An Acidity Function for Carbon Bases in Aqueous Sulfuric and Perchloric Acids

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Abstract: The degree of equilibrium protonation of eleven carbon-protonating bases (substituted azulenes, 1,1-diarylethylenes, and aromatic polyethers) has been determined as a function of the concentrations of aqueous sulfuric and perchloric acids. Plots of log ([BH$^+$]/[B]) against $-H_0$ for all bases are nearly parallel in regions of overlap, with slopes near 1.6 for sulfuric acid and 1.7 for perchloric acid. The data were used to determine the acidity constants of the indicator cations and to establish a new Hammett-type acidity function, H_C. In the concentration range from 1 to 14 moles/l., sulfuric acid is 0.2–0.9 unit less acidic on the H_C scale than on the $H_{R'}$ scale. We believe that H_C is more appropriate than $H_{R'}$ to the protonation of carbon bases, and we obtained activity coefficient data to support this view.

The treatment of indicator protonation equilibria, as originally developed by Hammett and Deyrup,[2] included the expectation that in a given acidic solution, the degree of protonation would depend only on the acidity constant of the protonated indicator and its net electric charge. This led to the establishment of the acidity function H_0, to which all electrically neutral bases were expected to conform. Hammett's prediction of behavioral uniformity of uncharged bases, in media of high dielectric constant, at least, remained unchallenged for many years, but it is now abundantly evident that different structural classes of bases, even of a single charge type, do respond differently to changes in solvent acidity, thus generating their own peculiar acidity functions.[3] In recognition of this, a generalized acidity function definition for neutral Brønsted bases may be written (eq 1) with a subscript to emphasize the

$$-H_i \equiv \log a_{\mathrm{H^+}} - \log\left(\frac{f_{\mathrm{BH^+}}}{f_{\mathrm{B}}}\right)_i = -\mathrm{p}K_{\mathrm{BH^+}} + \log\left(\frac{[\mathrm{BH^+}]}{[\mathrm{B}]}\right)_i \quad (1)$$

importance of consistency in indicator structure. Furthermore, the belief that uniformity of charge type within a structural class of indicators is always necessary is erroneous. Long and Schulze found a cationic azulene base whose protonation behavior parallels that of several neutral indicators.[3a]

This behavioral specificity of various types of organic bases does not seriously impair the usefulness of acidity functions in the measurement of acidity constants, but does force attention on the question of how the inherent protonating power of strongly acidic media can most realistically be evaluated. Equation 1 shows that an ideal function would be one built with indicators whose acidic and basic forms experience identical changes in their activity coefficients as the composition of the medium is varied from that of the dilute aqueous reference state. This consideration, coupled with the findings of Boyd,[4] lead one to view H_0 as a rather unrealistic general measure of solvent acidity. Using aqueous sulfuric acid as a medium, Boyd measured the activity coefficients of a number of acidic cations (relative to a reference cation) and neutral bases that have been used as indicators for the H_0 and H_R functions. The conclusion to be drawn is that, for the H_0 function, the activity coefficient ratio in eq 1 increases rapidly with the sulfuric acid concentration because of both moderate salting in of the aniline bases used to establish H_0, and strong salting out of their conjugate acids. The salting out of the anilinium ions has been attributed[5] to their stabilizing formation of hydrogen bonds to water, which becomes decreasingly available with increasing sulfuric acid concentration. The salting in of aniline bases may be due to hydrogen bonding of the basic site, or of certain substituents (notably the nitro group,[4,6,7]) to the solvent acid.[3c]

In this paper data are presented on the equilibrium protonation of certain aromatic carbon bases, with which a new Hammett-type acidity function, H_C, has been constructed, in accordance with a suggestion by Long and Schulze.[3a] The choice of indicators for the new function was guided by the belief that the major cause of departure of the activity coefficient ratio in eq 1 from the "ideal" value of unity is specific interactions of certain substituents with the solvent, as discussed above. We used appropriately substituted azulenes, 1,1-diphenylethylenes, and aromatic polyethers. Several protonation studies of these types of bases have been previously reported,[3a,8-10] but not until now have they all been compared in a single set of experiments directly linked to the dilute aqueous reference state. The new acidity function, we believe, is essentially independent of specific solvation factors, and thus gives a more generally significant measure of solvent protonating power than previously described functions of the Hammett type.

