally so small that in a me-



dium containing an appreciable amount of water, such as 60% dioxane, the concentration of sulfinyl sulfone present at equilibrium is <0.01% of the concentration of the sulfinic acid.² We have now found, however, that in this same solvent in the case of naphthalene-1,8-disulfinic acid (1) and the cyclic sulfinyl sulfone 2, naphtho[1,8-*cd*]-1,2-dithiole 1,1,2-trioxide, the equilibrium (eq 2) strongly favors the sulfinyl sulfone, the equilibrium concentration of 2 being almost three times that of 1. The evidence for this is outlined in the following paragraphs.



A concentrated aqueous solution of sodium naphthalene-1,8-disulfinate (3)⁵ (synthesized by reaction of hydrogen peroxide anion with the known⁷ cyclic thioisulfonate, naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide) was acidified with hydrochloric acid in the expectation that 1 would precipitate. Instead of 1 the sulfinyl sulfone 2 precipitated in ~35% yield.⁸ That the isolation of 2 rather than 1 was not the result of a solubility phenomenon but rather because of 2 being favored over 1 at equilibrium was demonstrated in the following way.

Treatment of a very dilute ($1.7 \times 10^{-4} \text{ M}$) solution of 2 with excess standard sodium hydroxide in 60% dioxane resulted in immediate hydrolysis of 2 to 3, as evidenced by a change in the uv spectrum from that associated with 2 (curve A, Figure 1) to that for sodium naphthalene-1,8-disulfinate (curve B). This solution of the disulfinate was then acidified with sufficient concentrated perchloric acid to give a solution with $[\text{H}^+] = 0.01\text{--}0.10 \text{ M}$. Immediately after acidification, the spectrum of the solution was as shown in curve C. (This is presumably the spectrum associated with naphthalene-1,8-disulfinic acid, 1.) Upon standing the spectrum of the acid solution initially changed quite rapidly, but after ~60 min at room temperature one observed a final spectrum (curve D) that did not change further with time. This spectrum is very similar to, but not identical with, the spectrum of 2, and is consistent with that expected for an equilibrium mixture of 1 and 2 in which the majority of the material is present as 2. The

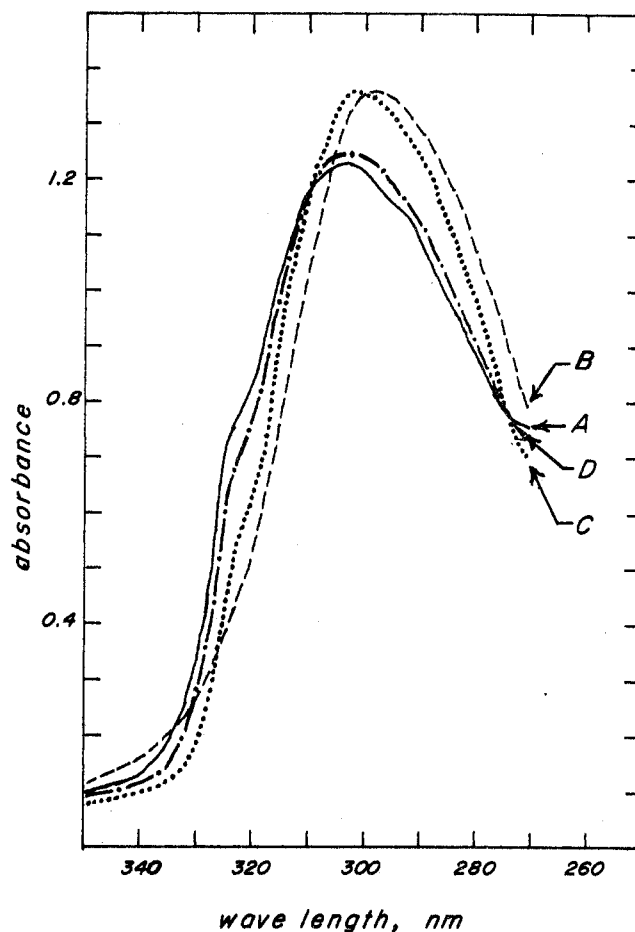
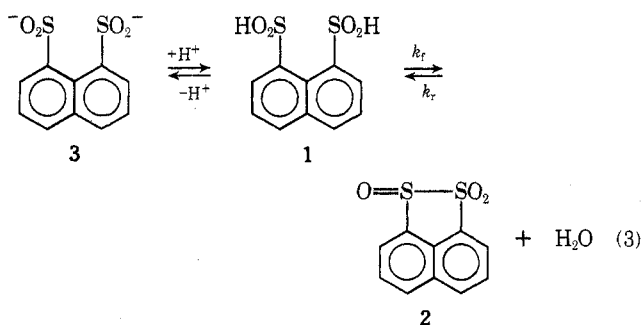


