[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Cryoscopic Behavior of Organic Compounds in Sulfuric Acid. II. Sulfides, Sulfoxides and Sulfones. Evidence for the Existence of New Sulfur Ions

BY H. HARRY SZMANT AND GENE A. BROST

The cryoscopic behavior of a number of sulfides, sulfoxides and sulfones in sulfuric acid was studied. In the absence of oxidation reactions aromatic sulfides produce a colored sulfonium ion (R_2SH^+). Evidence is presented to show that aromatic sulfoxides can give a sulfoxidonium ion (R_2SOH^+), or a sulfidonium ion (R_2S^{++}). The formation of sulfidonium ions from sulfoxidonium ions requires a more concentrated sulfuric acid medium. The sulfones are weak bases in sulfuric acid and give only partial protonation unless the sulfone function is conjugated with nitro groups.

The number of sulfur compounds which has been investigated cryoscopically in sulfuric acid is limited to a few aromatic sulfonic acids,[1] and recently phenyl sulfone was studied by Gillespie.[2] In this paper we wish to report the results obtained with a number of sulfides, sulfoxides and sulfones.

Experimental

The compounds employed in this study were either purchased or were prepared by methods described in the literature. The sources of the compounds are indicated as follows: phenyl sulfide (Eastman Kodak Co.); di-(*p*-nitrophenyl) sulfide,[3] benzyl sulfide (Eastman Kodak Co.); di-(*p*-nitrobenzyl) sulfide[4]; phenyl sulfoxide[5]; *p*-nitrophenyl phenyl sulfoxide[6]; di-(*p*-nitrophenyl) sulfoxide[6]; benzyl sulfoxide[7]; phenyl sulfone[5]; *p*-nitrophenyl phenyl sulfone[8]; di-(*p*-nitrophenyl) sulfone[6]; benzyl sulfone[7]; and di-(*p*-nitrobenzyl) sulfone.[9]

The apparatus and the experimental technique was described in a previous publication.[10]

Representative cryoscopic measurements obtained in this study are shown in Table I.

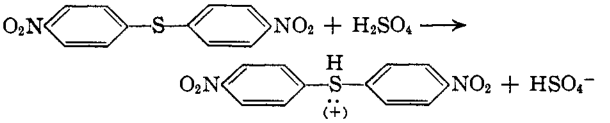
To recover the samples from the sulfuric acid reaction mixture the latter was poured onto crushed ice and the precipitated solid was filtered, washed, dried and identified.

TABLE I

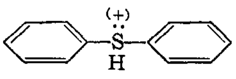
Δm	Hr.	Initial f. pt., (°C.)	ΔT	i	Color of solution	Remarks SO_2 evolution	Remarks Recovery
Phenyl sulfide							
0.03814	0.25	10.36	1.25	5.3	Red	Yes	No
Di-(*p*-nitrophenyl sulfide							
.01553	11-15	9.96	0.22	2.3	Red	No	Yes
Benzyl sulfide							
.03110	1.5	10.17	1.24	6.5	Light amber	Yes	No
Di-(*p*-nitrobenzyl) sulfide							
.01846	0.5	10.02	0.37	3.6	Light amber	Yes	No
Phenyl sulfoxide							
.008899	2-20	10.07	0.26	4.8	Green	No	Yes
p-Nitrophenyl phenyl sulfoxide							
.02526	29-49	10.21	0.39	2.5	Red	No	Yes
Di-(*p*-nitrophenyl) sulfoxide							
.02629	19-26	10.16	0.37	2.3	Red	No	Yes
Benzyl sulfoxide							
.02893	2.5	10.00	0.62	3.5	Light amber	Yes	No
Phenyl sulfone							
.04332	29-59	10.07	0.35	1.3	None	No	Yes
p-Nitrophenyl phenyl sulfone							
.01799	17-34	10.27	0.16	1.5	None	No	Yes
Di-(*p*-nitrophenyl) sulfone							
.01572	9-28	10.23	0.19	2.0	None	No	Yes
Benzyl sulfone							
.03280	20	10.09	1.18	5.8	Light amber	Yes	No
Di·(*p*-nitrobenzyl) sulfone							
.02902	3-6	10.15	0.18	1.0	Light amber	Slow	Yes

Discussion

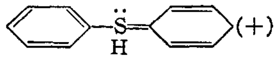
The results obtained with most of the sulfides can not be given an unambiguous interpretation since oxidation reactions (evidenced by an evolution of sulfur dioxide) and possibly also sulfonation reactions produced high *i* factors. The nature of the oxidation reactions could not be easily determined since the quenching of the sulfuric acid mixtures failed to result in water-insoluble products. The only compound which resisted the side reactions was di-(*p*-nitrophenyl) sulfide, and the *i* factor in this case indicates an ionization reaction represented as



