

## Experimental Section

FIK measurements were made with a modified double focusing Du Pont (CEC) 21-110B mass spectrometer.<sup>16</sup> Uncoated Schick stainless steel razor blades were used as emitters in the standard Du Pont FI/EI ion source. Curves of ion current vs. blade potential were measured on an XY recorder. The blade potential was scanned from 8 to 10 kV in steps of 10 V so that the curves are quasi-continuous.

The synthesis of the deuterated compound has been described.<sup>10</sup>

Total fragment ion currents formed between  $1 \times 10^{-11}$  and  $5 \times 10^{-6}$  sec following FI were estimated as follows. The logarithm of the rate constant  $k(t)$  calculated from eq 1 for the particular reaction of interest was plotted against  $\log t$ . The resulting graph had a series of points in the range  $10^{-11}$ – $10^{-9}$  sec and two additional points at  $1 \times 10^{-6}$  and  $2 \times 10^{-6}$  sec (from the metastables). A

curve was drawn through all these points interpolating between  $10^{-9}$  and  $2 \times 10^{-6}$  sec. With both  $m/e$  86 ( $C_3H_{10}O$ ) and  $m/e$  87 ( $C_3H_9DO$ ) from 7-methyl-4-octanone-7- $d_1$  these curves of  $\log k(t)$  vs.  $\log t$  could be approximated by straight lines. The area under the curves could then be estimated by analytical integration. The area under such a curve represents the total current due to a particular fragment ion (expressed as a fraction of the molecular ion current) formed between the time limits of integration.

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## Mechanistic Studies in Strong Acids. I. General Considerations. Catalysis by Individual Acid Species in Sulfuric Acid<sup>1</sup>

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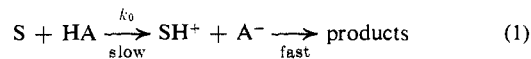
**Abstract:** The conditions under which general acid catalysis should be observable in concentrated sulfuric acid are considered. An examination of the log activities or concentrations of the individual species present in this medium, plotted against  $-H_0$ , leads to the conclusion that  $HSO_4^-$  rather than  $H_2O$  should act as a nucleophile or base in some reactions, especially above 80%  $H_2SO_4$ . As an example of general acid catalysis, the rearrangement of azoxybenzene to *p*-hydroxyazobenzene is shown to be catalyzed by the acid species  $H_2SO_4$  and  $H_3SO_4^+$ , but *not*  $H_3O^+$ , by log rate vs. log species activity correlations.

Acidity function correlations have been used for many years as mechanistic criteria for acid-catalyzed reactions,<sup>3</sup> and correlations of log reaction rates with log water activity in strong acids also provide valuable mechanistic insights.<sup>4,5</sup> However, little attempt seems to have been made to use correlations with the log activities of the many other species present in sulfuric or other acids to give mechanistic information. The most notable exception is the work of Cerfontain, *et al.*, which enabled these workers to elucidate the mechanisms of many sulfonation processes.<sup>6</sup>

In particular, data of this type have not been used in distinguishing between specific and general acid catalysis in strong acid solutions. Although several workers have proposed,<sup>7,8</sup> and possibly demonstrated,<sup>9</sup> general acid catalysis in strong acids, the possibility of this type

of mechanism is not often considered. The notable exception here is the valuable work of Kresge, *et al.*, concerning rate-determining proton transfer in aromatic systems.<sup>9</sup>

General acid catalysis means that a proton transfer is involved in the rate-determining step of the reaction. An example is the so-called A-SE2 mechanism,<sup>3</sup> e.g., eq 1 (S = substrate, HA = general acid). The rate of this



process can be expressed in the usual way<sup>3</sup> as follows, where  $k_\psi$  is the observed pseudo-first-order rate constant, and the other symbols have their usual meaning.<sup>3</sup> Equation 2 suggests that a plot of  $\log k_\psi$  vs.  $\log a_{HA}$

$$\text{rate} = -\frac{dC_S}{dt} = k_\psi C_S = k_0 C_S a_{HA} (f_S/f_\pm) \quad (2)$$

$$\log k_\psi = \log a_{HA} + \log k_0 + \log (f_S/f_\pm)$$

should be a straight line of slope one for this process, assuming constancy for the activity coefficient term, as is often done.<sup>3,5</sup> The difficulty in using this equation in strong acids is that the acid is usually fully dissociated, when, assuming that  $h_0$  is an applicable acidity function, eq 3 applies.<sup>3</sup> Substituting eq 3 into eq 2 gives eq 4,

$$a_{HA} = a_{H^+} = h_0(f_{BH^+}/f_B) \quad (3)$$

$$\log k_\psi = -H_0 + \log k_0 + \log (f_S f_{BH^+}/f_\pm f_B) \quad (4)$$

(1) Presented in part at the 56th CIC Chemical Conference, Montreal, June 1973; E. Bunzel, R. A. Cox, and A. J. Dolenko, paper No. 177.

