aminophenyldiphenylmethane, the compound was equilibrated with diphenylmethane and 0.2 ml of tetramethylethylenediamine was also added to the equilibration solution. Quenching and work-up in the usual way gave 29% deuteration of the triarylmethane and 45% monodeuteration of the diphenylmethane, from which the pK_a of *p*-dimethylaminophenylmethane is taken to be 33.8, assuming that diphenylmethane has a pK_a of 33.5. A solution of tris(*p*-dimethylaminophenyl)methane in tetrahydrofuran with tetramethylethylenediamine and diethylamine was heated with methyllithium at 60-65° for 30 min and quenched with D_2O. No detectable deuteration of the triarylmethane occurred, so this compound could not be equilibrated with the other anions.[41]

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(41) Support of this work by the National Institutes of Health is gratefully acknowledged.

Medium Dependence of Acidity Functions and Activity Coefficients in Perchloric Acid

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Abstract: The H_A and H_0''' acidity scales have been established for 0–75% aqueous perchloric acid solutions, using pK measurements on eight substituted amides and 13 substituted tertiary amines. Activity coefficients of four typical neutral indicator bases and four typical pentacyanopropenide salts have been measured in the same acid region by the solubility technique. Acidity function differences ($H_X - H_0$), based on directly measured values of the acidity functions H_0, H_A, H_0''', H_I, and H_R', can be semiquantitatively reproduced in both $HClO_4$ and particularly H_2SO_4 using the above and other available activity coefficient data. Use of representative activity coefficient and typical acidity function data yields estimates of hydronium ion activities in 0–60% H_2SO_4 and $HClO_4$ solutions which are remarkably independent of the method used to obtain them. The utility of these data is discussed.

It is now clear that the conformity of neutral organic bases to the H_0 acidity function[2] is more the exception than the rule. The only bases that can be expected to follow H_0 closely in their protonation behavior are probably nitroanilines of the type used to make up the set of indicators on which the H_0 scale is based. Other structural classes of base are known to generate their own characteristic acidity functions, such as tertiary anilines[3a] (H_0'''), amides[3b] (H_A), and indoles[4] (H_I) for example. These, and other acidity scales, have been shown to differ considerably from H_0 and from each other in several aqueous mineral acid systems. The failure of the protonation of neutral Brønsted bases to conform to a unique acidity scale, such as H_0, has been termed by Arnett and Mach[5] "acidity function failure." This in our view is a rather misleading terminology, since what has really occurred is not the failure of acidity functions to measure some property of an acidic medium, but a breakdown of the earlier hoped for generality of the H_0 function as a unique measure of the protonating ability (or acidity) of a medium toward all neutral organic bases. What has failed in a general sense is the Hammett activity coefficient postulate,[6] namely that log $(f_{XH^+}f_Y/f_Xf_{YH^+})$ will be essentially medium independent for any pair of organic bases X and Y. It is easy to see in retrospect that such a postulate was bound to fail in the broadest sense, although it is quite probable that it holds within a reasonable degree of precision for each of a number of restricted structural classes of base. Furthermore, it is clear that any hoped for generality of H_0, or any other one acidity function, was also bound to break down in the sense that the acidity of any medium can never be defined uniquely, but only in terms of the particular bases with which it is reacting.

Hopefully, acceptance of this limitation and future measurement and analysis of acidity function behavior in different acid systems will eventually lead to a quantitative understanding of typical activity coefficient behavior of organic bases and their conjugate acids. A knowledge of typical medium variation of these activity coefficients may lead not only to more quantitatively sound measures of acid–base equilibria, but also to increased understanding of the solvent–solute interactions which cause these variations. It is not unreasonable that estimates of typical activity coefficient behavior, combined with observed rate acidity dependences, may even lead to quantitative estimates of transition-state–solvent interactions and thus to a better understanding of the mechanisms of acid-catalyzed reactions.

It is thus important to obtain more extensive data on acidity function and activity coefficient behavior, particularly in media other than aqueous sulfuric acid which has tended to be the predominantly used medium. This is important, not only for making comparisons between the strengths of various acids, but also to extend and test the generality of any conclusions regarding the factors which cause general acidity function breakdown. Apart from acidity functions which deal with

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(1) Deceased.

(2) For a recent and complete review of acidity functions and their measurement see C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

(3) (a) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964); (b) K. Yates, A. R. Katritzky, and J. B. Stevens, *Can. J. Chem.*, 42, 1957 (1964).