A significant difference, however, was observed between those sulfides in which the sulfur atom is directly attached to an aromatic ring and those in which the aromatic ring and the sulfur atom are insulated by a methylene group: the first group of compounds produced brilliantly colored solutions (red) whereas the compounds of the second type gave practically colorless solutions. We believe that this difference can be attributed to the existence of resonance stabilization in a diarylsulfonium ion with contributing structures such as I. It is noteworthy that the oxygen analog of



IA



IB

phenyl sulfide dissolves in cold 100% sulfuric acid slowly on shaking and with the formation of a colorless solution, while phenyl sulfide gives an immediate cherry-red solution. The inability of the protonated phenyl ether to participate in a resonance phenomenon represented by I is a reasonable explanation of the difference in its behavior.

The most interesting results of this study were

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(1) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); **65**, 41 (1912); *Ber.*, **55B**, 953 (1922); **63B**, 1782 (1930).

(2) R. J. Gillespie, *et al.*, *J. Chem. Soc.*, 2473 (1950).

(3) C. C. Price and G. W. Stacey, *Org. Syntheses*, **28**, 82 (1948).

(4) Jahoda, *Monatsh.*, **10**, 874 (1889).

(5) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., 1948, 2nd ed., p. 138.

(6) H. H. Szmant and J. J. McIntosh, THIS JOURNAL, in press.

(7) R. L. Shriner, *et al.*, *ibid.*, **52**, 2060 (1930).

(8) E. Bourgeois and P. Huber, *Rec. trav. chim.*, **31-2**, 37 (1913).

(9) W. Reid, THIS JOURNAL, **45**, 2406 (1923).

(10) H. H. Szmant, O. M. Devlin and G. A. Brost, *ibid.*, **73**, 3059 (1951).

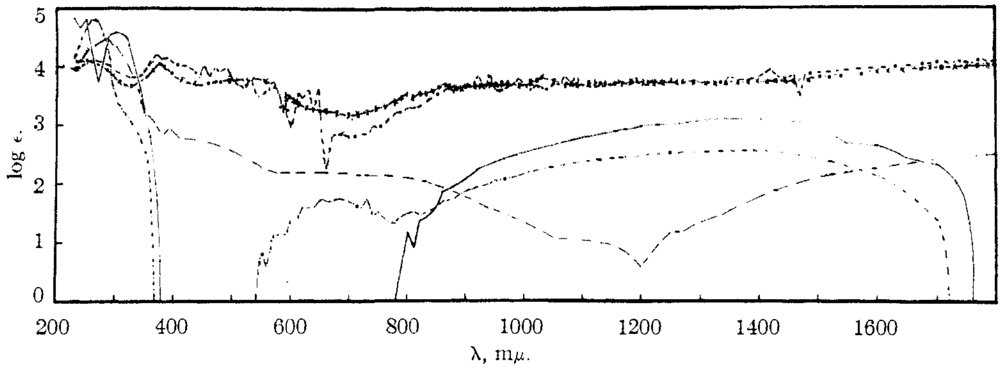


Fig. 1.—Absorption spectra in sulfuric acid: —, phenyl sulfide; —·—·, phenyl sulfoxide; - - - -, di-(*p*-nitrophenyl) sulfide; -x-x-, phenyl *p*-nitrophenyl sulfoxide; — —, di-(*p*-nitrophenyl) sulfoxide.

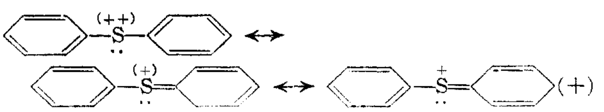
obtained with the sulfoxides. All of the aromatic sulfoxides were recovered from the sulfuric acid reaction mixture in essentially quantitative yields thus proving that no irreparable damage occurred during the complex ionization reactions. The benzyl sulfoxides, unfortunately, underwent undesirable side reactions which make the interpretation of the experimental *i* factors difficult, but again, as in the case of the benzyl sulfides, practically colorless solutions were obtained.

Phenyl sulfoxide gave a large and reproducible freezing point depression ($i = 4.7$) with the formation of a brilliant green solution. The nitro-substituted phenyl sulfoxides gave deep red solutions but the freezing point depressions were smaller ($i = 2.3$–2.5). The green solution of phenyl sulfoxide in 100% sulfuric acid faded on addition of water (or ordinary concentrated sulfuric acid) and, if not extensively diluted, assumed a reddish color. As mentioned above, the phenyl sulfoxide could eventually be recovered upon quenching of the reaction mixture.

