

Heats of Hydrolysis of Phenyl α -Disulfone and Phenyl Benzenesulfinyl Sulfone^{1a}

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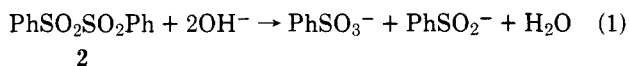
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Phenyl benzenesulfinyl sulfone (PhS(O)SO₂Ph, **1**) is very unstable thermally^{2a} ($t_{1/2} \approx 30$ min at 50 °C) compared to phenyl α -disulfone^{2b} (PhSO₂SO₂Ph, **2**) ($t_{1/2} \approx 13$ h at 145 °C). The sulfinyl sulfone also undergoes either spontaneous^{3a} or alkaline^{3b} hydrolysis about 10 000 times faster than the α -disulfone.⁴ Combined with its much greater thermal instability, one might tend to get the impression from this that the sulfinyl sulfone was much less thermodynamically stable relative to its hydrolysis products than is the α -disulfone.

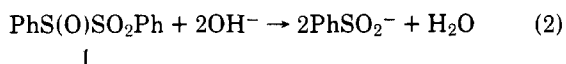
We have now carried out measurements of the heats of hydrolysis of both **1** and **2** which show that this is not the case, and that sulfinyl sulfones (sulfinic anhydrides) are apparently significantly more stable relative to their hydrolysis products than is true of the most acid anhydrides.

Results and Discussion

The heats of reaction, ΔH_{rxn} , for the alkaline hydrolyses of both phenyl α -disulfone (eq 1) and phenyl benzenesulfinyl sulfone (eq 2)

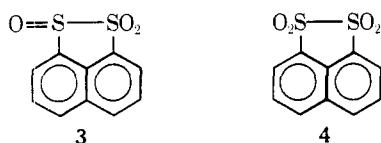


$$\Delta H^\circ_1 = -57.3 \pm 0.2 \text{ kcal/mol}$$



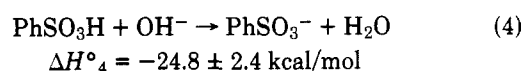
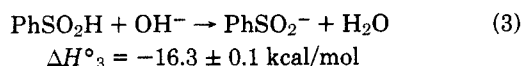
$$\Delta H^\circ_2 = -34.1 \pm 2.0 \text{ kcal/mol}$$

were measured by determining the amount of heat liberated when a weighed sample of the sulfur compound was added to 60% dioxane containing excess 0.1 M sodium hydroxide. To obtain ΔH° for each reaction one must also obtain the heat of solution, ΔH_{soln} , for each of the sulfur compounds in 60% dioxane, since $\Delta H^\circ = \Delta H_{rxn} - \Delta H_{soln}$. While the heat of solution of the α -disulfone ($\Delta H_{soln}^\circ = 5.90 \pm 0.06$ kcal/mol) was easily determined, the rapid spontaneous hydrolysis of **1** in aqueous dioxane^{3a} makes it impossible to measure ΔH_{soln} for **1** directly. However, since we could show that ΔH_{soln} for the cyclic sulfinyl sulfone **3** (which is stable to hydrolysis in acidic



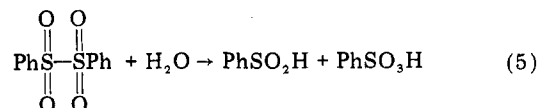
aqueous dioxane^{5a}) was virtually the same as ΔH_{soln} for the analogous cyclic α -disulfone **4**,^{5b} we believe that it is reasonable^{5c} to assume that ΔH_{soln} for **1** in 60% dioxane is essentially the same as ΔH_{soln} for **2**, and we have accordingly used an estimated value of $\Delta H_{soln}^\circ = 6 \pm 2$ kcal/mol in calculating ΔH° for reaction **2** from ΔH_{rxn} for the alkaline hydrolysis of **1**. The values for ΔH° for the alkaline hydrolyses of **1** (eq 2) and **2** (eq 1) are shown under the respective equations. One sees that the alkaline hydrolysis of the α -disulfone is more exothermic than that of the sulfinyl sulfone by somewhat over 20 kcal/mol.

