

# Equilibria and Reactions of Organic Sulfoxides in Moderately Concentrated Acids

Gianfranco Scorrano

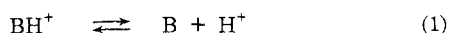
Centro CNR Meccanismi di Reazioni Organiche, Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy.

Received October 24, 1972

In the early years of the century Fromm<sup>1</sup> and Finzi<sup>2</sup> recognized that sulfoxides (R<sub>2</sub>SO) behave as weak bases. The interest in the properties of this class of compounds notwithstanding,<sup>3</sup> quantitative study of their acid-base equilibria, which is fundamental to understanding their acid-catalyzed reactions, was started only several years later. As has often happened with weak bases, widely different pK<sub>BH+</sub> values were reported; some of them are collected in Table I.<sup>4-14</sup>

The reasons for these differences, as well as of those found for other bases, lie both on experimental and theoretical grounds.<sup>15,16</sup>

The equilibrium constant<sup>17</sup> for generalized acid-



base reaction 1 can be written as

$$K_{\text{BH}^+} = \frac{a_{\text{B}}a_{\text{H}^+}}{a_{\text{BH}^+}} = \frac{c_{\text{B}}c_{\text{H}^+}f_{\text{B}}f_{\text{H}^+}}{c_{\text{BH}^+}f_{\text{BH}^+}} \quad (2)$$

In dilute acids, where the activity coefficients can be taken to be unity, eq 2 reduces to a familiar expression (eq 3) from which the pK<sub>BH+</sub> of the base is

$$\text{p}K_{\text{BH}^+} = \text{pH} + \log(c_{\text{BH}^+}/c_{\text{B}}) \quad (3)$$

easily evaluated by measuring the ionization ratio  $I = c_{\text{BH}^+}/c_{\text{B}}$ . Moreover, the difference in the pK<sub>BH+</sub> of two bases is simply given by the difference of the log  $I$  at a given pH (eq 4). From a known pK<sub>(BH<sup>+</sup>)<sub>1</sub></sub>

$$\text{p}K_{(\text{BH}^+)_1} - \text{p}K_{(\text{BH}^+)_2} = \log \frac{c_{(\text{BH}^+)_1}}{c_{(\text{B})_1}} - \log \frac{c_{(\text{BH}^+)_2}}{c_{(\text{B})_2}} \quad (4)$$

value one could derive the pK<sub>(BH<sup>+</sup>)<sub>2</sub></sub> of a weaker base, through eq 4, and therefore extend the acidity scale (eq 3) in stepwise fashion to more concentrated acid solutions. This is the basis of acidity measurements with indicators using the so-called overlap method.

When the base is protonated in more concentrated acids, however, the activity coefficients can no longer be taken to be unity and the equilibrium constant should be expressed as eq 5. Hammett and Deyrup<sup>18</sup>

$$-\log K_{\text{BH}^+} = -\log a_{\text{H}^+} + \log \frac{c_{\text{BH}^+}}{c_{\text{B}}} + \log \frac{f_{\text{BH}^+}}{f_{\text{B}}} \quad (5)$$

introduced the acidity function concept to reduce eq 5 to a more amenable expression

$$\text{p}K_{\text{BH}^+} = H_0 + \log(c_{\text{BH}^+}/c_{\text{B}}) \quad (6)$$

where

$$H_0 = -\log a_{\text{H}^+} + \log(f_{\text{BH}^+}/f_{\text{B}}) \quad (7)$$

The evaluation of pK<sub>BH+</sub> from differences in log  $I$  values, therefore, is now more complicated since

$$\text{p}K_{(\text{BH}^+)_1} - \text{p}K_{(\text{BH}^+)_2} = \log \frac{c_{(\text{BH}^+)_1}}{c_{(\text{B})_1}} - \log \frac{c_{(\text{BH}^+)_2}}{c_{(\text{B})_2}} + \log \frac{f_{(\text{BH}^+)_1}f_{(\text{B})_2}}{f_{(\text{B})_1}f_{(\text{BH}^+)_2}} \quad (8)$$

One must also take into account the last term on the right of eq 8, which contains activity coefficients. It was long believed<sup>19</sup> that this term would cancel since the ratio of activity coefficients,  $f_{\text{BH}^+}/f_{\text{B}}$ , for a given base could be considered constant and equal to that for primary anilines, which were used to develop the first acidity function  $H_0$ . It was assumed that

$$f_{(\text{B})_1}/f_{(\text{BH}^+)_1} = f_{(\text{B})_2}/f_{(\text{BH}^+)_2} \quad (9)$$

- (1) E. Fromm, *Ann. Chem.*, **396**, 75 (1913).
- (2) C. Finzi, *Gazz. Chim. Ital.*, **46**, 186 (1916).
- (3) C. R. Johnson and J. C. Sharp, *Quart. Rep. Sulfur Chem.*, **4**, 1 (1969).
- (4) C. A. Streuli, *Anal. Chem.*, **30**, 997 (1958).
- (5) K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).
- (6) P. Nylen, *Z. Anorg. Allg. Chem.*, **246**, 227 (1941).
- (7) G. Wada, *Bull. Chem. Soc. Jap.*, **42**, 890 (1969).
- (8) D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, **91**, 6703 (1969).
- (9) W. L. Reynolds and K. A. Lampe, *J. Inorg. Nucl. Chem.*, **30**, 2860 (1968).
- (10) P. Haake and R. D. Cook, *Tetrahedron Lett.*, 427 (1968).
- (11) P. O. I. Virtanen and J. Korpela, *Suomen Kemistilehti B*, **41**, 326 (1968).
- (12) N. C. Marziano, G. Cimino, U. Romano, and R. C. Passerini, *Tetrahedron Lett.*, 2833 (1969).
- (13) C. Klofutar, F. Krasovec, and M. Kusar, *Croat. Chem. Acta*, **40**, 23 (1968).
- (14) S. Oae, K. Sakai, and N. Kunieda, *Bull. Chem. Soc. Jap.*, **42**, 1964 (1969).
- (15) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970.
- (16) M. Liler, "Reaction Mechanisms in Sulphuric Acid," Academic Press, London, 1971; C. H. Rochester, "Acidity Functions," Academic Press, London, 1970.
- (17) BH<sup>+</sup> and B are the protonated and free base, respectively;  $a$ ,  $c$ , and  $f$ , represent activity, concentration, and activity coefficients of the indicated species.
- (18) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).
- (19) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