We interpret these experimental facts by assuming that the following reaction occurs in the formation of the green solution

$$(C_6H_5)_2SO + 3H_2SO_4 \longrightarrow (C_6H_5)_2S\!:^{++} + H_3O^+ + 3HSO_4^- \quad (1)$$
$$(i = 5)$$

The double positive sulfur ion, presumably a new species, can be named the **diphenyl sulfidonium** ion, and its green color may result from the contribution of resonance structures such as II.

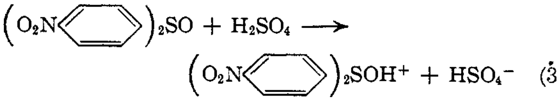


II

The sulfidonium ion in the presence of water restores the original sulfoxide according to equation (2).

$$(C_6H_5)_2S^{++} + 3H_2O \longrightarrow (C_6H_5)_2SO + 2H_3O^+ \quad (2)$$

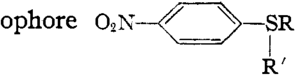
The introduction of one or two nitro groups onto the phenyl sulfoxide structure (only the para positions were studied) strengthens the sulfur-oxygen bond so that a less complex ionization reaction seems to take place. In the case of di-(*p*-nitrophenyl) sulfoxide, it is believed that the reaction is represented by equation (3) and a positive ion such as that formed in (3) can be named a **sulfoxidonium ion.**



(3)

The strengthening of the sulfur-oxygen bond in the nitro-substituted phenyl sulfoxides may be attributed to the polar effect of the nitro group. The existence of sulfoxidonium ions is not surprising in view of the well-known basicity of sulfoxides.[11]

The absorption spectra of several compounds described above were determined in sulfuric acid[12] and are shown in Fig. 1. It is noteworthy that the spectra of phenyl sulfide and phenyl sulfoxide resemble each other closely and thus it appears that the spectral properties of the diphenylsulfonium and diphenylsulfidonium ions are similar. The spectra of the other three compounds are also similar, presumably because of the common chromophore



$O_2N\text{—}C_6H_4\text{—}\underset{\textstyle R'}{\underset{|}{S}}R^+$

(R = phenyl, *p*-nitrophenyl; R′ = H, OH).

Our results with phenyl sulfone agree satisfactorily with those reported recently.[2] Of major interest, however, was the rise in the *i* factor observed by us when nitro-substituted phenyl sulfones were examined cryoscopically. The fractional *i* values in the case of weak bases are usually thought to be due to an equilibrium represented in the case of a sulfone by (4).

$$R_2SO_4 + H_2SO_4 \rightleftharpoons R_2SO_2H^+ + HSO_4^- \quad (4)$$

The rise in the *i* values upon introduction of nitro groups into the phenyl sulfone structure could be attributed to the shift in the equilibrium (4) due to a cumulative effect of the weakly basic nitro and sulfone groups. The magnitude of the rise of the *i* values upon the introduction of the second nitro group, however, was surprising and deemed worthy of investigating. We examined, therefore, the compound di-(*p*-nitrobenzyl) sulfone, a structure in which there are also present two nitro groups

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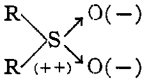
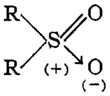
[11] D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

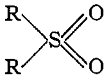
[12] Approximately 10% fuming sulfuric acid was employed in order to avoid excessive dilution by moisture take-up during the operations. The absorption curves were determined without delay in a Beckman DU spectrophotometer and each curve was checked by means of a new solution. (Work by Mr. H. J. Planinsek)

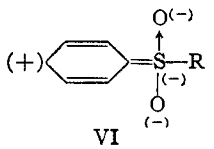
in addition to the sulfone function, and surprisingly enough we found the i value in this case to be considerably smaller than that of di-(p-nitrophenyl) sulfone,[13] In view of the behavior of the nitrobenzyl sulfone one can not attribute the sharp rise of the i values in the phenyl sulfone series to a simple accumulative effect of the basic groups. The sharply rising basicity of the nitrophenyl sulfones apparently is related to the existence of conjugation between the nitro and sulfone groups. The following explanation is offered for the purpose of correlating the experimental observations.

