Thermal Decomposition of Sulfinic Acids[1]

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The thermal decomposition of sulfinic acids has been investigated at 275° at reduced pressures. The gaseous decomposition products, collected and identified by infrared and mass spectrometer analysis, were found to consist primarily of sulfur dioxide and olefins. Small quantities of carbon dioxide, carbon monoxide, carbonyl sulfide, sulfur, hydrocarbons, hydrogen, and water were also found, indicative of oxidation-reduction side reactions occurring in the presence of free radicals and sulfur dioxide. The absence of thiolsulfonates, sulfonic acids, sulfides, and disulfides indicates an unimolecular free-radical decomposition of sulfinic acid into the final products. Further confirmation of this mechanism was obtained by studying the decomposition of benzhydrylsulfinic acid.

The instability of sulfinic acids is well known; aliphatic sulfinic acids are less stable than aromatic sulfinic acids and short-chain aliphatic acids are less stable than are the longer-chain acids.[2] The disproportionation of sulfinic acids into thiosulfonates and sulfonic acids at 25 to 100° has been reported by many investigators[3] to occur according to the equation

$$3RSO_2H \longrightarrow RSO_2SR + RSO_3H + H_2O \qquad (1)$$

Variations in this disproportionation in terms of different reactive intermediates responsible for the formation of thiolsulfonates and sulfonic acids have been suggested. Thus Hinsberg[4] claims the disproportionation of the sulfinic acid to a sulfenic and a sulfonic acid as the initial step, followed by thiolsulfonate formation

$$2RSO_2H \longrightarrow RSOH + RSO_3H \qquad (2)$$

$$RSOH + RSO_2H \longrightarrow RSO_2SR + H_2O \qquad (3)$$

Sulfinyl sulfone formation from sulfinic acid in nonaqueous media and further disproportionation in an excess of the sulfinic acid gave the products shown, which were isolated.[5]

$$2RSO_2H \longrightarrow RSO_2SOR + H_2O \qquad (4)$$

$$RSO_2SOR + RSO_2H \longrightarrow RSO_2SR + RSO_3H \qquad (5)$$

On the basis of the work of Knoevenagel and Polack[6] who found that *p*-toluenesulfinyl tolyl sulfone was unstable at room temperature in the presence of moisture, Allen and Reich,[7] in their study of the disproportionation of *p*-toluenesulfinic acid in aqueous solution, favored a mechanism involving the decomposition of the postulated intermediate sulfinyl sulfone to sulfenic and sulfonic acids. The sulfenic acid was believed then to react with more sulfonic acid as in equation 3 to give the thiolsulfinate.

The rate-determining step in the decomposition of 2,2′-biphenyldisulfinic acid is reported[8] to involve thiolsulfonate formation with elimination of the elements of hydrogen peroxide, which accounts also for the formation of sulfonic acid by oxidation of sulfinic acid; thiolsulfonate is also said to form by a rearrangement of a disulfoxide formed initially.

In general the decomposition of sulfinic acids at temperatures below 100° and in aqueous or nonaqueous solutions has been shown to give the thiolsulfonate by a disproportionation second-order in sulfinic acid.[5,7]

In the present work an attempt has been made to elucidate the thermal decomposition of sulfinic acids by studying the products resulting when four acids of quite different stability were heated above 200° in the absence of a solvent. For our study we chose the following for the differences in structure and therefore in stability: benzenesulfinic acid, 1-butanesulfinic acid, 1,4-butanedisulfinic acid, and 1-dodecanesulfinic acid.

Experimental

Preparation and Purification of Sulfinic Acids. (a) **Benzenesulfinic acid** was prepared in 92% yield by the reduction of benzenesulfonyl chloride, by an adaptation of the method of Smiles and Bere.[9] The cold sodium benzenesulfinate solution was acidified with cold hydrochloric or sulfuric acid. After crystallization had started, acid was again slowly added with stirring until no more precipitate formed. The acid was removed by filtration, recrystallized twice from water, and washed with cold petroleum ether. The acid, m.p. 85–86°, was dried under reduced pressure at room temperature for 24 hours and stored under nitrogen at Dry Ice temperature. The compound is stable for several days at 25°.

Anal. Calcd. for $C_6H_6O_2S$: C, 50.70; H, 4.22; S, 22.54. Found: C, 51.36; H, 4.05; S, 22.84.