Gianfranco Scorrano was born in Pescara, Italy, in 1939. After receiving his degree in chemistry at the University of Bologna, he joined the research group of Professor G. Modena at the University of Bari. In 1968 he did postdoctoral work at the University of California, Santa Cruz, and then went to the University of Padova where he is Lecturer in Organic Chemistry. His research interest center on the mechanisms of reactions of sulfur compounds.

**Table I**  
 **$pK_{BH^+}$  Values Reported for Dimethyl and Diphenyl Sulfoxide**

$pK_{BH^+}$	Method <sup>a</sup>	Ref
	(CH <sub>3</sub> ) <sub>2</sub> SO	
1.0	TNAS	4
0.91	TNAS	5
0.0	TNAS	6
-1.04	Uv	7
-1.80	Nmr	8
-2.09	Uv	9
-2.78	Nmr	10
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO	
-2.07	SE	11
-2.54	Uv	8
-2.85	Uv	12
-3.19	SE	13
-3.58	TNAS	5
-4.97	Uv	14

<sup>a</sup> TNAS = titration in nonaqueous solvent; SE = solvent extraction.

Unfortunately, time has proved that eq 9 holds for very similar classes of compounds only. In fact, several different acidity scales have been developed for different bases such as aromatic tertiary amines ( $H_0'''$ ),<sup>20</sup> amides ( $H_A$ ),<sup>21</sup> carbinols ( $H_{R+}$ ),<sup>22</sup> indoles ( $H_I$ ),<sup>23</sup> and so on.<sup>15,24</sup> Therefore, once the ionization ratio for a given base is measured, a chemist is faced with the problem of deciding which acidity function should be taken to represent the proton activity and the activity coefficient ratio (eq 7).

A rigorous approach to this problem would be to define an acidity function for each class of structurally similar bases, if not for every single base. This tedious and almost worthless work (no meaningful comparison between different classes of base would then be possible) can be avoided by using empirical relationships found by Yates and McClelland<sup>25</sup> and by Bunnett and Olsen.<sup>26</sup>

Yates and McClelland reported<sup>25</sup> that, since all known acidity functions ( $H_X$ ) are almost linearly correlated with the  $H_0$  acidity functions (eq 10), eq 6

$$H_X = mH_0 \quad (10)$$

can be rewritten as

$$pK_{BH^+} = mH_0 + \log(c_{BH^+}/c_B) \quad (11)$$

A plot of  $\log I$  vs.  $H_0$  allows one to evaluate  $pK_{BH^+}$  values as the  $H_0$  intercept (when  $\log I = 0$ ) times the slope  $m$ .

Bunnett and Olsen<sup>26</sup> found that linear relationships exist between the logarithms of the equilibrium

quotient ( $Q = c_{BH^+}/c_{BC_{H^+}}$ ) for diverse bases in solutions of the same mineral acid. By taking as reference the behavior of an amine for which a plot of  $\log I$  vs.  $-H_0$  is linear with slope 1.00 and  $pK_{BH^+}$  zero, one could write eq 12, where  $1 - \phi$  is an arbitrary

$$\log(c_{BH^+}/c_B) - \log c_{H^+} =$$

$$(1 - \phi)(-H_0 - \log c_{H^+}) + \text{constant} \quad (12)$$

choice of slope parameter. Equation 12 can be easily transformed in the standard formulation of the Bunnett and Olsen linear free energy relationship (eq 13)

$$\log(c_{BH^+}/c_B) + H_0 = \phi(H_0 + \log c_{H^+}) + pK_{BH^+} \quad (13)$$

by adding to each side  $H_0 + \log c_{H^+}$  and by evaluating the constant at  $H_0 = -\log c_{H^+}$ , that is, at infinite dilution in water.

Therefore, on plotting ( $\log I + H_0$ ) vs. ( $H_0 + \log c_{H^+}$ ) one can obtain the  $pK_{BH^+}$ , referred to infinite dilution in water, as the intercept for ( $H_0 + \log c_{H^+}$ ) = 0, and, as slope, the parameter  $\phi$  which expresses the response of the equilibrium to changing acid concentration. Equation 12 is equivalent to eq 14, where  $H_X$  is the acidity function followed by the base B.

$$H_X + \log c_{H^+} = (1 - \phi)(H_0 + \log c_{H^+}) \quad (14)$$

Compared with eq 10, eq 14 contains terms in  $\log c_{H^+}$ . This could probably justify<sup>15</sup> the fact that plots based on eq 14 give smooth straight lines to the origin of coordinates, whereas plots of  $H_X$  vs.  $H_0$  have sharp curvature in this region. In general, eq 13 gives more linear plots than eq 10. For this reason, and for the fact that the Bunnett and Olsen equation lies in the framework of the well-known linear free energy relationships, we have adopted eq 13 in the work described below. However, as described by Greig and Johnson,<sup>27</sup> substantially similar results can be obtained by means of the Yates treatment. It must also be pointed out that the Bunnett and Olsen equation makes somewhat clearer the limitations of the  $H_0$  acidity function.