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[2] L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

[3] See for discussion (a) F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964); (b) E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964); (c) E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., 1963.

[4] R. H. Boyd, *J. Am. Chem. Soc.*, **85**, 1555 (1963).

[5] R. W. Taft, Jr., *ibid.*, **82**, 2965 (1960).

[6] N. C. Deno and C. Perizzolo, *ibid.*, **78**, 1345 (1956).

[7] L. P. Hammett and R. Chapman, *ibid.*, **56**, 1282 (1934).

[8] N. C. Deno, P. T. Groves, and G. Saines, *ibid.*, **81**, 5790 (1959).

[9] A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962).

[10] W. M. Schubert and R. H. Quacchia, *ibid.*, **84**, 3776 (1962).

Experimental Section

Materials. Solvents used for the purification of indicators, and the perchloric and sulfuric acids used for preparation of solutions, were reagent grade. The following indicators, listed by name and symbol, were purchased from Aldrich Chemical Co.: azulene (Az), 1-methylazulene (MeAz), 1,1-diphenylethylene (DPE), 1,3,5-trimethoxybenzene (TMeOBz), and 2,6-dimethoxytoluene (DMeOTl). Compounds obtained by custom synthesis were 1-chloroazulene (ClAz) (Reef Laboratories, Lafayette, Ind.) and 1-*p*-anisyl-1-phenylethylene (APE) (Frinton Laboratories, South Vineland, N. J.). Professor A. G. Anderson donated 1-cyanoazulene (CNAz), and 1-cyano-4,6,8-trimethylazulene (CNTMeAz) was supplied by Professor K. Hafner. Professor N. C. Deno kindly provided samples of 1,1-di-*p*-anisylethylene (DAE) and 1,1-di-*p*-chlorophenylethylene (DClPE).

Azulenes were purified by chromatography on neutral alumina, followed by vacuum sublimation. The melting points and ultraviolet spectra agreed within experimental error with published data. Azulenes were used immediately after purification, since some of them (notably ClAz) are rather unstable. TMeOBz, DMeOTl, APE, DClPE, and naphthalene were recrystallized to constant melting point from anhydrous methanol and vacuum sublimed. DPE was purified by molecular distillation *in vacuo*.

Indicator Ratio Measurement. A series of solutions of each indicator in varying concentrations of aqueous mineral acid (sulfuric or perchloric) was prepared by one of two methods.

Method A. A fixed quantity of a stock solution of the unprotonated indicator in water or in standard mineral acid was added from a calibrated volumetric pipet to a volumetric flask containing a weighed quantity of the standard acid. The slightly warm solution was quickly brought to *ca.* 25°, then adjusted to volume by addition of a little water.

Method B. A fixed quantity of a stock solution of the indicator in glacial acetic acid was added from a micropipet to a volumetric flask nearly filled with water and a weighed quantity of the standard acid. Final volume adjustment was made with a little water. The acetic acid content of the final solution was less than 0.5%. Method B was used when method A was precluded by excessive heat of mixing or by too low solubility of the indicator in aqueous media.