We have also measured the heats of reaction associated with neutralization of PhSO₂H (eq 3) and PhSO₃H (eq 4)

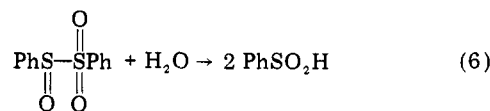


by hydroxide ion in 60% dioxane. While ΔH_{soln} for PhSO₂H (4.02 \pm 0.04 kcal/mol) in 60% dioxane could be determined accurately by measuring the heat of solution of the compound in 60% dioxane containing 0.3 M HClO₄, a medium of sufficient acidity that dissociation of PhSO₂H is negligible, the same was not true for PhSO₃H, for even in the presence of added perchloric acid the dissociation of PhSO₃H (PhSO₃H \rightarrow PhSO₃⁻ + H⁺) was still virtually complete. For this reason we had to estimate ΔH_{soln} for PhSO₃H in 60% dioxane. We have used a value of 4.0 \pm 2.0 kcal/mol, trusting that in all likelihood ΔH_{soln} for the sulfonic acid should be similar to that for the sulfinic acid in this medium.⁶ The values of ΔH° for reactions **3** and **4** computed from the measured ΔH_{rxn} for each process and the measured (PhSO₂H) and estimated (PhSO₃H) ΔH_{soln} s are shown under the respective reactions.

From the ΔH° s for reactions **3** and **4** and those for reactions **1** and **2** one can calculate ΔH° for the hydrolysis of both the α -disulfone (eq 5) and the sulfinyl sulfone (eq 6).



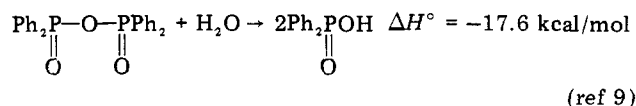
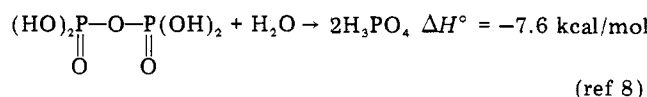
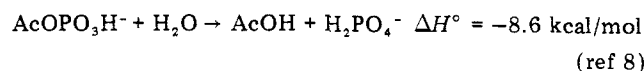
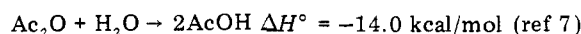
$$\Delta H^\circ_5 = \Delta H^\circ_1 - \Delta H^\circ_3 - \Delta H^\circ_4 = -16.2 \pm 2.5 \text{ kcal/mol}$$



$$\Delta H^\circ_6 = \Delta H^\circ_2 - 2\Delta H^\circ_3 = -1.5 \pm 2.1 \text{ kcal/mol}$$

The ΔH° s for eq 5 and 6 show that the hydrolysis of the α -disulfone (eq 5) is much more exothermic than the hydrolysis of the sulfinyl sulfone (eq 6). The estimated difference is 15 \pm 5 kcal/mol. Clearly the high kinetic reactivity of the sulfinyl sulfone compared to the α -disulfone in hydrolysis reactions has *nothing* to do with any greater thermodynamic instability of **1** relative to its hydrolysis products.

Both the sulfinyl sulfone and the α -disulfone can be considered "anhydrides", the sulfinyl sulfone being the anhydride of benzenesulfinic acid, and the α -disulfone being a mixed anhydride of benzenesulfonic and benzenesulfinic acids. Heats of hydrolysis of a number of other anhydrides are known, albeit in water rather than 60% dioxane as solvent. Values are shown below.



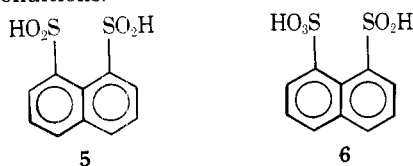
While the difference in solvent (water vs. 60% dioxane) makes it risky to draw any detailed quantitative conclusions from comparison of these values with those in eq 5 and 6, the results would seem to at least suggest that the heat of hydrolysis of the sulfinyl sulfone is probably smaller than those for most anhydrides and that, for an anhydride, particularly considering its thermal instability, a sulfinyl sulfone is from a thermodynamic point of view surprisingly stable relative to its hydrolysis products.

Table I. Calorimetric Data for Individual Runs

Registry no.	Reaction	Heats of Reaction		
		mmol of substrate	q'_{main} , cal	ΔH , kcal/mol
10409-06-0 (2) 14280-30-9 (OH ⁻)	2 + OH ⁻	0.25135	-12.9087	-51.36
		0.24972	-12.7970	-51.25
		0.25135	-12.9863	-51.66
				av -51.42 ± 0.15
784-81-6	1 + OH ⁻	0.24890	-6.9037	-27.74
		0.24962	-7.0481	-28.24
		0.24711	-6.9859	-28.27
				av -28.08 ± 0.23
618-41-7	PhSO ₂ H + OH ⁻	0.25103	-3.0933	-12.32
		0.25723	-3.1761	-12.35
		0.25505	-3.1144	-12.21
				av -12.29 ± 0.06
98-11-3	PhSO ₃ H + OH ⁻	0.25310	-5.3594	-21.17
		0.25817	-5.2321	-20.27
		0.26756	-5.6060	-20.95
				av -20.79 ± 0.35