From the discussion above it appears that two quantities are needed to define an acid-base equilibrium, that is, the  $pK_{BH^+}$  and  $\phi$  (or  $m$ ) values, which give an indication of the solvation requirements of the base.

### Measurements of Ionization Ratios and Evaluation of $pK_{BH^+}$ of Sulfoxides

The most reliable measurements of ionization ratios are those based on the evaluation of some spectroscopic property of the base and the conjugate acid.<sup>15,16</sup>

In the case of sulfoxides, we have been able to use, and compare, ultraviolet (uv),<sup>8</sup> nuclear magnetic resonance (nmr),<sup>8</sup> and circular dichroism (CD)<sup>28</sup> spectroscopy. Each technique has its own advantages and drawbacks.

(27) C. C. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, **90**, 6453 (1968).

(28) U. Quintily and G. Scorrano, *Chem. Commun.*, 260 (1971); P. Bonvicini, A. Levi, and G. Scorrano, *Gazz. Chim. Ital.*, **102**, 621 (1972).

(20) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964).

(21) K. Yates, J. B. Stevens, and A. R. Katritzky, *Can. J. Chem.*, **42**, 1957 (1964).

(22) N. C. Deno, J. J. Jaruzelski, and A. Schreisheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

(23) R. L. Hinman and J. Long, *J. Amer. Chem. Soc.*, **86**, 3796 (1964).

(24) R. H. Boyd in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

(25) K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, **89**, 2686 (1967).

(26) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899 (1966).

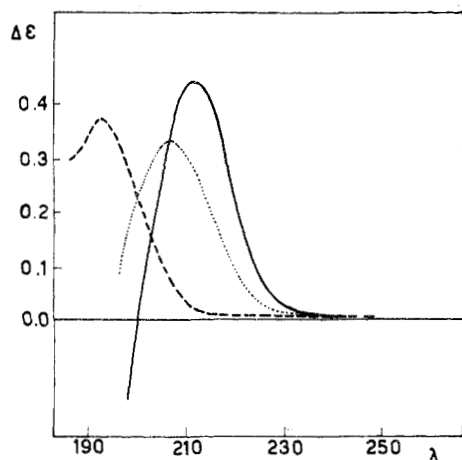


Figure 1. Circular dichroism spectra of (+)-methyl *tert*-butyl sulfoxide partially resolved (ca. 43% optically pure) in  $\text{H}_2\text{SO}_4$ : (—) 1.7 M; (···) 4.8 M; (---) 13.3 M.

The uv spectra, measured in solutions of different acid concentration, are, as often happens for this kind of measurement,<sup>15</sup> somewhat difficult to interpret. They change, in fact, both because of protonation and of solvent effects. Several empirical methods have been proposed to account for these effects.<sup>15,16</sup> We obtained good results<sup>8</sup> by following the approach of Davis and Geissman,<sup>29</sup> which involves evaluation of differences in optical densities at two wavelengths, characteristic of the free and protonated base. Since the identification of these two wavelengths is not always straightforward, we felt it necessary to compare uv data with those obtained by other spectroscopic methods.

The comparison has been particularly interesting as far as the nmr method is concerned. It involves measurements of chemical shifts of protons,  $\alpha$  to the SO group, in acid solution with respect to a suitable internal standard, such as the trimethylammonium ion,<sup>8,10</sup> chosen to minimize solvent effects. These measurements are made at much higher concentrations than those used with the other spectroscopic methods. Some doubt could, therefore, be raised as to whether the relatively high base concentration necessary has a salt effect, making the effective acidities significantly different from the measured ones. The fact that identical results, within experimental error, have been obtained with the nmr and the uv and CD techniques<sup>8</sup> provides clear evidence that the effect of higher base concentration on the acidity is negligible, when compared with other sources of error inherent in these measurements.

Some problems, however, are also encountered in the nmr measurements.<sup>30</sup> Indeed, different ionization ratios have been evaluated at the same acidity for methyl methylphenylphosphinate by following the  $\text{CH}_3$  or  $\text{OCH}_3$  proton resonance chemical shifts, with respect to the trimethylammonium ion.<sup>30</sup> Probably, the  $(\text{CH}_3)_3\text{NH}^+$  ion is able to compensate for solvent effects of the methyl, but not of the methoxyl group, where a basic oxygen atom separates the  $\text{CH}_3$

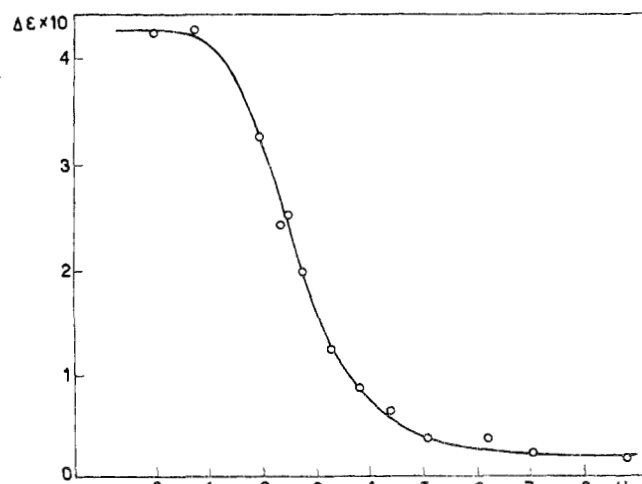


Figure 2. Correlation of  $\Delta\epsilon$  values with  $-H_0$  for methyl *tert*-butyl sulfoxide in sulfuric acid solutions.

group from the protonation center. The nmr method is, moreover, limited to compounds having a hydrogen  $\alpha$  to the SO group.