Figure 1. Curve A (—): 2, $1.7 \times 10^{-4} \text{ M}$ in dioxane. Curve B (---): 2, $1.7 \times 10^{-4} \text{ M}$ in 60% dioxane after addition of sodium hydroxide to hydrolyze 2 to 3. Curve C (····): solution of curve B immediately after addition of sufficient concentrated perchloric acid to give final $[\text{H}^+] = 0.1 \text{ M}$. Curve D (-·-·-): solution of curve C after standing for 60 min at 25°.

same change was observed when solutions of the disulfinate were added to trifluoroacetate buffers having a pH from 2.81 to 3.81. Kinetic measurements showed that the experimental first-order rate constant for the approach to equilibrium, k_{exptl} , was independent of pH and equal to $2.5 \pm 0.2 \times 10^{-3} \text{ sec}^{-1}$ at 25°.

When the disulfinate was added to a chloroacetate buffer having a pH of 5.18, there was no spectral change indicating the formation of 2. On the other hand, when 2 was added to this buffer or to more alkaline chloroacetate or formate buffers having pH's from 5.48 to 6.8 a spectral change occurred that indicated that 2 was undergoing irreversible hydrolysis. Its rate of hydrolysis under these conditions contains both a pH-independent term and one whose rate is proportional to the concentration of the buffer anion. The pH-independent term, which is presumably equal to the rate of spontaneous hydrolysis of 2 under these conditions, has a value of $0.7 \pm 0.1 \times 10^{-3} \text{ sec}^{-1}$.

These various results are all accommodated by the scheme shown in eq 3. In reasonably acid solutions (pH ≤ 3.8) 3 is protonated to 1, and 1 is in equilibrium with 2, with 2 being markedly favored at equilibrium. The measured rate constant for approach to equilibrium, k_{exptl} , will be equal⁹ to $k_f + k_r$. At pH ≥ 5.2 the hydrolysis of 2 is irreversible because 1 is deprotonated as soon as it is formed. The pH-independent rate of hydrolysis under these conditions should be equal to k_r . From the measured values of $(k_f + k_r)$ and k_r , K_2 (eq 2) is estimated to be 2.6 ± 0.4 , indi-



cating that at equilibrium in 60% dioxane the concentration of 2 will be about three times that of 1.

As noted earlier, a sulfanyl sulfone is the anhydride of the corresponding sulfinic acid. Given the thermodynamics associated with other acid-anhydride equilibria,¹⁰ it is most remarkable, even allowing for the intramolecular nature of sulfanyl sulfone formation in eq 2, that 2 should actually be favored over 1 at equilibrium in aqueous dioxane. It becomes even more striking when one recalls the marked thermal instability of aryl sulfanyl sulfones.¹¹

The behavior of the $1 \rightleftharpoons 2$ equilibrium suggests that the enthalpy difference between ArSO_2H and $\text{ArS(O)SO}_2\text{Ar}$ in sulfinic acid-sulfanyl sulfone equilibria generally must be considerably less than in usual acid-anhydride equilibria, such as those involving carboxylic acids and their anhydrides. We have confirmed that this is indeed the case by measuring ΔH° for the reaction $\text{PhS(O)SO}_2\text{Ph} + \text{H}_2\text{O} \rightarrow 2\text{PhSO}_2\text{H}$ in 60% dioxane. This turns out to be only -0.3 ± 2.0 kcal/mol, far less than ΔH° of -14.0 kcal/mol for the hydrolysis of acetic anhydride^{10a} or the ΔH° of -16.3 ± 2.0 kcal/mol that we find for the hydrolysis of phenyl α -disulfone ($\text{PhSO}_2\text{SO}_2\text{Ph} + \text{H}_2\text{O} \rightarrow \text{PhSO}_3\text{H} + \text{PhSO}_2\text{H}$) in 60% dioxane.¹²

These various results and conclusions have a number of important consequences for the chemistry of mono- and disulfonic acids. Reports in the literature of inability to isolate certain disulfonic acids^{14a,b} or of their exhibiting peculiar behavior^{14c} could well be due to a favorable equilibrium constant for formation of the cyclic sulfanyl sulfone and subsequent decomposition reactions of the sulfanyl sulfone. These points are under further investigation and will be reported in detail in subsequent publications.

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References and Notes

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