Registry No.	Compd	Heats of Solution		
		mmol of compd	q'_{main} , cal	ΔH , kcal/mol
	2	0.25057	1.4851	5.93
		0.25057	1.4582	5.82
		0.24837	1.4815	5.97
				av 5.90 ± 0.06
	PhSO ₂ H	0.26537	1.0682	4.03
		0.30383	1.2033	3.96
		0.31418	1.2812	4.08
				av 4.02 ± 0.04
57821-65-5	3	0.22608	0.9421	4.07
		0.22566	1.0136	4.49
		0.22322	1.0394	4.66
				av 4.44 ± 0.21
62609-77-2	4	0.19799	0.7506	3.79
		0.19732	0.8090	4.10
		0.19976	0.8283	4.15
				av 4.01 ± 0.15

If that is true, then in general K_{eq} , the equilibrium constant for formation of a sulfinyl sulfone from the corresponding sulfonic acid, is likely to be considerably more favorable than the equilibrium constants for formation of most other types of anhydrides. One manifestation of this which has already been reported^{5a} is the fact that in the equilibrium between naphthalene-1,8-disulfonic acid (5) and 3 in aqueous dioxane at equilibrium $[3]/[5] \approx 3$, while there is no evidence for any detectable amount of the analogous α -disulfone 4 in equilibrium with naphthalene-1-sulfonic-8-sulfonic acid (6) under the same conditions.



Experimental Section

Preparation and Purification of Materials. Phenyl α -disulfone and dioxane were purified as previously described.^{4a} Benzenesulfonic acid was prepared from commercial sodium benzenesulfinate (Aldrich Chemical Co.) by dissolving the salt in the minimum amount of distilled water and then slowly adding 50% sulfuric acid with stirring in the cold until the solution was strongly acid (pH < 1). The sulfonic acid which precipitated was filtered off, washed carefully with a small amount of ice-cold water, and then redissolved in ether. The ether solution was dried over sodium sulfate to remove water and the ether then removed under reduced pressure. The residue was recrystallized from chloroform-hexane to give benzenesulfonic acid, mp 82–83 °C (lit.¹⁰ 85 °C), which was shown by titration to be greater than 99% pure. Phenyl benzenesulfinyl sulfone^{2a} was synthesized from ben-

zenesulfonic acid using the general procedure developed by Lerch and Moffat.¹¹ To 1.42 g of benzenesulfonic acid in 25 mL of dry methylene chloride was added 1.03 g of dicyclohexylcarbodiimide. After stirring for 10 min the precipitated dicyclohexylurea was filtered off and the filtrate evaporated to dryness under reduced pressure. The pure sulfinyl sulfone was obtained by recrystallization of the residue from chloroform-hexane. The benzenesulfonic acid used was anhydrous, electronic grade (Eastman Kodak Co.). Titration with sodium hydroxide showed it to be at least 99% pure. All handling of this deliquescent material was carried out in a dry nitrogen atmosphere. Compounds 3 and 4 were samples prepared in other work.⁵

Procedure for Calorimetric Measurements. All the thermochemical data were obtained using a commercial LKB 8700-1 calorimetry system.¹² All experiments were carried out in a single 100-mL calorimeter vessel of standard design. To reduce experimental deviations the mechanical ampule breaking device was employed. The ampules used were the commercial LKB 8727-1 with a 1-mL capacity.

Ampules were weighed accurately and filled carefully with approximately 0.25 mmol of the proper compound. Great care was taken in all weighings to obtain the precise weight of the substance in the ampule to ± 0.01 mg. For those substances which tended to be hygroscopic, weighings were carried out in a dry nitrogen atmosphere. The unsealed ampules were placed in a specially designed cold-water jacket that made it possible to seal the opening of the ampule with hot, molten glass (cold seal) without affecting the substance contained in the ampule.

Heats of reaction were determined by measuring the heat evolved upon breaking a filled ampule in the calorimeter vessel containing 100 mL of a 60% dioxane solution which was 0.1 N in sodium hydroxide. At least three different determinations were made for each substance.

The heat of solution for phenyl α -disulfone was determined by measuring the heat absorbed upon breaking an ampule containing 2 in the calorimeter vessel containing 100 mL of 60% dioxane. For

benzenesulfinic acid the heat of solution was determined in 60% dioxane containing 0.34 M perchloric acid, in order to suppress any tendency for PhSO_2H to dissociate. Dissociation of benzenesulfonic acid could not be suppressed by this same procedure, and so the heat of solution of PhSO_3H itself in 60% dioxane could not be measured experimentally. Because of its rapid spontaneous hydrolysis, the heat of solution of sulfinyl sulfone 1 also could not be determined experimentally. Since cyclic sulfinyl sulfone 3 does not undergo appreciable hydrolysis in acidic 60% dioxane its heat of solution could be determined satisfactorily. Since it was found to be essentially the same (4.4 ± 0.21 kcal/mol) as that of cyclic α -disulfone 4 (4.01 ± 0.15 kcal/mol), we assumed that, to an excellent approximation, ΔH_{soln} for 1 would be the same as the measured ΔH_{soln} for α -disulfone 2.