These limitations forced us to explore the CD technique. It requires, albeit in small amounts, optically active sulfoxides, which can be easily prepared by Andersen's method.<sup>31</sup> It has, on the other hand, some advantages. Well-resolved CD spectra have been obtained with all the sulfoxides and phosphine oxides so far examined,<sup>28</sup> and, apparently, the solvent effects cause smaller changes than those caused by protonation. This allows a simple data treatment. For instance, the  $\Delta\epsilon$  values evaluated at 212 nm from the CD spectra in sulfuric acid solution of (+)-methyl *tert*-butyl sulfoxide (see Figure 1) give a good sigmoid curve when plotted vs. the medium acidity as evaluated, for example, by the  $H_0$  acidity function (see Figure 2).

The  $c_{\text{BH}^+}/c_{\text{B}}$  values obtained as described above fit nicely with eq 13 to give good straight lines from which  $\text{p}K_{\text{BH}^+}$  and  $\phi$  values can be evaluated. The results obtained in perchloric or sulfuric acids, with one or more of the above techniques, all lie within experimental error, which we estimated as  $\pm 0.2$   $\text{p}K_{\text{BH}^+}$  unit. Some mean  $\text{p}K_{\text{BH}^+}$  and  $\phi$  values are collected in Table II.<sup>8,28,32,33</sup>

The  $\phi$  values, within the scope of the linear free energy relationship developed by Bunnett and Olsen,<sup>26</sup> have a meaning similar to that of Hammett's  $\rho$ ,<sup>15</sup> in the sense that they represent the response of the equilibrium quotient to changing of the medium (*i.e.*, to increasing acid concentration, and hence decreasing  $a_{\text{H}_2\text{O}}$ ).

Most of the medium effect, but not all, is certainly due to hydration changes,<sup>26</sup> and this will be reflected by the magnitude of the  $\phi$  values. Taking as reference the protonation of a primary aniline (Hammett base) for which  $\phi = 0$ , positive  $\phi$  values are expected

(29) C. T. Davis and T. A. Geissman, *J. Amer. Chem. Soc.*, **76**, 3507 (1954).

(30) R. Curci, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, in press.

(31) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, **86**, 5637 (1964).

(32) D. Landini, G. Modena, U. Quintily, and G. Scorrano, *J. Chem. Soc. B*, 2041 (1971).

(33) G. Modena, U. Quintily, and G. Scorrano, *J. Amer. Chem. Soc.*, **94**, 202 (1972).

Table II  
Average Values Describing the Acid-Base Equilibria of Sulfoxides (R-SO-R') in Perchloric and Sulfuric Acids<sup>a</sup>

R	R'	$pK_{BH^+}^b$	$\phi^b$	$(H_A)_{1/2}^c$	$s^c$	Method	Ref
Me	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	-2.05	0.41	-2.29	1.08	Uv, nmr	8
Me	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	-2.22	0.47	-2.61	1.12	Uv, nmr	8
Me	Ph	-2.27	0.51	-2.72	0.98	Uv, nmr	8
Me	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	-2.45	0.53	-2.89	0.96	Uv, nmr	8
Me	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	-2.61	0.50	-2.99	1.05	Uv, nmr	8
Me	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	-2.96	0.53	-3.37	1.07	Uv, nmr	8
<i>i</i> -Pr	Ph	-2.13	0.47	-2.50	1.04	CD, uv, nmr	28, 32
<i>t</i> -Bu	Ph	-1.79	0.49	-2.26	1.03	CD, uv	28, 33
Ph	Ph	-2.54	0.59	-2.93	0.92	Uv	8
Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	-2.39	0.55	-2.80	0.98	Uv, CD	8, 28
Me	Me	-1.80	0.46	-2.11	0.95	Nmr	8
Me	<i>t</i> -Bu	-1.66	0.46	-1.93	1.05	Nmr, CD	8, 28

<sup>a</sup> Actual  $pK_{BH^+}$  values obtained in the two acids with different techniques differ from the means by less than  $\pm 0.2$  unit. <sup>b</sup> Obtained as intercept ( $pK_{BH^+}$ ) and slope ( $\phi$ ) from a plot of  $(\log I + H_0)$  vs.  $(H_0 + \log c_{H^+})$  (eq 13). <sup>c</sup>  $H_A$  values at half-protonation  $(H_A)_{1/2}$  are evaluated by plotting  $\log I$  vs.  $-H_A$ ;  $s$ , slopes.

when bases have a greater solvation requirement than anilines and negative  $\phi$  values when hydration of  $BH^+$  is relatively low.