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

(5) E. M. Arnett and G. W. Mach, *ibid.*, **88**, 1177 (1966).

(6) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932); see also M. Liler, "Reaction Mechanisms in Sulphuric Acid," Academic Press, New York, N. Y., 1971, Chapter 2, for a recent discussion of this postulate.

carbonium ion equilibria, there are four major acidity functions which are based on typical ammonium or oxonium ion equilibria, namely H_0, H_0''', H_A, and H_I.[2] Of these only the first[7] and last[4] have been investigated in perchloric acid. This paper describes the measurement of H_0''' and H_A over an extensive range of aqueous perchloric acid and a general comparison of acidity function and activity coefficient behavior in concentrated perchloric and sulfuric acid systems. These comparisons lead to some remarkably simple and potentially useful general relationships between acidity functions, activity coefficient ratios, and acid concentrations.

Table I. pK_a Values[a] of Substituted Amides at 25°

	pK_a values[b]		
Indicator	$HClO_4$	H_2SO_4[c]	HCl[d]
2-Pyrrolecarboxamide	−1.30 ± 0.05[e]	−1.23	−1.23
4-Methoxybenzamide	−1.54 ± 0.02	−1.44	−1.46
3,4,5-Trimethoxybenzamide	−1.93 ± 0.01	−1.82	−1.86
3-Nitrobenzamide	−2.35 ± 0.07	−2.42	−2.25
3,5-Dinitro-4-methylbenzamide	−3.06 ± 0.04	−2.69	−2.77
2,3,6-Trichlorobenzamide	−3.38 ± 0.08	−3.30	−3.10
2,4-Dichloro-3,5-dinitrobenzamide	−3.70 ± 0.04	−3.73	
2,4,6-Trinitrobenzamide	−4.05 ± 0.08	−4.08	

[a] All pK values are referred to a primary value of −0.29 for 2-nitroaniline, the "best" value in the compilation of M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957). [b] Defined for the acid dissociation of the conjugate acid form of the indicator. [c] Reference 3b. [d] K. Yates and J. C. Riordan, *Can. J Chem*, **43**, 2329 (1965). [e] Mean deviations based on values calculated from overlapping data (from 5 to 18 points) in different acid concentrations.

Table II. pK_a Values of Substituted Tertiary Amines at 25°

	pK_a values				
Indicator	$HClO_4$	H_2SO_4[a]	H_3PO_4[b]	HCl[b]	HOTs[b]
N,*N*-Dimethyl-2-nitroaniline	0.67	0.66	0.66	0.66	0.66
N,*N*-Diethyl-4-nitroaniline	0.27 ± 0.02[c]	0.21			
N-(2,4-Dinitrophenyl)piperidine	−0.41 ± 0.07	−0.38	−0.44	−0.46	−0.34
N,*N*-Dimethyl-2,6-dinitro-4-methylaniline	−1.59 ± 0.04	−1.66	−1.73	−1.81	
N,*N*-Dimethyl-2,4-dinitro-1-naphthylamine	−2.45 ± 0.07	−2.59	−2.72	−2.74	
N,*N*-Dimethyl-4-chloro-2,6-dinitroaniline	−3.09 ± 0.07	−3.12	−3.12		
N-Methyl-4-nitrodiphenylamine	−3.57 ± 0.04	−3.42	−3.42	−3.31	
N-Methyl-4′-bromo-4-nitrodiphenylamine	−4.29 ± 0.03	−4.21	−4.11	−4.16	
N,*N*-Diethyl-2,4,6-trinitroaniline	−5.52 ± 0.13	−5.71	−5.81	−6.02	
N,*N*-Dimethyl-2,4,6-trinitroaniline	−6.46 ± 0.05	−6.55			
N-Methyl-4-bromo-2′,4′-dinitrodiphenylamine	−6.96 ± 0.02	−6.93			
N-Methyl-*x*′,4′-dibromo-2,4-dinitrodiphenylamine	−8.28 ± 0.01	−8.17			
N-Methyl-2,4,2′,4′-tetranitrodiphenylamine	−11.1[d]	−10.56			

[a] Reference 3a. [b] Reference 5. [c] Mean deviation based on overlapping points in different acids. [d] Obtained by a short extrapolation of log *I* values from previous two indicators.