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(3) For instance, see (a) C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970; (b) M. Liler, "Reaction Mechanisms in Sulfuric Acid," Academic Press, New York, N. Y., 1971.

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

(5) K. Yates, *Accounts Chem. Res.*, **4**, 136 (1971).

(6) H. Cerfontain and C. W. F. Kort, *Int. J. Sulfur Chem., Part C*, **6**, 123 (1971), and earlier papers.

(7) W. M. Schubert and P. C. Myhre, *J. Amer. Chem. Soc.*, **80**, 1755 (1958).

(8) E. Bunzel and W. M. J. Strachan, *Can. J. Chem.*, **48**, 377 (1970).

(9) A. J. Kresge, S. G. Mylonakis, and L. E. Hakka, *J. Amer. Chem. Soc.*, **94**, 4197 (1972), and earlier papers by Kresge, *et al.*

which is indistinguishable from the usual Hammett equation for an A1 process, *i.e.*, a prior equilibrium proton transfer, followed by rate-determining reaction of  $\text{SH}^+$ .<sup>3</sup>

It follows that in order to use eq 2, acid solutions which do *not* consist entirely of "solvated protons" must be used. This is the usual case in dilute solutions of carboxylic acids, in which catalysis by undissociated  $\text{RCO}_2\text{H}$  and by " $\text{H}^+$ " can be easily distinguished by using various buffer solutions.<sup>10</sup> It should also be the case in the acidity region near 100% pure acid, which consists mainly of undissociated acid molecules. The system  $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{H}_2\text{S}_2\text{O}_7$ , which has been widely studied, forms the subject of this first report.

### Experimental Section

Concentrations of the species  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  in aqueous  $\text{H}_2\text{SO}_4$  have been measured by Raman spectroscopy by Young, *et al.*,<sup>11</sup> and others.<sup>12</sup> Young's data were used in their work by Robertson and Dunford,<sup>13</sup> and for the sake of consistency the concentrations of  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  listed by the latter authors were used, with their values for  $\text{H}^+(\text{H}_2\text{O})_n$  concentrations, until better data become available. These data were converted from molarities to mole fraction concentration units, using densities from "International Critical Tables."<sup>14</sup> The concentration of autoprotolysis ions ( $\text{HSO}_4^-$  and  $\text{H}_3\text{SO}_4^+$ ) in 100%  $\text{H}_2\text{SO}_4$  is accurately available from conductivity measurements.<sup>15</sup>

Water activities are given by Giauque, *et al.*,<sup>16</sup> together with much accurate thermodynamic data for the  $\text{H}_2\text{SO}_4$  system. From these data Kort and Cerfontain calculated the activities of undissociated  $\text{H}_2\text{SO}_4$  at various temperatures,<sup>17</sup> and the activities of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}_2\text{O}_7$  in oleum at 25°. These values were used in this work. These authors also calculated (probably less reliable) values for the activity of  $\text{H}_3\text{O}^+$ .<sup>17</sup>

Values for  $\text{H}_3\text{SO}_4^+$  were calculated using the autoprotolysis (ap) equation (eq 5), anchoring the values on the known concentration of

$$K_{\text{ap}} = a_{\text{H}_3\text{SO}_4^+} a_{\text{HSO}_4^-} / (a_{\text{H}_2\text{SO}_4})^2 \quad (5)$$

$\text{H}_3\text{SO}_4^+$  in 100%  $\text{H}_2\text{SO}_4$ <sup>15</sup> (*i.e.*, using  $\log K_{\text{ap}} = -5.646$ ). Since the literature values<sup>17</sup> of  $a_{\text{HSO}_4^-}$  involve nonthermodynamic calculations, and stop at 98%  $\text{H}_2\text{SO}_4$  in any case, the mole fraction  $X_{\text{HSO}_4^-}$  was used in eq 5. Thus the data listed in Table I for  $\text{H}_3\text{SO}_4^+$  are concentrations rather than activities. In Figure 1,  $\text{H}^+(\text{H}_2\text{O})_n$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}_3\text{SO}_4^+$  are *concentrations* (mole fraction units), and  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_2\text{S}_2\text{O}_7$  are *activities*. Some of the data used between 95 and 100%  $\text{H}_2\text{SO}_4$ , not available in the literature, are given in Table I.