The  $\phi$  values found for sulfoxides lie in the range +0.4 to +0.6, which corresponds to strong solvation requirements of the conjugate acid  $R_2SOH^+$ . Inspection of data collected in the literature<sup>26</sup> showed that other classes of bases, in particular amides, have similar  $\phi$  values. Since the acidity function for amides is known ( $H_A$ ),<sup>21</sup> we checked whether the same function could be used to describe the acid-base behavior of sulfoxides. This is indeed the case, as shown (see Table II) by the almost unit slopes of the plots of  $\log I$  vs.  $-H_A$ . The  $H_A$  values at half-protonation should correspond to the  $pK_{BH^+}$  and in fact they do if we take into account that the  $H_A$  scale is, as a whole, probably shifted by 0.3 unit toward more negative values, possibly because of difficulties encountered in its anchorage to the pH scale.<sup>25,26</sup> Therefore we can use the acidity scale  $H_A$  as a reasonable approximation to the sulfoxide acidity scale.<sup>34</sup>

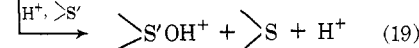
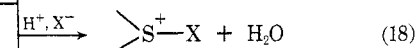
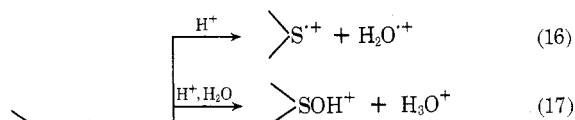
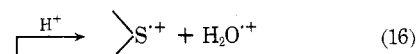
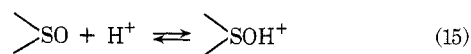
### Acid-Catalyzed Reactions of Sulfoxides

A knowledge of the acid-base equilibria of sulfoxides is of significance to an understanding of the chemical behavior of this class of compounds. The most obvious and pertinent application is in the area of their acid-catalyzed reactions.

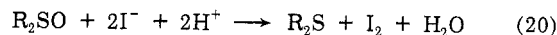
Several examples have been reported,<sup>3</sup> and in recent years reactions leading to oxygen exchange,<sup>38,39</sup>

racemization,<sup>38,40-42</sup> and reduction<sup>41,43,44</sup> have been studied in detail.

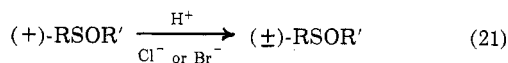
In these reactions the sulfur-oxygen bond breaking may occur either unimolecularly or by a bimolecular nucleophilic displacement (eq 15-19).



By far the best nucleophiles in these acid solutions are halide ions. It has been shown<sup>41</sup> that different halide ions react through similar pathways, although they lead to different products. Iodide ion causes reduction to sulfides (eq 20), whereas bromide and



chloride ions cause oxygen exchange and racemization (eq 21).



These reactions, studied in some detail in our laboratory,<sup>32,41</sup> may be taken as examples of the importance of the evaluation of the acid-base behavior in defining a reaction mechanism.<sup>15</sup> A knowledge of the position of equilibrium 15 allowed us to recognize that sulfoxides are substantially protonated in the range of acid concentration ( $\text{HClO}_4$  0.5-8 M) in

(34) Recently, Olah, *et al.*,<sup>35</sup> have reported that sulfoxides protonate in "magic acid" on sulfur, rather than on oxygen, since the chemical shift for the acidic proton lies in the range for  $-\text{SH}^+$  chemical shifts observed in protonated thiols and sulfides. This has been criticized by Olofsson, *et al.*,<sup>36</sup> also because of the lack of coupling between the acidic proton and an  $\alpha$  methyl group, although the corresponding proton-proton coupling in sulfides and thiols has been found to be about 8 Hz.<sup>37</sup> We feel that Olah's claim needs to be further substantiated (for a more detailed discussion see G. Modena, *Int. J. Sulfur Chem.*, in press) and will therefore treat protonated sulfoxides as "oxonium" compounds.

(35) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3904 (1970).

(36) Q. Appleton, L. Bernander, and G. Olofsson, *Tetrahedron*, **27**, 5921 (1971).

(37) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

(38) S. Oae, *Quart. Rep. Sulf. Chem.*, **5**, 53 (1970).

(39) I. Ookuni and A. Fry, *J. Org. Chem.*, **36**, 4097 (1971).

(40) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964).

(41) D. Landini, F. Montanari, G. Modena, and G. Scorrano, *J. Amer. Chem. Soc.*, **92**, 7168 (1970).

(42) S. Allenmark and C. Hagberg, *Acta Chem. Scand.*, **22**, 1461, 1694 (1968).

(43) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

(44) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

which their rates of reduction and of racemization are suitable for accurate measurements. Therefore, these rates must be expressed as a function of protonated sulfoxide concentration (eq 22). The rate coef-

$$\text{rate} = k_1[\text{R}_2\text{SOH}^+] \quad (22)$$

ficients  $k_1$ , easily derived from the experimental rate coefficient ( $k_{\text{obsd}}$ ) (eq 23), are found<sup>41</sup> to depend

$$k_1 = \frac{\text{rate}}{[\text{R}_2\text{SOH}^+]} = k_{\text{obsd}} \frac{h_A + K_{\text{BH}^+}}{h_A} \quad (23)$$

upon the first power of the concentration of the halide ion and to increase with acid concentration. We were then faced with the problem of correlating  $k_1$  (which already takes into account the protonation of the substrate) with the solvent acidity.