Immediately after the preparation of each indicator solution, its absorbance was measured on a Beckman DU or Cary 14 spectrophotometer, usually the latter. The solutions in both spectrophotometer cells were identical, except that the one in the reference cell contained no indicator. Indicator concentrations were frequently limited to *ca.* 1×10^{-6} mole/l. by low solubility, or to retard bimolecular decomposition of the diarylethylenes.[8] Solutions were investigated in 1-cm cells, sometimes with tenfold expansion of the absorbance scale, or in 10-cm cells. With DClPE and DPE, decomposition occurred rapidly enough that absorbances had to be extrapolated to time of mixing. Solutions were thermostated at 25 ± 0.2° by circulation of water through a hollow brass cell holder. Values of $[BH^+]/[B]$ were calculated by the method of Paul and Long.[11] For each indicator the wavelength chosen for the calculation (see Table I) was that of an absorption maximum of either B or BH^+ whose position was independent of the composition of the medium. Values of pK_{BH^+}, listed in Table I, were obtained by the stepwise comparison procedure,[11] and are ultimately referred to MeAz ($pK_{BH^+} = -0.83$[3a]).

Table I. Acidity Constants of H_C Indicators

Base	No.	λ_{max}, mμ	pK_{BH^+} H_2SO_4	pK_{BH^+} $HClO_4$
MeAz[a]	1	365	0.83	0.83
Az[a,b]	2	352	1.70	1.67
ClAz[b]	3	360	3.25	3.33
DAE	4	495	4.45	4.34
TMeCNAz[a]	5	305		5.62
TMeOBz	6	346	6.14	6.17
APE	7	445	6.30	
CNAz[a,b]	8	362	8.41	7.90[c]
DPE	9	430	9.40	
DMeOTl	10	340	10.26	
DClPE	11	466	10.28	

[a] Solutions were prepared by method A. [b] Data for this compound in perchloric acid are those of Long and Schulze.[3a,12] [c] The value quoted in ref 3a as *ca.* 1 logarithmic unit too low, evidently because of an arithmetical error.[12]

Activity Coefficients of Naphthalene. Each of a series of aqueous solutions containing 0–8 *M* standard sulfuric acid was saturated with naphthalene by 72 hr of vigorous mechanical stirring with a large excess of finely divided solid, in a bath at 25 ± 0.1°. After gravity filtration through sintered glass, each solution was kept thermostated until its ultraviolet spectrum could be recorded, with a solvent blank in the reference cell. The activity coefficient in each solution was taken as the ratio of the absorbance (276-mμ maximum) in pure water to that in the solution. Data are presented in Table III.

Results and Discussion

Most of the present work was conducted in aqueous sulfuric acid, though some of the indicators were also studied in perchloric acid. The results are summarized in Tables I and II. The indicator equilibria in sulfuric and in perchloric acids are described graphically in Figures 1 and 2, respectively, in which $\log([BH^+]/[B])$ (hereafter, $\log I$) is plotted against solvent acidity, arbitrarily expressed as $-H_0$. Some of the data used for calculation of H_C values of perchloric acid solutions are those of Long and Schulze.[3a,12] The temperature control was less precise in their experiments than in the present work, and to that extent, the H_C scale is regarded as being more firmly established for sulfuric than for perchloric acid. The indicator pK_{BH^+} values obtained with the two solvent systems are virtually the same for all compounds except CNAz. However, the discrepancy in this case need necessarily affect neither the calculated values of H_C nor those pK_{BH^+} values (for DPE, DMeOTl, and DClPE) found by comparison to CNAz, since the behavior of $\log I$ for CNAz parallels that of adjacent indicators in both sulfuric and perchloric acids.

Table II. H_C Values of Aqueous Sulfuric and Perchloric Acid Solutions

Acid concn, moles/l.	H_C H_2SO_4	H_C $HClO_4$	Acid concn, moles/l.	H_C H_2SO_4	H_C $HClO_4$
0.5	−0.07	0.00	7.5	5.88	6.87
1.0	+0.43	0.48	8.0	6.30	7.41
1.5	0.83	0.98	8.5	6.73	7.97
2.0	1.21	1.43	9.0	7.16	8.60
2.5	1.62	1.84	9.5	7.53	9.26
3.0	1.98	2.25	10.0	7.98	
3.5	2.39	2.65	10.5	8.42	
4.0	2.71	3.06	11.0	8.86	
4.5	3.05	3.54	11.5	9.32	
5.0	3.47	4.08	12.0	9.73	
5.5	4.01	4.60	12.5	10.16	
6.0	4.44	5.19	13.0	10.57	
6.5	5.03	5.76	13.5	11.02	
7.0	5.47	6.31	14.0	11.43	