The  $H_0$  scales used throughout this work are those of Katritzky, *et al.*,<sup>19</sup> at various temperatures, up to 98%  $\text{H}_2\text{SO}_4$ , and of Gillespie, *et al.*,<sup>20</sup> beyond this value. The two scales are contiguous. Although the latter is not strictly an  $H_0$  scale, involving aromatic nitro compound rather than primary aromatic amine indicators, it was anchored on a known amine indicator and shows good in-

(10) For instance, see J. Warkentin and R. A. Cox, *J. Org. Chem.*, **33**, 1301 (1968), and references cited therein.

(11) T. F. Young, L. F. Maranville, and H. M. Smith in "The Structure of Electrolyte Solutions," W. J. Hamer, Ed., Wiley, New York, N. Y., 1959, pp 35-63; T. F. Young and G. E. Walrafen, *Trans. Faraday Soc.*, **57**, 34 (1961).

(12) N. G. Zarakhani and M. I. Vinnik, *Russ. J. Phys. Chem.*, **37**, 260 (1963).

(13) E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, **86**, 5080 (1964).

(14) "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1930, p 56.

(15) Reference 3b, pp 76-79.

(16) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, **82**, 62 (1960).

(17) C. W. F. Kort and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **87**, 24 (1968).

(18) C. W. F. Kort and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **88**, 1298 (1969).

(19) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

(20) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, **93**, 5083 (1971).

**Table I.** Species Concentration Data for 95-100%  $\text{H}_2\text{SO}_4$  w/w at 25°<sup>a</sup>

% $\text{H}_2\text{SO}_4$	$-\log X_{\text{HSO}_4^-}$	$-\log X_{\text{H}_3\text{SO}_4^+}$	$-H_0$
95.00	0.655	5.469	9.81
95.50	0.693	5.373	9.89
96.00	0.736	5.272	9.98
96.50	0.785	5.171	10.08
97.00	0.843	5.061	10.18
97.50	0.913	4.945	10.30
98.00	1.001	4.805	10.44
98.20	1.042	4.748	10.50
98.40	1.089	4.683	10.56
98.60	1.142	4.614	10.63
98.80	1.204	4.536	10.71
99.00	1.277	4.449	10.82
99.20	1.367	4.343	10.93
99.40	1.483	4.211	11.05
99.60	1.646	4.032	11.19
99.80	1.916	3.746	11.40
99.90	2.164	3.490	11.64
99.92	2.238	3.416	11.68
99.94	2.326	3.326	11.74
99.96	2.438	3.212	11.80
99.97	2.507	3.143	11.84
99.98	2.589	3.059	11.87
99.99	2.690	2.958	11.90
100.00	2.823	2.823	11.93

<sup>a</sup>  $X$  = mole fraction. For references and details of calculation, see Experimental Section.

dicator overlap. It is probably the best acidity scale available in oleum.

Data for the azoxybenzene rearrangement, taken from the literature,<sup>8,21</sup> were plotted according to the  $H_0$  scales discussed above, at the appropriate temperature.