During the years the method of correlating reaction rates with acidity underwent a development similar to that described above for  $\text{p}K_{\text{BH}^+}$  evaluation.<sup>15,16</sup> It was thought, at first, that the log of pseudo-first-order rate constants should be linear either with  $-H_0$  or  $\log c_{\text{H}^+}$ .<sup>45</sup> Time proved this hypothesis unjustifiable,<sup>15,46</sup> both experimentally and theoretically. New correlations were then searched for; the two most recent treatments have been proposed by Yates, *et al.*<sup>46,47</sup> (eq 24), and by Bunnett and Olsen<sup>48</sup> (eq 25). The Yates treatment,<sup>49</sup> derived

$$\log k_{\text{obsd}} + H_X = r \log a_{\text{H}_2\text{O}} + \text{const} \quad (24)$$

$$\log k_{\text{obsd}} + H_0 = \phi(H_0 + \log c_{\text{H}^+}) + \text{const} \quad (25)$$

from a correlation found previously by Bunnett,<sup>50</sup> allows evaluation of the water activity dependence  $r$ , which should correspond to the number of water molecules involved in the conversion of the protonated substrate to the transition state, that is, the approximate "order" of the reaction in water.

The Bunnett and Olsen equation<sup>51</sup> has been derived following a similar line of reasoning as described above for the linear free energy relationship treatment of equilibria.<sup>48</sup> The  $\phi$  parameters thus evaluated may, as do the analogous  $\rho$  and  $\alpha$  parameters defined in the Hammett and Bronsted relationships,<sup>15</sup> vary widely for reactions having the same mechanisms.

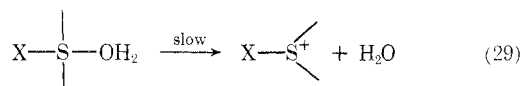
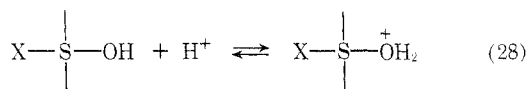
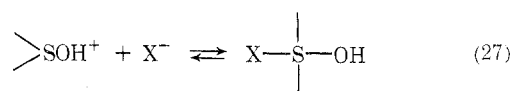
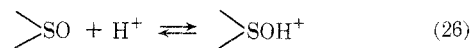
Reactions have been, on the basis of available data, grouped in three classes, corresponding to different degrees of participation of water molecules in the reaction scheme:  $\phi < 0.0$  are found when water is not involved in the rate-limiting step;  $\phi = +0.22$  to  $+0.56$  for water acting as a nucleophile in the rate-

limiting step;  $\phi > +0.58$  for water acting as a proton-transfer agent in the rate-limiting step.

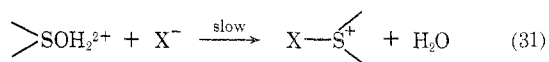
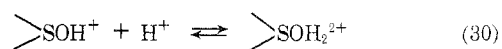
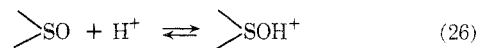
We used the Bunnett and Olsen approach and, by considering our reaction as the acid-catalyzed transformation of the protonated sulfoxide to give products, we plotted  $\log [(k_1/[\text{Hal}^-]) + H_0]$  vs.  $(H_0 + \log c_{\text{H}^+})$ .<sup>41</sup> Data collected in Table III show that  $\phi$  values lie, for methyl sulfoxides, in the range  $+0.06$  to  $-0.21$ , suggesting that the water molecule does not participate in the rate-determining step.<sup>41</sup>

The evaluation of  $k_1$  rate coefficients showed that the change of overall rates ( $k_{\text{obsd}}$ ), in the reduction of phenyl methyl sulfoxides in  $\text{HClO}_4$ , with the nature of the substituent in the phenyl ring ( $k_{\text{p-OMe}} > k_{\text{p-NO}_2}$ ) is due to differences in basicity rather than to different reactivities of the protonated sulfoxides.<sup>41</sup> On the other hand, the depression in rate constant found in reactions of alkyl phenyl sulfoxides with branched alkyl groups<sup>52</sup> does depend on the differences in rates from the protonated stage onward. We found<sup>52</sup> that isopropyl phenyl sulfoxide reacts *ca.* one-sixtieth as fast as the methyl derivative, whereas the *tert*-butyl compound undergoes fragmentation faster than either reduction or racemization. A lower limit for the ratio  $k_{\text{Me}}/k_{\text{t-Bu}}$  has been estimated as  $10^4$ .<sup>33</sup> Similar steric retardations were observed in other reactions at sulfur center,<sup>40,44,53</sup> and they have been taken as indications that the attack of the halide ions occurs at the sulfur atom.<sup>40,41,44</sup> Equations 26-31 seem adequate to accommodate the above results.

A



B



(45) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(46) K. Yates, *Accounts Chem. Res.*, **4**, 136 (1971), and references therein.

(47) K. Yates and J. B. Stevens, *Can. J. Chem.*, **43**, 529 (1965); K. Yates and J. C. Riordan, *ibid.*, **43**, 2328 (1965).

(48) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).

(49)  $H_X$  is the acidity function strictly appropriate to the type of substrate being investigated,  $k_{\text{obsd}}$  is the experimental pseudo-first-order rate coefficient, and  $a_{\text{H}_2\text{O}}$  is the water activity.

(50) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961).

(51) Slight modifications are required in the left-hand part of eq 25, which holds for reactions of weakly basic compounds, when we are dealing with moderate ( $\log k_{\text{obsd}} + \log ([\text{BH}^+]/[\text{B}])$ ) or strongly ( $\log k_{\text{obsd}}$ ) basic substrates.

(52) D. Landini, F. Montanari, G. Modena, and G. Scorrano, *Chem. Commun.*, **3** (1969).

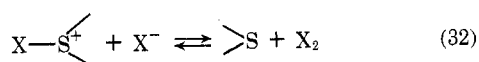
(53) A. Fava, A. Iliceto, and E. Camera, *J. Amer. Chem. Soc.*, **79**, 833 (1957); A. Fava and A. Iliceto, *ibid.*, **80**, 3478 (1958).