(b) **1-Butanesulfinic acid** was prepared by acidification of an aqueous solution of lithium butanesulfinate, prepared from butyllithium and sulfur dioxide. The cold solution

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TABLE I

THERMAL DECOMPOSITION OF SULFINIC ACIDS AT 275° FOR 1 HOUR

Acid	Mole-% Decom-position[a]	Mole-% Sulfur Dioxide[b]	Other Major Products	Minor Products
Benzenesulfinic acid	20.5	23	Benzene	COS, CO_2, H_2
1-Butanesulfinic acid	>90	>80	1,3-Butadiene, *cis*-2-butene	H_2O, C_4H_{10}, CO_2, COS, S, H_2
1-4-Butanedisulfinic acid	63	9	*cis*-2-Butene, 1,3-butadiene	H_2O, C_4H_{10}, CO_2, CO, COS, S, H_2
1-Dodecanesulfinic acid	63	85–90	Benzene	S, CO_2, H_2, COS

[a] The decomposition in mole % is based on the weight loss of the sulfinic acid during decomposition. [b] The mole % of sulfur dioxide was found from a calibration curve prepared from sulfur dioxide.

was extracted with ether and dried over anhydrous sodium sulfate. The product was obtained as a colorless oil by stripping the ether in a nitrogen stream under reduced pressure. The oil was stored under nitrogen at Dry Ice temperature. This compound has been obtained before as a pale yellow oil.[3e] Rapid decomposition at room temperature prevented the securing of meaningful analytical data. Infrared analysis confirmed the identity of this compound.

(c) **1,4-Butanedisulfinic acid** was prepared in 60% yield by the reduction of 1,4-butanedisulfonyl chloride.[10] The free acid was recrystallized twice from water and dried under reduced pressure at 65° for 24 hours. The compound, m.p. 123–124°, is very stable at room temperature. It was stored under nitrogen in a vacuum desiccator.

Anal. Calcd for $C_4H_{10}O_4S_2$: C, 25.80; H, 5.37; S, 34.40. Found: C, 25.69; H, 5.73; S, 34.30.

(d) **1-Dodecanesulfinic acid** was prepared in 75% yield by the method of Marvel and Johnson[2] by the acidification of a water solution of magnesium dodecylsulfinate prepared from dodecylmagnesium bromide and sulfur dioxide. The cold acidified solution was extracted with ether and dried over anhydrous sodium sulfate. The free acid, m.p. 35–36°, obtained by stripping the ether in a nitrogen stream under reduced pressure, was stored under nitrogen at Dry Ice temperature. It remained stable for a month at room temperature.

Anal. Calcd. for $C_{12}H_{26}O_2S$: C, 61.53; H, 11.11; S, 13.67. Found: C, 60.83; H, 11.37; S, 13.36.

Decomposition of Sulfinic Acids.—The acids were carefully purified immediately before use, and stored under nitrogen at low temperatures. For decomposition, the acids were weighed in a tared Pyrex glass tube (a glass wool plug was inserted to prevent mechanical loss during heating) and the sample tube was attached to a vacuum manifold. Also connected to the manifold were a mercury manometer, an infrared gas cell with cold-finger condenser, and a McLeod gauge. The manifold was fitted with the usual stopcocks and traps. The sample tubes were heated by an insulated glass tube of larger diameter wrapped with a heating tape. The temperature was regulated to ± 3° by a variable transformer connected to a Thermocap relay switch.

The entire apparatus was evacuated, and the temperature around the sample was quickly raised to 275° and held there for one hour. During decomposition of the sample, the gaseous products were condensed into the cold finger of the infrared gas cell cooled with liquid nitrogen. The decomposition products were immediately investigated by infrared and mass spectrometry. The residues were weighed after decomposition and the percent loss in weight was determined.

The decomposition of 1,4-butanedisulfinic acid, the most easily prepared and purified, was investigated first. Two different methods of decomposition were used. In method A, carried out in degassed closed breakseal tubes, the products of decomposition remained in contact with the decomposing sulfinic acid during the decomposition period. In the second method, B, the decomposition products were constantly removed during the one-hour period by condensing them in a cold-finger trap immersed in liquid nitrogen. The decomposition products of 1,4-butanedisulfinic acid by method A were large amounts of hydrogen sulfide and carbonyl sulfide, together with minor amounts of carbon dioxide, carbon monoxide, water, *cis*-2-butene, sulfur, hydrogen, and butane. These results are to be compared with the decomposition products by method B, listed in Table I.

The absence of sulfur dioxide and the large amounts of hydrogen sulfide found by method A and the reverse findings for method B indicate oxidation-reduction reactions when the decomposition products remain in contact with the decomposing acid. Removal of the products from the decomposition site results in a cleaner decomposition with less oxidation-reduction. The decomposition of all other sulfinic acids was therefore carried out by method B; the results are summarized in Table I.