### Results and Discussion

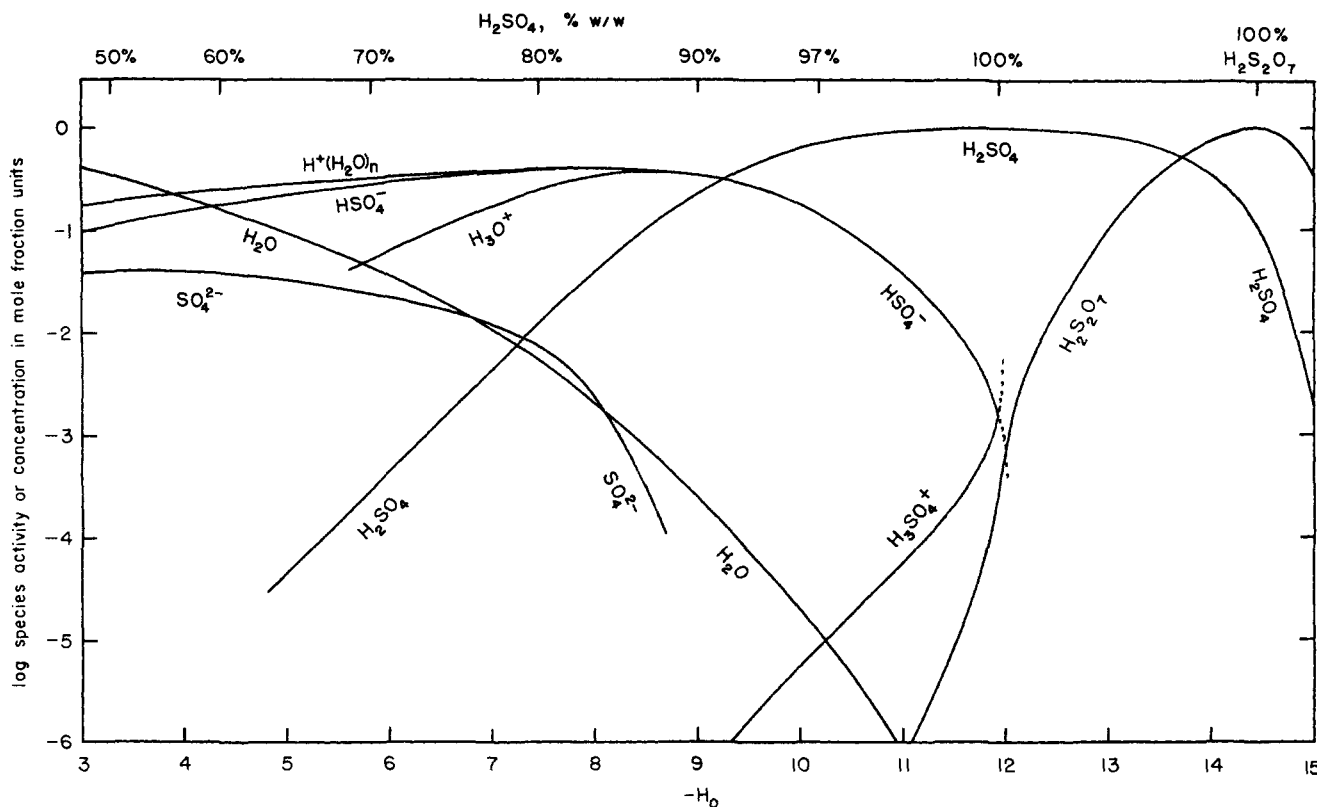
The concentrations, or activities where available, of the different species present in sulfuric acid, are plotted as a function of  $-H_0$  in Figure 1. The acidity function is used to facilitate comparisons between these curves and log rate *vs.*  $-H_0$  plots. The concentration units used are log mole fractions, which have the advantage of being directly comparable with the units generally used for water and sulfuric acid activities. The  $\text{H}_2\text{SO}_4$  concentration range extends from 50% to pure  $\text{H}_2\text{S}_2\text{O}_7$  (see the top scale of Figure 1). Various species present in oleum are not included, either because data are not available, *e.g.*, for  $\text{H}_3\text{SO}_4^+$  and  $\text{HS}_2\text{O}_7^-$ , or because the species themselves are not clearly defined (various poly(sulfuric acids)).

In 50-70%  $\text{H}_2\text{SO}_4$  the major species are  $\text{H}_2\text{O}$ ,  $\text{H}^+(\text{H}_2\text{O})_n$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$ . As the acidity increases,  $\text{H}_2\text{O}$  and  $\text{SO}_4^{2-}$  decrease,  $\text{H}^+(\text{H}_2\text{O})_n$  becomes  $\text{H}_3\text{O}^+$ , and undissociated  $\text{H}_2\text{SO}_4$  molecules become important. At 100%  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{SO}_4^+$  has become appreciable, and  $\text{H}_2\text{S}_2\text{O}_7$  has appeared.

**Nucleophiles and Bases.** The first noteworthy point is that  $\text{HSO}_4^-$  is present in much greater amount than  $\text{H}_2\text{O}$ , above about 60%  $\text{H}_2\text{SO}_4$ . Even  $\text{SO}_4^{2-}$  appears to be more concentrated than water around 80%  $\text{H}_2\text{SO}_4$ .<sup>22</sup> Thus, for reactions involving nucleophilic attack,  $\text{HSO}_4^-$  presents itself as a possible nucleophile. This possibility depends on the difference in nucleophilicity between  $\text{H}_2\text{O}$  and  $\text{HSO}_4^-$ ; one early report states that

(21) E. Buncl and B. T. Lawton, *Can. J. Chem.*, **43**, 862 (1965).

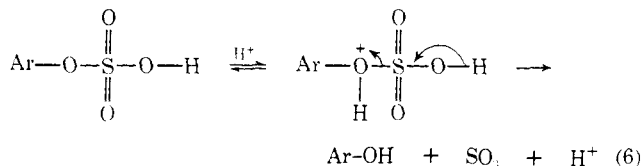
(22) The data for  $\text{SO}_4^{2-}$  are not very reliable.