Table III  
Correlations between Rate Coefficients and Acidity for  
Reactions of Sulfoxides (R-SO-R') with Halide Ions

R	R'	Hal <sup>-</sup>	Acid	$\phi^a$
Me	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Cl <sup>-</sup>	HClO <sub>4</sub>	+0.06
		Br <sup>-</sup>	HClO <sub>4</sub>	-0.12
		I <sup>-</sup>	HClO <sub>4</sub>	-0.01
		I <sup>-</sup>	H <sub>2</sub> SO <sub>4</sub>	-0.21
Me	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	I <sup>-</sup>	HClO <sub>4</sub>	-0.06
Me	Me	I <sup>-</sup>	HClO <sub>4</sub>	+0.02
<i>i</i> -Pr	Ph	Cl <sup>-</sup>	HClO <sub>4</sub>	+0.30
		Cl <sup>-</sup>	H <sub>2</sub> SO <sub>4</sub>	+0.25

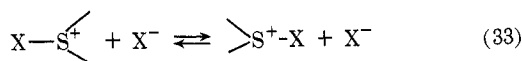
<sup>a</sup>  $\phi$  values are slopes of the plots  $\log [(k_1/[\text{Hal}^-]) + H_0]$  vs.  $(H_0 + \log c_{\text{H}^+})$ .

fide, with equilibrium 32 completely shifted to the

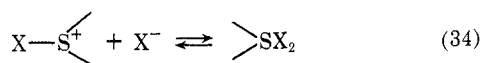


right in the reaction with iodide ion or to the left with bromide and chloride ion. Direct evidence of this equilibrium (from right to left) has been obtained by studying the oxidation of sulfides with bromine.<sup>54</sup>

However, other pathways, such as fast halogen exchange<sup>40</sup> (eq 33) or formation of a dihalo sulfide (eq



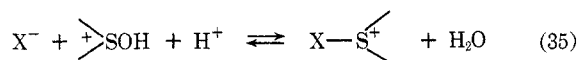
34) followed by a fast hydrolysis could lead to racem-



ized sulfoxides as well. Since reactions 32-34 occur after the rate-determining formation of the halosulfonium ion, the nature of the product-forming steps is open to speculation.

Although a choice between path A and B is quite difficult, some considerations favor path A. A change in the acid dependence of  $\log k_1$  had been found between the chloride ion catalyzed racemization of (+)-isopropyl phenyl sulfoxide ( $\phi = +0.30$ ) and (+)-methyl *p*-tolyl sulfoxide ( $\phi = +0.06$ ).<sup>32</sup> Path B would not predict any change in the acid dependence, since both protons are involved prior to the attack of the halide ion and hence only a decrease in reaction rate should be observed with the isopropyl derivative. Path A, on the other hand, is consistent with a change in the acid dependence since the steric crowding around the sulfur should retard reaction 27 and accelerate reaction 29.

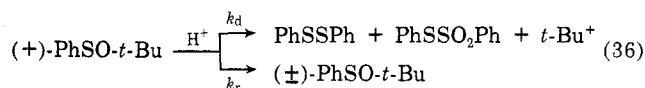
Thus, if the rates of steps 27-29 are comparable, the reactions perhaps are better represented in terms of a general-acid-catalyzed process (eq 35). This is



in agreement with the trend in  $\phi$  values which become more positive with increased crowding around sulfur.

(54) U. Miotti, G. Modena, and L. Sedea, *J. Chem. Soc. B*, 802 (1970).

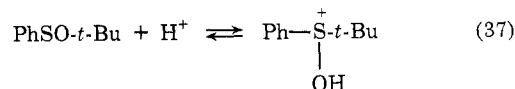
Unfortunately, the *tert*-butyl derivative cannot be studied under these conditions. It undergoes,<sup>33</sup> as mentioned above, acid-catalyzed fragmentation and racemization which are not influenced by the presence of halide ions (eq 36).



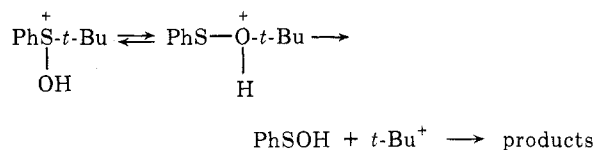
The two reactions follow the same kinetic path with reaction rates depending only on the concentration of sulfoxide and acid. Moreover, the plots of  $\log k_1$  vs.  $(H_0 + \log c_{\text{H}^+})$  gave  $\phi$  values in the range -0.20 ( $k_r$ ) to -0.25 ( $k_d$ ). These values are expected for reactions in which the water does not participate in the transition state and suggest that only one proton intervenes in the reaction.

The diprotonation of sulfoxides appears, therefore, very improbable, and it may occur, in line with path A, only after the first positive charge is neutralized by a suitable nucleophile. Furthermore stable tetravalent sulfur species are well known nowadays.<sup>55</sup>

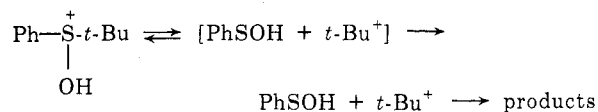
The racemization occurring without intervention of nucleophiles offers some interesting mechanistic problems. The mechanism should also account for the concurrent reaction, leading to products of carbon-sulfur bond breaking, which follows the same pathway up to the rate-determining step. Two possible ways, both involving preliminary protonation of the substrate, can be conceived.<sup>33</sup>



C



D



In path C the protonated sulfoxide isomerizes to protonated sulfenic ester which then unimolecularly hydrolyzes to products, whereas in path D the sulfoxide gives an ion-molecule pair between sulfenic acid and *tert*-butyl cation, whose diffusion in the solvent would give the fragmentation products.