The electronic structures proposed for the sulfone group range from those in which both sulfur–oxygen bonds are doubly covalent to those in which both bonds are semipolar.[11,14] Presumably the actual structure of sulfones is a hybrid of several resonance structures, and the relative contribution of the individual forms III-V depends on the particular structural features present in a given molecule. If one examines the three contributing structures one notices a gradual decrease in the positive charge on the sulfur atom as we proceed from III to V. In sulfones in which nitro groups are conjugated with the sulfone function, the negative electromeric effect of the nitro group causes an electron deficiency near the sulfone group and this in turn would be expected to cause increasing contributions of structures IV and V to the ground state of the molecule. The benzyl sulfones, on the other hand, can be represented more accurately in terms of a structure such as III, and phenyl sulfone and sulfones containing electron-donating substituents are best represented by resonance structures such as VI. From the experimental i values of the sulfones investigated in this work it would seem that the relative basicities of sulfones increase as the electron distribution changes in the order: III < VI < IV < V. If this conclusion is correct, it follows that the basicity of the sulfone function depends more on the resonance stabilization of the protonated structure than on the fractional negative charge present initially on the oxygen atom.[15] We hope to investigate additional sulfones cryoscopically in order to ascertain the relationship between the basicities of sulfone groups and the structural features which could influence the relative contributions of the various sulfone resonance hybrids.[16]


III


IV


V


VI

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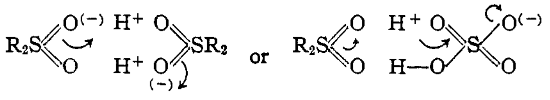
[13] Because of the critical significance of the i values of di-(p-nitrobenzyl) sulfone several careful experiments were carried out using fresh batches of sulfuric acid in each case. Within several hours upon the completion of the solution of each sample the experimental i factor had the value of nearly unity. As noted in Table I a slow oxidation side reaction then began which caused a noticeable evolution of sulfur dioxide and a gradual rise in the i values. Nearly quantitative recovery of the sulfone was possible after 12 hours: in an isolation experiment carried out with great care 0.681 g. of the initial 0.708 g. of sulfone was recovered. On the basis of these observations we believe the i value of di-(p-nitrobenzyl) sulfone to be nearly unity. In this connection we found the oxidation of benzyl sulfone to be too rapid for the determination of the i value of the simple ionization process, and this sulfone could not be recovered from the reaction mixture.

[14] (a) E. D. Amstutz, *et al.*, *Science*, **111**, 305 (1950); (b) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 234 (1949); *ibid.*, **72**, 1292 (1950); (c) H. P. Koch, *J. Chem. Soc.*, 408 (1949).

[15] A referee made the excellent suggestion that the protonated sulfone structure may be dimeric in line with the results of J. Walker (*ibid.*, 1996 (1949)) with amidinium complexes. Thus, the protonated sulfone may be best visualized as a resonating complex



[16] ADDED IN PROOF—Additional i values determined more recently support the above ideas: 4,4′-dichlorodiphenyl sulfone (i = 1.0): 3,3′-dinitro-4,4′-dichlorodiphenyl sulfone (i = 1.2).

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[CONTRIBUTED FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Electromotive Force Studies in Aqueous Solutions of Hydrochloric Acid and *d*-Fructose at 25°

BY H. D. CROCKFORD AND ALEXANDER A. SAKHNOVSKY

The values of the electromotive force at 25° of cells of the type H_2 |HCl (m), d-fructose (x), H_2O (y) |AgCl, Ag were determined with acid concentrations to approximately 0.12 m and in 5 and 10% d-fructose solutions. From the data obtained the standard cell potentials were calculated. An ion size parameter of 6.6 Å. was found for hydrochloric acid in the solutions studied. The mean activity coefficients of hydrochloric acid in the two solvents were determined at rounded molalities. These were found to agree closely with those calculated by the Debye–Hückel equation.

The work reported on in this paper is a continuation of the studies being carried on in this Laboratory on the effect of mixed solvents on the thermodynamic properties of hydrochloric acid solutions. In this work electromotive force measurements were made on the cell

$$H_2 \mid HCl\ (m),\ d\text{-fructose}\ (x),\ H_2O\ (y) \mid AgCl\text{–}Ag$$

at 25° in solutions containing 5 and 10% of d-fructose by weight with acid concentrations ranging from approximately 0.005 to 0.12 m. From the data obtained have been calculated the activity coefficients, the standard cell potentials, and the value of the ion size parameter.

This work was undertaken for the purpose of studying ion size parameter values of hydrochloric acid in solutions of hydroxyorganic compounds. Work with d-glucose was reported by Williams, Knight and Crockford.[1] They found a value of 6.6 Å. for the ion size parameter, a value much higher than the 4.3 Å. value found by other investigators

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[1] Williams, Knight and Crockford, THIS JOURNAL, **72**, 1277 (1950).