The ultraviolet and nmr spectral changes accompanying the protonation of azulenes bearing a chlorine, an alkyl, or a cyano substituent in the 1 position have been described,[13] and show that the proton is accepted on the 3-carbon, giving an azulenium ion, I. The 1,1-diarylethylene bases used in this work were shown by Deno, *et al.*, to protonate only on the methylene carbon,[8] and Kresge and coworkers found that TMeOBz protonates on the 2-carbon, and not on oxygen.[9] Evidence that

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[11] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[12] F. A. Long and J. Schulze, private communication.

[13] J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, **86**, 322 (1964).

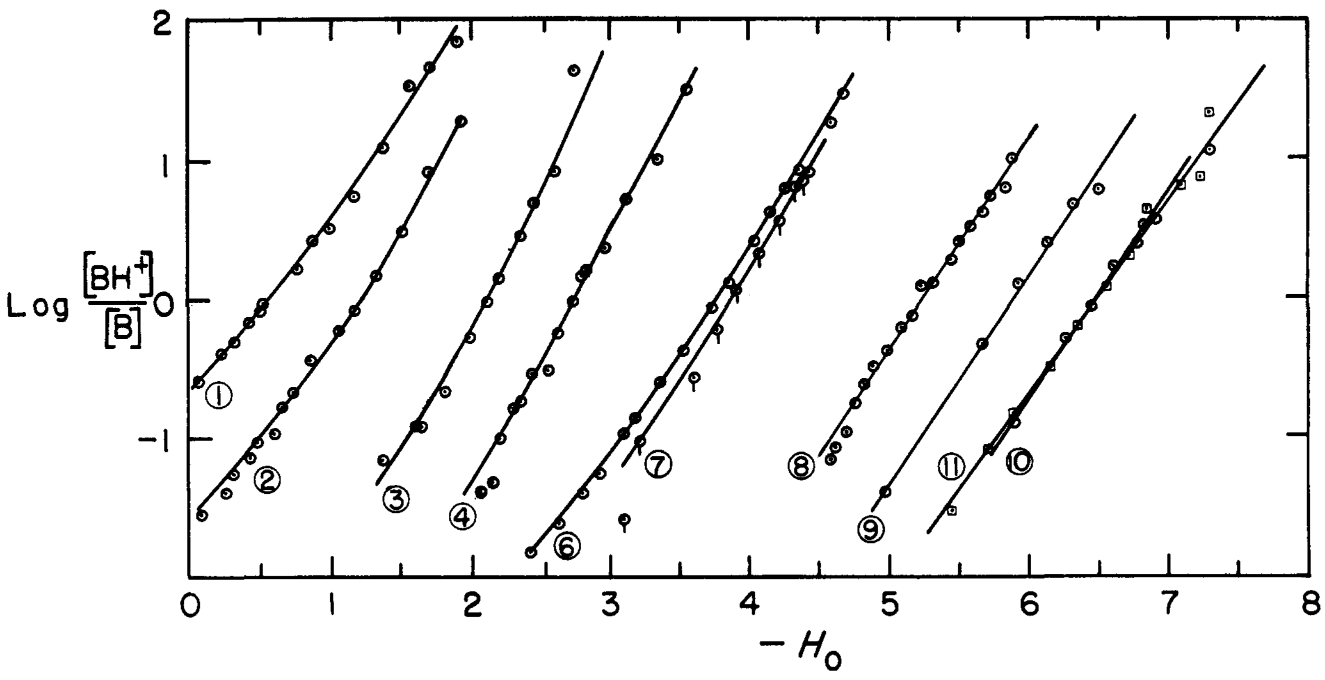


Figure 1. Log *I* *vs.* sulfuric acid concentration: compound no. 7, ⊙; no. 11, ⊡.