**Figure 1.** The species present in sulfuric acid. Concentrations of  $\text{H}^+(\text{H}_2\text{O})_n$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}_3\text{SO}_4^+$ , and activities of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{O}^+$ , and  $\text{H}_2\text{S}_2\text{O}_7$ , in log mole fraction units, plotted against  $-H_0$ , for the system  $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{H}_2\text{S}_2\text{O}_7$  at  $25^\circ$ .

$\text{H}_2\text{O}$  is the better nucleophile by a factor of 100.<sup>23</sup> If this is so, it means that  $\text{HSO}_4^-$  will be the predominant nucleophile from that point in Figure 1 at which the distance between the  $\text{HSO}_4^-$  and  $\text{H}_2\text{O}$  curves becomes greater than 2 log units. This occurs at about 80%  $\text{H}_2\text{SO}_4$ . It is interesting that many reactions, for instance ester hydrolyses,<sup>5</sup> undergo mechanistic changes at about this acidity.

It may not be possible to tell from product analysis studies whether the original nucleophile was  $\text{H}_2\text{O}$  or  $\text{HSO}_4^-$ . For instance, it has been demonstrated that the process shown in eq 6 is faster than nucleophilic



attack on the aryl group, in at least one case.<sup>24</sup>

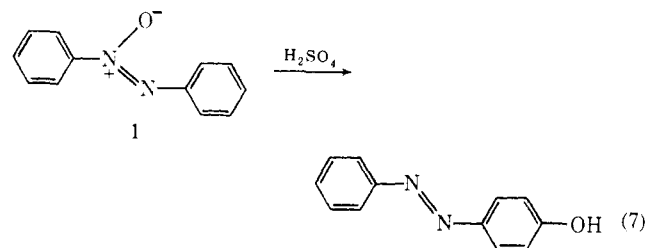
Regarding the roles of  $\text{HSO}_4^-$  and  $\text{H}_2\text{O}$  as bases, one can only say that since  $\text{H}_2\text{SO}_4$  is a stronger acid than  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}$  should be the better base. At what acidity  $\text{HSO}_4^-$  will take over as a base because of its higher concentration is not clear. The subject of  $\text{H}_2\text{O}$  vs.  $\text{HSO}_4^-$  as base or nucleophile will be explored in more detail in future publications. At this point it is worth stating that the practice of plotting log reaction rates against log water activity, used for distinguishing between A1 and A2 processes<sup>3,5</sup> and for determining the role of water in the reaction,<sup>4</sup> should be used with some care above 80%  $\text{H}_2\text{SO}_4$ .

(23) C. G. Swain and A. S. Rosenberg, *J. Amer. Chem. Soc.*, **83**, 2154 (1961).

(24) E. Buncl and W. M. J. Strachan, *Can. J. Chem.*, **47**, 911 (1969).

**General Acid Catalysis.** Insofar as proton transfers are generally "fast," the study of general acid catalyzed reactions requires that certain conditions be met if the reactions are to proceed at a conveniently measurable rate. One possibility is that the proton transfer could be concerted with some other process. Another is that, if a proton transfer to one of the *less* basic of several available sites is required for reaction, the probability of observing general acid catalysis should be increased. Also the second protonation of a monoprotonated substrate is a likely possibility.

The Wallach rearrangement<sup>25</sup> of azoxybenzene to *p*-hydroxyazobenzene (eq 7) has been the subject of sev-



eral mechanistic studies. At least three different mechanisms have been proposed.<sup>8,26</sup> It is known from isotopic substitution studies that: (a) the product OH group is solvent derived; (b) the OH group is equally likely to appear at either para position; and (c) unreacted **1** does not undergo oxygen exchange or migra-

(25) For reviews, see E. Buncl in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 61-119; H. J. Shine, "Aromatic Rearrangements," Elsevier, New York, N. Y., 1967, pp 272-284.

(26) C. S. Hahn, K. W. Lee, and H. H. Jaffé, *J. Amer. Chem. Soc.*, **89**, 4975 (1967); D. Duffey and E. C. Hendley, *J. Org. Chem.*, **33**, 1918 (1968).