Discussion of Results

The homogeneous decomposition of thiolsulfonates in several inert solvents at elevated temperatures (130–200°) has been found to be an ionic first-order process.[11] Sulfinic acids produced during this decomposition by a side reaction were postulated to decompose to sulfur dioxide and hydrocarbons by a free radical mechanism.

We have investigated for the first time the thermal decomposition of sulfinic acids at temperatures above 200°, in the absence of solvent, to determine the course of decomposition. Under the experimental conditions, sulfur dioxide and olefins are the major decomposition products. Minor products are water, carbon dioxide, carbon monoxide, carbonyl sulfide, and elemental sulfur formed by oxidation-reduction side reactions which occur in the presence of free radicals and sulfur dioxide.[12,13] *cis*-2-Butene is presumably formed by the isomerization of 1-butene in the presence of sulfur dioxide.[13]

Thiolsulfonates and their decomposition products, sulfonic acids, sulfides, and disulfides were not detected either in the gas phase or in the residues. Hydrogen sulfide and mercaptans, though not present in measurable quantity, are known to be present in small amounts, based on the method A experiments. The decomposition of sulfinic acids at 275° is evidently not the result of disproportionation to thiolsulfonates since none of the major products, except sulfur dioxide, reported for the de-

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composition of thiolsulfonates were found in our study.

On the basis of our experimental conditions and products obtained we suggest an unimolecular decomposition by a free radical mechanism. The initiating step may be represented by equation 6 in consideration of the relative bond strength of the C—S and S—H bonds and the differences in bond strength ascribable to the alkyl or aryl groups involved.[14] The propagation step may be represented by equation 7. Olefin formation results from transfer reactions followed by elimination such as indicated by equations 9 and 10.

$$\text{Initiation:}\quad RSO_2H \longrightarrow R\cdot + \cdot SO_2H \qquad (6)$$

$$\hookrightarrow SO_2 + H\cdot$$

$$\text{Propagation:}\quad RSO_2H + R\cdot \text{ or } H\cdot \longrightarrow RSO_2\cdot + RH + H_2 \qquad (7)$$

$$RSO_2\cdot \longrightarrow R\cdot + SO_2 \qquad (8)$$

$$\text{Transfer:}\quad R'\text{—}CH_2\text{—}CH_2SO_2H + R\cdot \text{ or } H\cdot \longrightarrow R'\underset{\cdot}{C}H\text{—}CH_2\text{—}SO_2H + RH \text{ or } H_2 \qquad (9)$$

$$R'\underset{\cdot}{C}H\text{—}CH_2SO_2H \longrightarrow R'CH{=}CH_2 + \cdot SO_2H \qquad (10)$$

$$\hookrightarrow SO_2 + H\cdot$$

A free radical mechanism of decomposition is supported by the work of Dainton and Ivin[15] who have prepared sulfinic acids by ultraviolet irradiation of hydrocarbons and sulfur dioxide. It is also similar to the thermal decomposition of alkanesulfonyl chlorides, postulated to proceed by a free-radical mechanism.[16]

To confirm this mechanism, benzhydrylsulfinic acid, not previously reported in the literature, was prepared by transmetallation of diphenylmethane with butyllithium and sulfinated at 20° in ether to give benzhydryllithium sulfinate (identified by infrared analysis). Acidification of the sulfinate at 0° with cold hydrochloric acid gave the free acid, a white crystalline solid at this temperature which showed absorption typical of a sulfinic acid at 9.6 μ. Unfortunately, rapid decomposition of this compound at 25° prevented elemental analysis.

The acid was found to decompose rapidly at room temperature and at 275° to give the same products: sulfur dioxide and diphenylmethane. These are the products which would be expected by the proposed mechanism for decomposition. The absence of both tetraphenylethane and hydrogen indicates that the decomposition propagates rapidly (equation 7) as compared with the rate of initial decomposition (equation 6). Sulfur dioxide was identified by mass spectrometer, and diphenylmethane was confirmed by its infrared spectrum and by elemental analysis. (*Anal.* Calcd. for $C_{13}H_{12}$: C, 93.4; H, 6.54. Found: C, 93.2; H, 7.27).

We conclude that the decomposition of sulfinic acids in the gas phase at 275° is a free radical unimolecular process resulting in sulfur dioxide, olefins, hydrocarbons, hydrogen, and decomposition products produced in minor amount by secondary reactions.

One unexplained fact remaining is the observation that benzene was obtained in two instances. This is not an error, since the result was reconfirmed several times by infrared analysis. Strong absorption at 14.9 μ, characteristic of benzene in the gas phase, was observed.

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