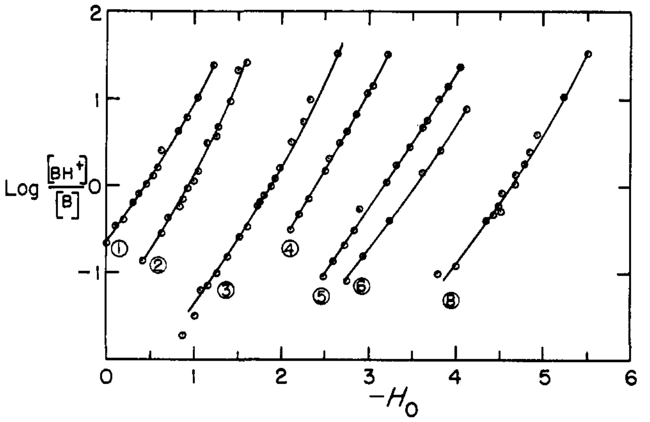
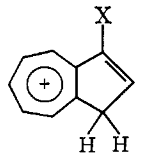


Figure 2. Log *I* *vs.* perchloric acid concentration.

DMeOTl also experiences ring carbon protonation is that it shows a variation in log *I* with solvent acidity which parallels that found for adjacent carbon bases (DPE and DClPE, see Figure 1). Furthermore, solu-



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tions of DMeOTl and TMeOBz in sulfuric acid have very similar ultraviolet spectra. Protonation produces strong maxima ($\epsilon \simeq 10^4$) at 340 and 346 mμ, respectively. Absorption bands in this region do not appear in the spectra of oxygen-protonated alkoxybenzenes.[9] The ultraviolet spectral features of the diphenylethylenes,[8] like those of the polymethoxybenzenes, were ideally suited for this work, since the conjugate acids of both types of bases have stable, intense maxima in the near-ultraviolet or visible region, where the conjugate bases do not absorb.

The unifying structural feature of the bases used to establish H_C is that they protonate on carbon to form a cation with a widely dispersed charge which is probably not specifically solvated. Substituents such as nitro, hydroxyl, and amino groups that would be expected to form hydrogen bonds with the solvent were purposely avoided. In principle, a set of unsaturated hydrocarbons would have served as ideal indicators for the new acidity function, but an acidity scale based solely on hydrocarbons was unattainable because of the dearth of such compounds that are measurably protonated at intermediate solvent acidities.[14] However, the work presented here shows that the presence of cyano, methoxyl, and chloro substituents do not alter the protonation pattern of a carbon base from what would be expected of a hydrocarbon. Figure 1 shows a strongly basic hydrocarbon (Az) and a weakly basic one (DPE), both of which display changes in log *I* with changes in solvent acidity that parallel those of adjacent indicators containing these substituents. Thus the present work corroborates earlier findings of Deno[8] and of Long and Schulze[3a] that certain carbon bases containing heteroatoms belong to the same indicator class as hydrocarbons, and it seems likely that other substituted carbon bases (*e.g.*, aromatic bromo and iodo compounds) will also show hydrocarbon-like protonation behavior.

The distinguishing behavioral characteristic of the H_C indicators is the large slopes of their log *I* *vs.* $-H_0$ plots, compared with those of the amines and ketones used to establish H_0, for which $-\mathrm{d}(\log I)/\mathrm{d}H_0 = 1$. The H_C bases have values of $-\mathrm{d}(\log I)/\mathrm{d}H_0$ near 1.6 and 1.7 in sulfuric acid and in perchloric acid, respectively. Boyd's work[4] shows that, qualitatively, this is the result to be expected from a set of indicators for which the value of f_{BH^+}/f_B is less sensitive to changes in the solvent composition than for the H_0 indicators.

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(14) For a summary of the basicity of hydrocarbons, see ref 3c.