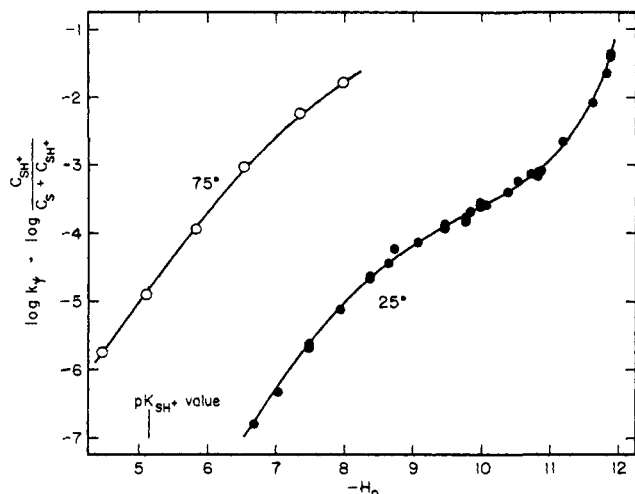
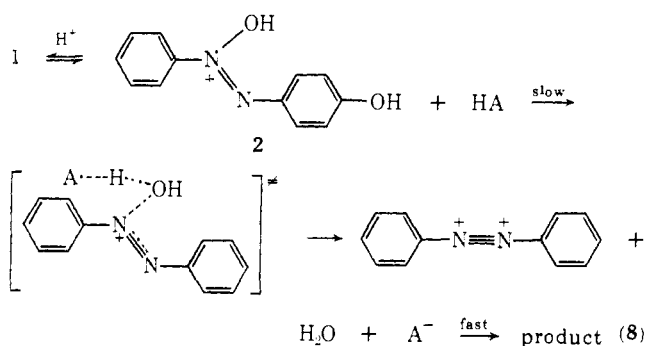


Figure 2. Graphs of  $\log k_\psi - \log (C_{SH^+}/C_S + C_{SH^+})$  vs.  $-H_0$ , for the rearrangement of azoxybenzene in  $H_2SO_4$  at 25 and 75°. Rate data from ref 8 and 21,  $H_0$  scales from ref 19 and 20.

tion to the other nitrogen under the reaction conditions.<sup>25,27</sup> One mechanism meeting these requirements proposed by Buncl and Strachan<sup>8</sup> involves general acid catalysis (eq 8). If this mechanism is



correct, it fulfills at least two of the conditions discussed above, since water loss is concerted with proton transfer, and a second protonation of monoprotonated substrate is occurring.

A plot of log reaction rate,<sup>8,21</sup> corrected via the term  $\log (C_{SH^+}/C_S + C_{SH^+})$  for the small amount of substrate not fully protonated at the lower acidities, against  $-H_0$  for the azoxybenzene rearrangement is shown in Figure 2. It is immediately apparent that more than one proton is involved, since the rate continues to increase with acidity after the  $pK_{SH^+}$  value of  $-5.15$  for monoprotonation of the substrate on oxygen<sup>21</sup> has been passed, and that the second protonation is not another prior equilibrium process. If it were, the plot would probably be a straight line; it would almost certainly not exhibit the double curvature of Figure 2. The slope would probably not be unity, as the acidity function would not necessarily be  $H_0$ , but the plot would likely be linear, since several acidity functions have been shown to be linear functions of one another.<sup>28</sup>

A comparison of Figure 2 (25° data) with Figure 1

(27) M. M. Shemyakin and V. I. Maimind in "Recent Progress in the Chemistry of Natural and Synthetic Coloring Matters and Related Fields," T. S. Gore, Ed., Academic Press, New York, N. Y., 1962, pp 441-449, and earlier papers.

(28) K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, **95**, 418 (1973); K. Yates and R. A. McClelland, *ibid.*, **89**, 2686 (1967).