The procedure by which either heats of solution or heats of reaction were obtained was as follows. With calorimeter, solvent, and filled ampule in place, the change in resistance, R , with time was measured (foredrift). The reaction was then activated by breaking the ampule (main experiment). A fast change in resistance was observed, followed by a slower change which was again monitored (afterdrift). The thermistor for the calorimetry system is of such a type that a decrease in temperature (endothermic process) within the calorimeter vessel results in an increase in resistance across the thermocouple. After the reaction was over (stable afterdrift), an exact amount of electrical energy (heat) was pumped into the calorimeter and the change in resistance with time was recorded (calibration run). Using a linear regression program and the data from the calibration run, q_{calib} was calculated (Hewlett-Packard 9100-A calculator, Program No. 70803). This value was then correlated with ΔR for the main experiment to give q_{main} . Minor corrections were then made for sample buoyancy and vaporization of solvent to give q'_{main} . Dividing q'_{main} by the number of moles of substance used in the main experiment gives ΔH . The same procedure was followed whether obtaining ΔH_{soln} or ΔH_{rxn} . The data for the individual runs are given in Table I. A more detailed description of the data handling procedures used is given elsewhere.¹³

References and Notes

- (1) (a) This research was supported by the National Science Foundation, Grant GP 35927X. (b) Address correspondence to this author at the Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.
- (2) (a) J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964); (b) J. L. Kice and N. A. Favritsky, *J. Org. Chem.*, **35**, 114 (1970).
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- (5) (a) J. L. Kice and H. Margolis, *J. Org. Chem.*, **40**, 3623 (1975). (b) H. Margolis, Ph.D. Thesis, University of Vermont, 1976. (c) A referee has suggested that ΔH_{soln} for 1 might be significantly different than that for 2, because 2 has a much higher melting point than 1 and could therefore have a significantly higher crystal lattice energy. However, since 4 also has a much higher melting point than 3 and yet shows virtually the same ΔH_{soln} as 3, we personally doubt that ΔH_{soln} for 1 differs much from that of 2.
- (6) This assumption could be subject to a few kilocalories error, but, even if it is, it is certainly not going to be large enough to change significantly the basic and important conclusion, namely, that the heat of hydrolysis of the α -disulfone is substantially more exothermic than that of the sulfinyl sulfone.
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Conversion of Triflones to Ketones

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The trifluoromethanesulfonyl group (triflyl, CF_3SO_2-) has found extensive utility as an activating group in organic syn-

Table I. Synthesis of Ketones from Vinyl Azides

Vinyl azide	Registry no.	Ketone	Registry no.	Yield, %
	61795-22-0		451-40-1	85 ^a
	16717-64-9		98-86-2	93
	34910-43-5		591-78-6	86
	40934-24-5		502-49-8	91
	16719-57-6		83-33-0	87

^a Yield from iodoazide.

Table II. Synthesis of Ketones from Triflones

Triflone	Registry no.	Ketone	Registry no.	Yield, %
	52208-98-7			76
	62654-00-6		495-40-9	83
	62654-01-7		123-19-3	86

thesis, especially in the formation of carbon-carbon bonds.¹⁻³ One prerequisite for any such group is that after the construction step it must be easily removed or converted into other desired functionality. Previously, it was known that triflones ($\text{C}-\text{SO}_2\text{CF}_3$) could be reduced to the parent alkanes or thiols, or thermally eliminated to give olefins.² In addition, it was recently shown that triflones could react with toluenesulfonyl azide in the presence of 2 equiv of base (NaH/glyme) to give vinyl azides in good yield (Scheme I).³ Reduction of these compounds with lithium aluminum hydride gave the corresponding saturated amines.

Initial attempts to hydrolyze vinyl azides to the corresponding ketones with acid were only partially successful.³ In addition to ketones, amides were also produced via Schmidt rearrangement of the protonated vinyl azide.^{3a} We reasoned that to avoid this we must first extrude the nitrogen that acts as the initiating leaving group for the rearrangement. Accordingly, we investigated the Staudinger reaction of azides with phosphines.^{5,6} Although many kinds of azides have been studied, there appear to be few prior examples of the reaction with simple, unconjugated vinyl azides to form iminophosphoranes.⁷

Scheme I