It must be stressed that bases with substituents such as hydroxyl groups that form hydrogen bonds to the solvent cannot be expected to comply with H_C, even if protonation takes place on carbon. An example of such a base is phloroglucinol, whose equilibrium is described approximately by H_0.[9] Although methoxyl groups cannot participate as donors in hydrogen bonding, they are potential hydrogen bond acceptors. It may then be asked why the presence of methoxyl groups in a carbon base does not alter its response to solvent acidity changes from that expected of a hydrocarbon with the same value of pK_{BH^+}. This is probably best answered by pointing out that with amines, the sensitivity of f_{BH^+}/f_B to changes in the medium is apparently due less to the acceptor in hydrogen bonding (B) than to the donor (BH^+).[4] Since ethers are much less basic than amines, it is hardly surprising that the involvement of the methoxyl groups of a carbon base as hydrogen bond acceptors is too weak to effect measurably the dependence of log I on solvent acidity.

Deno, Groves, and Saines proposed the acidity function $H_{R'}$, defined as $H_R - \log a_{H_2O}$, to describe the equilibria of diarylolefins with diarylalkyl cations.[8] This was, in effect, a device for indirectly connecting the pK_{BH^+} values of the olefins to the pure water reference state, and was perhaps motivated by the fact that none of the olefins was basic enough to be studied in dilute aqueous solution. Deno's treatment is valid only to the extent that in a given solution, $f_{R^+}/f_{ROH} = f_{AH^+}/f_A$, where ROH is a triarylcarbinol indicator used to evaluate H_R and A is a diarylolefin. The assumption[8] that $f_{R^+} = f_{AH^+}$ seems a reasonable one, but it would not be expected that $f_{ROH} = f_A$, since the activity coefficient of the carbinol might be influenced by hydrogen bonding.[15] In this light it is not surprising that the new H_C function, established in part with diarylolefin indicators, differs significantly from $H_{R'}$.

The behaviors of H_C, $H_{R'}$, and H_0 in aqueous sulfuric acid are compared in Figure 3. It is clear that $H_{R'}$ and H_C change with solvent composition at approximately the same rate over most of the range of acid concentrations, so the fact[8] that for the protonation of a diarylolefin, $H_{R'} + \log I$ had an approximately constant value in the small solvent composition range over which it was measured is understandable. This constant was equated with pK_{AH^+} on the assumption that the last term in eq 2 equals zero, but our results lead us to conclude

$$H_{R'} + \log\left(\frac{[AH^+]}{[A]}\right) = pK_{AH^+} + \log\left(\frac{f_{R^+}f_A}{f_{ROH}f_{AH^+}}\right) \quad (2)$$

that this assumption was inaccurate. An estimate of the actual magnitude of this term for a given olefin can be obtained by subtraction of its pK_{AH^+} value on the H_C scale from $H_{R'} + \log([AH^+]/[A])$. In sulfuric acid solutions, $\log(f_{R^+}f_A/f_{ROH}f_{AH^+})$, estimated in this way, is approximately 0.65 for DAE, and 0.72 for DClPE.[16]

$$-H_{R'} - (-H_C) = \log\left(\frac{f_{CH^+}}{f_{R^+}}\right) + \log f_{ROH} - \log f_C \quad (3)$$

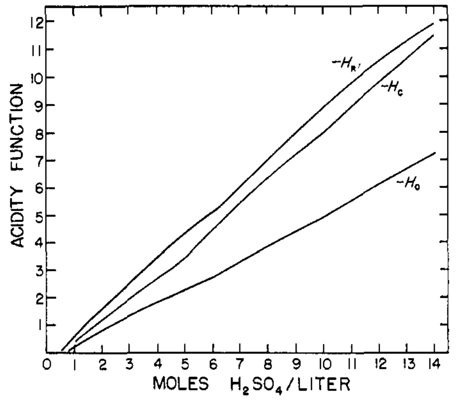

Figure 3. A comparison of the acidity functions H_0, H_C, and $H_R{}'$ in aqueous sulfuric acid.