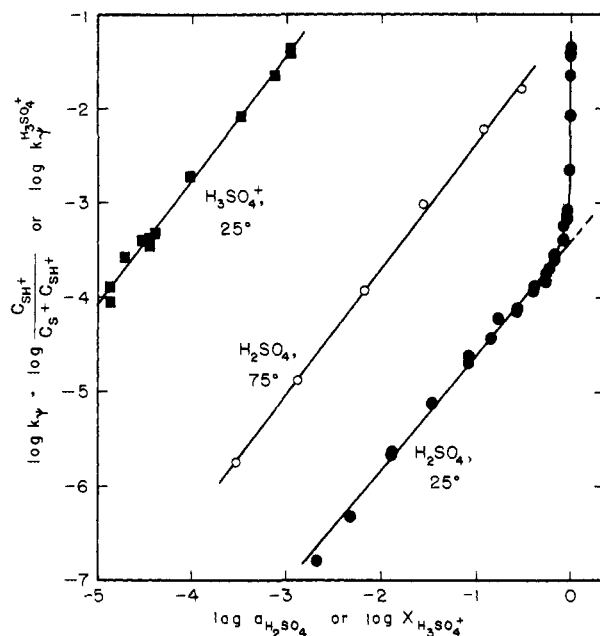


Figure 3. Graphs of  $\log k_\psi - \log (C_{SH^+}/C_S + C_{SH^+})$  at 25° (●) and 75° (○) vs.  $\log a_{H_2SO_4}$ , and of  $\log k_\psi^{H_3SO_4^+}$  at 25° (■) vs.  $\log X_{H_3SO_4^+}$ , for the rearrangement of azoxybenzene in  $H_2SO_4$ .

reveals that the slope of the log rate vs.  $-H_0$  curve strongly resembles a superimposition of the  $H_2SO_4$  and  $H_3SO_4^+$  curves of Figure 1. A plot of the log rates vs.  $\log a_{H_2SO_4}$  and  $\log X_{H_3SO_4^+}$  is shown in Figure 3. The 75° data are a good linear function of  $\log a_{H_2SO_4}$  (at the same temperature); slope  $1.335 \pm 0.017$ , correlation coefficient 0.999. The 25° data below 96.5%  $H_2SO_4$  are also a good linear function of  $\log a_{H_2SO_4}$ , slope  $1.214 \pm 0.017$ , correlation coefficient 0.997. Deviation becomes serious above this acidity, and so the points above this value were corrected for the amount of reaction involving  $H_2SO_4$ , via  $k_\psi = k_\psi^{H_2SO_4} + k_\psi^{H_3SO_4^+}$ . A plot of  $\log k_\psi^{H_3SO_4^+}$  vs.  $\log X_{H_3SO_4^+}$  gives a good straight line, slope  $1.177 \pm 0.036$ , correlation coefficient 0.995. Within experimental error the slopes for the two acid species at 25° are the same as one another. All other correlations tried either gave curves, or lines with slopes very different from the predicted value of unity. At a log activity value of  $-3$ , the ratio  $k_\psi^{H_3SO_4^+}/k_\psi^{H_2SO_4}$  is  $10^{5.6}$ , which means that  $H_3SO_4^+$  is a stronger acid toward 2 than  $H_2SO_4$  by about this value. This seems quite reasonable.

The observed slopes are significantly different from the value of unity predicted by eq 2, although the difference is not large. This is probably a consequence of the effect of the activity coefficient term,  $\log (f_s/f_\pm)$ , which has been ignored up to now. It is an observational fact that the existence of these terms does not affect observed linearities in many correlations of log rate with acidity functions or water activity.<sup>3,5</sup> Although there is no particular reason to suppose that  $\log (f_s/f_\pm)$  should be a linear function of acidity, it is evident that in most cases it does not deviate sufficiently from this behavior to affect observed linearities.<sup>29</sup> This is evidently the case here also.

The slope of the  $\log k_\psi^{H_3SO_4^+}$  vs.  $\log X_{H_3SO_4^+}$  correlation would probably be slightly affected when better

(29) Always a reasonable assumption in log-log plots of this type.

values of  $\log a_{\text{H}_2\text{SO}_4}$ , used in the derivation of  $\log a_{\text{H}_3\text{SO}_4^+}$ , become available. It is doubtful, however, that the linear behavior would be affected by using accurate  $\log a_{\text{H}_3\text{SO}_4^+}$  values rather than the  $\log X_{\text{H}_3\text{SO}_4^+}$  values used here. Using  $\log X_{\text{H}_3\text{SO}_4^+}$  means that an additional activity coefficient term,  $\log (f_{\text{H}_3\text{SO}_4^+}/f_{\text{H}_2\text{SO}_4})$ , is present in eq 2. This term could well cancel to zero, since one species is increasing and the other decreasing (see Figure 1). The observed similarity of slopes for the correlations with  $\log a_{\text{H}_2\text{SO}_4}$  and  $\log X_{\text{H}_3\text{SO}_4^+}$  in Figure 3 is a point in favor of this possibility.

It would appear that the Bunce-Strachan mechanism<sup>8</sup> for the azoxybenzene rearrangement, involving general acid catalysis, is correct. This reaction requires the strongest acids of the system, *i.e.*,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{SO}_4^+$ , in order for the reaction to go. The solvated proton  $\text{H}_3\text{O}^+$  is *not a strong enough acid* to catalyze the reaction. Undissociated  $\text{H}_2\text{SO}_4$  ( $K_a = 2550$ )<sup>30</sup> is a much better proton donor than  $\text{H}_3\text{O}^+$  ( $K_a = 1$ )<sup>31</sup> at these acidities. According to Figure 1,  $\text{H}_3\text{O}^+$  should be the better proton donor, because of greater concentration, only at acidities below about 67%  $\text{H}_2\text{SO}_4$ .