Two experiments seem to favor path D: (i)  $\alpha$ -phenylethyl phenyl sulfoxide optically active both at sulfur and carbon gives racemization at both centers, with sulfur losing its chirality *ca.* 3.5 times faster than carbon;<sup>33</sup> (ii) the  $\beta$  deuterium isotope effect in *tert*-butyl-*d*<sub>9</sub> phenyl sulfoxide is  $k_{\text{H}}/k_{\text{D}} \approx 2$ ,<sup>56</sup> which

(55) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969); C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5398 (1969); I. Kapovits and A. Kalman, *Chem. Commun.*, 649 (1971); I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **94**, 5010 (1972), and previous papers.

(56) P. Bonvicini, A. Levi, and G. Scorrano, unpublished results.

is in agreement with the formation of a carbonium ion rather than with a concerted 1,2 shift.<sup>57</sup>

### Conclusions

The above discussion emphasizes that the application of the appropriate acidity function, and hence a knowledge of the acid-base behavior of substrates, is *conditio sine qua non* to deduce mechanistic implications even from otherwise accurate kinetic analysis of acid-catalyzed reactions. As shown by the case of substituent effects on the reduction by iodide ions of sulfoxides, the observed rate changes as a function of structural factors often result from a combination of effects on basicity and on reaction rates.

On the other hand, it is clear that there is no meaning in an "absolute" measure of the strength of a base or an acid,<sup>15</sup> since solvation phenomena have a very large effect in determining the ionization ratios of each class of base (or each base) in every solvent. As an example we recently observed<sup>58,59</sup> that solvation requirements of dialkyl ethers ( $\phi$  ca. +0.8)<sup>59</sup> and sulfides ( $\phi$  ca. -0.2)<sup>58</sup> are very different. They make the log *I* values of sulfides larger than those of ethers in the stronger acid solutions (H<sub>2</sub>SO<sub>4</sub>

(57) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold Co., New York, N. Y., 1970.

(58) P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972).

(59) P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, manuscript in preparation.

> 65%). These results match well with the recent findings that, whereas dialkyl ethers are more basic than sulfides in dilute acids by ca. 4 pK<sub>BH+</sub> units,<sup>59</sup> the reverse is true in the gas phase where the proton affinity of H<sub>2</sub>S is ca. 14 kcal/mol higher than that of H<sub>2</sub>O.<sup>60</sup>

It is precisely the comparison between the liquid and gas phase, made possible by recent improvements in experimental techniques,<sup>61</sup> which could well lead to the most important progress in the field of acid-base equilibria, hopefully making possible a dissection of the thermodynamic quantities ( $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$ ) into ionization and solvation terms.<sup>62</sup> This will lead to a greater understanding of solvent effects in organic chemistry, which is the ultimate purpose of most acid-base equilibrium investigations.<sup>15</sup>

*Most of the work here described has been made possible through a close collaboration with Professors D. Landini, G. Modena, and F. Montanari, to whom I am greatly indebted. The collaboration of other people of this research group, whose names are cited in the references, and the financial support of the Consiglio Nazionale delle Ricerche are also gratefully acknowledged.*

(60) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(61) J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); P. Kebarle in "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Vol. 1, Wiley-Interscience, New York, N. Y., 1972.

(62) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

## Long-Lived States in Atom-Molecule Collisions

David A. Micha

*Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32601*

*Received August 28, 1972*

Encounters involving an isolated pair of atoms or molecules may be characterized by collision times,  $\tau_c$ . The collision time is the delay suffered by these particles with respect to their free-passage time through the collision region, as a result of their interaction.

A collision time depends on the relative velocity,  $v$ , of the pair, on the impact parameter,  $b$ , and on the intermolecular forces at play. For most values of  $v$  and  $b$ , reactants transform into products by a di-

rect process and  $\tau_c$  is a smooth function of these variables, approximately equal to the period of rotation of the pair of  $\tau_{dir} \approx 2\pi b/v$ .

However, in the neighborhood of certain velocities  $v_r$  and impact parameters  $b_r$  a resonance process may take place, at which  $\tau_c$  shows a sharp peak and increases over its previous value by a quantity  $\tau_{res} \gg \tau_{dir}$  at the maximum. This second process corresponds physically to formation of a temporarily bound complex whose nature depends on whether the collision partners contain open or closed shells, and on quantities such as ionization potentials and electron affinities. The pair may temporarily form a chemical bond, a charge-transfer complex, or a van der Waals complex, in the last case as a result of the attraction of fluctuating charge distributions. Examples of these different types are provided by K + RbCl, K + SO<sub>2</sub> and Ar + H<sub>2</sub>.

David A. Micha was born in Argentina, where he did his undergraduate studies at the University of Cuyo, Bariloche. He received the Filosofie Licenciati (1965) and Filosofie Doctor (1966) degrees at Uppsala University. He then worked at the Theoretical Chemistry Institute of the University of Wisconsin (Madison) and at the Institute for Pure and Applied Physical Sciences of the University of California, La Jolla. He became a Docent of Uppsala University in 1968, was Visiting Lamberg Professor at the University of Gothenburg in 1970, and is now Associate Professor at the University of Florida. He is interested in molecular electronic structure and dynamics and related computational methods.