A means of testing our criticism of the $H_{R'}$ function is provided by eq 3, in which the subscripts C and CH^+ represent the basic and acidic forms of the H_C indicators. If we make the reasonable assumption that $\log(f_{CH^+}/f_{R^+}) \simeq 0$, it should be possible to predict the approximate difference between $H_{R'}$ and H_C by comparison of the logarithms of the activity coefficients of triarylcarbinols with those of H_C indicator bases. Table III shows such a comparison for sulfuric acid solutions, of $-H_{R'} - (-H_C)$, with a model of $\log f_{ROH} - \log f_C$ constructed from activity coefficients of triphenylcarbinol[17] (TPC) as representative of ROH bases, and of naphthalene (Nap) as representative of C bases. Naphthalene was chosen because it is a typical aromatic hydrocarbon and is isomeric with azulene. At no acid concentration are the values in the third and fourth columns of Table III exactly equal, but such equality would hardly be expected, since this would require that all the relevant indicator species fall in one of three groups [(1) R^+ and CH^+, (2) ROH, and (3) C], with individual activity coefficients in each group totally independent of structure. The activity coefficients of the H_0 bases do depend on structure,[4] and the same is probably true of the $H_{R'}$ and H_C indicators. Even so, the data in the table clearly indicate a parallel relationship between $-H_{R'} - (-H_C)$ and $\log f_{TPC} - \log f_{Nap}$; the average difference between these values over the acid concentration range covered in Table III is less than 0.2 logarithmic unit. This hardly exceeds the experimental error limit usually associated with the stepwise determination

Table III. A Comparison of $H_R{}'$ and H_C with Activity Coefficients

$[H_2SO_4]$, M	f_{Nap}	$-H_R{}' - (-H_C)$	$\log f_{TPC} - \log f_{Nap}$
2.00	1.96	0.30	0.17
3.00	2.40	0.45	0.27
4.00	2.69	0.60	0.35
5.00	2.85	0.80	0.37
6.00	2.76	0.45	0.38
7.00	2.49	0.40	0.36

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[15] (a) W. F. McDevit and F. A. Long, *J. Am. Chem. Soc.*, **74**, 1773 (1952); (b) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

[16] Data used for calculation of $H_R{}'$ in aqueous sulfuric acid: N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *ibid.*, **82**, 62 (1960).

[17] Activity coefficients of triphenylcarbinol in aqueous sulfuric acid were taken from ref 4.

of pK_{BH^+} values. The data in Table III therefore seem concordant with our view that the H_C scale is more appropriate to the protonation of carbon bases of the type discussed in this paper than the $H_{R'}$ scale, or any acidity scale that has been presented to date.

Acknowledgment. I wish to thank Professor F. A. Long for suggesting this project, for providing his laboratory facilities, and for very many helpful discussions. This work was supported by a grant from the Atomic Energy Commission to Cornell University.

Quantitative Comparison of Nucleophilic Substitution at Sulfonyl *vs.* Sulfinyl Sulfur. The Hydrolysis of Aryl α-Disulfones in Aqueous Dioxane[1a]