In connection with the above is an interesting observation that the Wallach rearrangement does not go in perchloric acid,<sup>32</sup> even at an  $H_0$  of  $-10.2$  (78%  $\text{HClO}_4$ ).<sup>33</sup> Now it should be borne in mind that perhaps  $\text{HClO}_4$  is not such a strong acid regarding oxygen protonation (Wallach rearrangement) as it is toward nitrogen protonation ( $H_0$  scale measurement). However, one could argue as follows. At this  $H_0$  in perchloric acid the stoichiometric concentration of  $\text{H}_2\text{O}$

(30) P. A. H. Wyatt, *Trans. Faraday Soc.*, **56**, 490 (1960).

(31) Since the reaction is  $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O} + \text{H}_3\text{O}^+$ .

(32) R. Bolduc, E. Bunce, R. A. Cox, and R. B. Kitzul, submitted for publication.

(33) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

is greater than that of  $\text{HClO}_4$ , which is not the case in  $\text{H}_2\text{SO}_4$ . Thus all the acidity is due to solvated protons; the undissociated  $\text{HClO}_4$  concentration is negligible,<sup>34</sup> both for this reason and because as a stronger acid than  $\text{H}_2\text{SO}_4$  it is more dissociated. So the rearrangement does not go, since  $\text{H}_3\text{O}^+$  is not strong enough to catalyze the reaction, and the strong acid species  $\text{HClO}_4$  is not present in high enough concentration.<sup>34</sup> It would undoubtedly be present at  $\text{HClO}_4$  concentrations around 100% acid,<sup>35</sup> but as yet no one has had the temerity to carry out mechanistic studies in the 100%  $\text{HClO}_4$  medium.

### Summary

This study probably represents the least ambiguous demonstration so far presented of general acid catalysis in the 80–100%  $\text{H}_2\text{SO}_4$  acidity region. The utility of correlations between log rate and log species activity is clear. Other examples of general acid catalyzed reactions are undoubtedly amenable to similar treatment (the Beckmann rearrangement in the 100%  $\text{H}_2\text{SO}_4$  region is one possibility<sup>36</sup>) and will hopefully be explored in future publications.

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(34) Extrapolation of Duerst's data<sup>35</sup> shows that the undissociated perchloric acid concentration probably only becomes significant above 82%  $\text{HClO}_4$ . The stable solid hydrate at 84.8% has the formula  $\text{H}_3\text{O}^+\text{ClO}_4^-$ .

(35) R. W. Duerst, *J. Chem. Phys.*, **48**, 2275 (1968).

(36) M. I. Vinnik and N. G. Zarakhani, *Russ. J. Phys. Chem.*, **38**, 491 (1964).

## Solvolysis of 8-Vinyl-*exo*-8-bicyclo[3.2.1]octyl 3,5-Dinitrobenzoate. Evidence for Stabilization by Carbon-Carbon Hyperconjugation in the Transition State for Formation of a Tertiary Allylic Cation

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**Abstract:** The high *exo/endo* reactivity ratio (8000) for acetolysis of the epimeric 8-bicyclo[3.2.1]octyl tosylates may derive from preferential "vertical" stabilization of the transition state for ionization of the *exo* tosylate by carbon-carbon hyperconjugation. Support for this suggestion is found in the observation that a high reactivity ratio is maintained and that high product stereospecificity is manifest in the solvolysis of the epimeric 8-vinyl-8-bicyclo[3.2.1]octyl 3,5-dinitrobenzoates ( $k_{\text{exo}}/k_{\text{endo}} = 515$ ). Since the "leveling capacity" ( $10^6$ ) of the vinyl group exceeds the *exo/endo* rate ratio exhibited by the secondary tosylates by a factor of  $10^4$ , incorporation of a vinyl substituent at the site of ionization should engender complete cessation of neighboring group participation if such participation were nonvertical in nature.

A comparison of the solvolytic behavior of a series of 7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates (**1a**) with that of their norbornenyl analogs (**2a**) has prompted Gassman and Fentiman<sup>1</sup> to suggest that there exists

a definite upper limit to the amount of stabilization an aryl group can provide by means of delocalization of

(1) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549, 2551 (1970); **91**, 1545 (1969).