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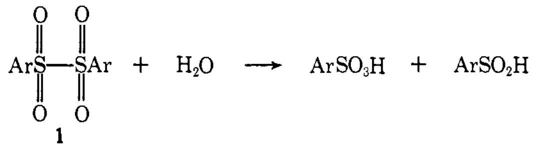
Abstract: The spontaneous (uncatalyzed) hydrolysis of aryl α-disulfones (eq 1) has been studied kinetically in acidic aqueous dioxane. Because this reaction differs from the previously investigated[2] spontaneous hydrolysis of aryl sulfinyl sulfones (eq 2) only in that eq 1 involves nucleophilic substitution at sulfonyl (>SO_2) sulfur while eq 2 involves substitution at sulfinyl (>SO) sulfur, the data for the two reactions (Table II) provide a *quantitative* comparison of the influence of various important reaction variables on nucleophilic substitution at sulfonyl *vs.* sulfinyl sulfur. This comparison reveals that, despite the fact that the substitution at sulfinyl sulfur is 10^4 times faster than the one at sulfonyl sulfur, the two reactions show a remarkable similarity in (1) dependence of rate on aryl group structure, (2) increase in rate with water content of the solvent, (3) solvent isotope effect, and (4) $\Delta S^{\ddagger}$. The large difference in rate arises solely as a result of a 6.0-kcal/mole difference in activation energy. The conclusion is that analogous nucleophilic substitutions at sulfonyl and sulfinyl sulfur do not differ significantly in their detailed mechanism: nucleophilic substitution at sulfonyl sulfur is much slower merely because of a less favorable activation energy. The large solvent isotope effect ($k_{H_2O}/k_{D_2O} = 2.3$) for α-disulfone hydrolysis indicates that a proton transfer is part of the rate-determining step of that reaction. Various mechanisms including this feature are discussed, and it is concluded that a mechanism (eq 8) involving a concerted proton transfer from the attacking water molecule to the departing $ArSO_2$ group is the most satisfactory one on the basis of presently available evidence. Finally, comparison of the spontaneous hydrolysis of α-disulfones with that of aryl sulfonic anhydrides (eq 3) shows that in reactions of the type under consideration a change in the character of the leaving group is apparently much more likely to lead to a significant change in mechanism than is a change in the site where substitution occurs from sulfonyl to sulfinyl sulfur.

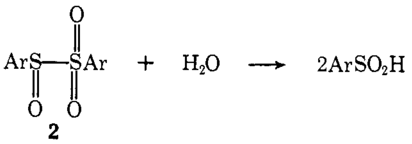
Quantitative comparison of various important characteristics of nucleophilic substitution reactions occurring at different oxidation states of sulfur should contribute much to a better understanding of some of the general principles governing such processes. One pair of oxidation states that it is of great interest to compare in this way is sulfinyl sulfur (>S=O) and sulfonyl sulfur (>SO_2).

For such a comparison to be truly meaningful one must take pains to select two reactions which differ *only* in the oxidation state of the sulfur being attacked, and where all else, such as the nature of the group being displaced, nature of the attacking nucleophile, solvent medium, etc., is identical. The principal deterrent which has prevented such a study in the past has undoubtedly been the fact that most sulfinyl compounds undergo substitution so much faster than their sulfonyl counterparts that it is not easy to find a pair of reactions where the rates for both sulfinyl and sulfonyl compound are accurately measurable under the same conditions.

We have now been able to make the first such quantitative comparison of substitution at sulfinyl and sulfonyl sulfur by obtaining data on the spontaneous hydrolysis of aryl α-disulfones (eq 1) in aqueous dioxane and comparing it with the extensive results already available[2] on the spontaneous hydrolysis of aryl sulfinyl sulfones (eq 2) in the same medium. As is readily evident the two



$$\underset{\mathbf{1}}{\mathrm{Ar}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\!-\!\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\mathrm{Ar}} + H_2O \longrightarrow ArSO_3H + ArSO_2H \qquad (1)$$



$$\underset{\mathbf{2}}{\mathrm{Ar}\underset{O}{\underset{\|}{S}}\!-\!\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\mathrm{Ar}} + H_2O \longrightarrow 2ArSO_2H \qquad (2)$$

reactions meet our requirements that the leaving group ($ArSO_2$), the solvent medium, and the substituting nucleophile (H_2O) should be exactly the same for both reactions and differ only in that eq 1 involves substitution at sulfonyl sulfur while eq 2 involves substitution at sulfinyl sulfur.

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[1] (a) This research supported by the National Science Foundation Grant GP-6952; (b) NDEA Fellow, 1966–1969.

[2] J. L. Kice and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4113 (1967).