Results and Discussion

Indicator pK_a Values. Values of the ionization ratios (*I*) measured at various perchloric acid concentrations were used to determine pK_a values for each of the eight amide indicators ($I_A = [AH^+]/[A]$) and each of the 13 tertiary amines ($I_{B'''} = [B'''H^+]/[B]$) by means of the standard stepwise procedure.[12] The reference pK for the first indicator in each series was obtained as usual from measurements extrapolated to infinite dilution in water, so that each set of pK_a's is anchored to the dilute aqueous standard state.[8-10] For the amide series, extensive overlap was obtained between successive indicator curves of log *I vs.* perchloric acid concentration using only log I_A values in the range ±1.0 (corresponding to 9–91% protonation). For the tertiary amines, which protonate more rapidly with increasing acid concentration, it was necessary to use log I_B values in the range ±1.2 (corresponding to 6–94% protonation) to achieve satisfactory overlap.[11]

Curves of log *I vs.* % $HClO_4$ for each series showed good to excellent parallelism between successive indicators. The approximately constant vertical difference between successive curves demonstrates that the necessary condition for the Hammett activity coefficient postulate[6] is satisfied by each set of indicators.

The pK_a values for the amides are listed in Table I, with values reported for these bases in H_2SO_4 and HCl solutions for comparison. Values for the tertiary amines are given in Table II, with available values in other acids for comparison.

It has been pointed out previously[12] that pK_a values such as the above may not necessarily be thermodynamically valid quantities, because of the possibility of anomalous activity coefficient behavior outside the range of directly observable ionization ratios. Despite this, one can derive some confidence that the measured pK_a values are quantitatively reasonable from their concordance from one mineral acid to another. Since all the pK's are ultimately referred to a dilute aqueous standard state, the pK_a value of any one indi-

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

(8) The reference pK in the amide series for 2-pyrrolecarboxamide has necessarily been referred to that of 2-nitroaniline, as described previously,[3b] since no sufficiently basic amide has yet been found which will measurably ionize in the very dilute acid region. Bunnett and Olsen[9] have suggested that because of this, the H_A scale in sulfuric acid may be in error by 0.3 unit. The same criticism would apply to the present scale in perchloric acid. However more recently, Katritzky and coworkers[10] have failed to confirm this estimated error, by use of more basic pyridine 1-oxides (which follow H_A), and have suggested that the original H_A scale is valid, despite its being anchored to 2-nitroaniline as primary indicator.

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

(10) C. D. Johnson, A. R. Katritzky, and N. Shakir, *J. Chem. Soc. B.*, 1235 (1967).

(11) Tables giving detailed values of log *I* for all 21 indicators will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-418. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche.

(12) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

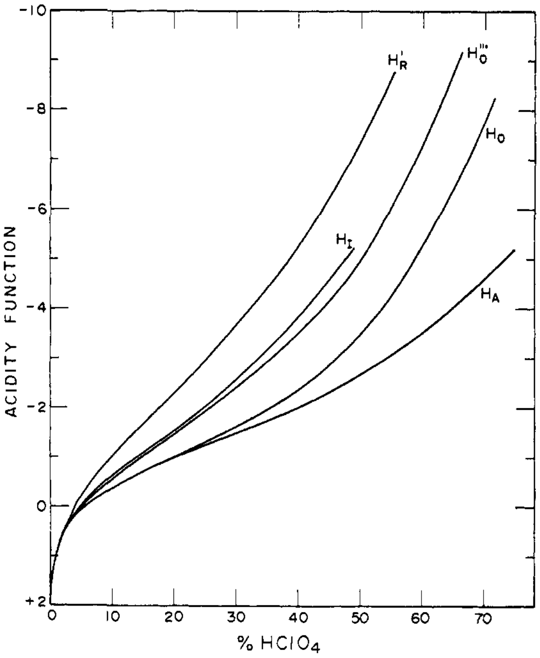

Figure 1. Curves of acidity function variation as a function of perchloric acid concentration (smoothed curves based on data from ref 4, 7, and 26 for H_0, H_I', and H_R'; data for H_0''' and H_A from this work).

cator should be independent of the particular acid used to determine it. Examination of the values in Tables I and II obtained in different acid systems shows that this is the case to within a good degree of approximation. The average difference between the pK_a values in HClO$_4$ compared with those in other acids is of the order of 0.1 pK unit or less, and in only two cases is it significantly outside this range. Therefore the agreement between the various independently determined values must be considered very satisfactory. Thus a second *necessary* condition (in addition to the activity coefficient postulate), that the pK_a values be considered thermodynamically meaningful quantities, is satisfied.

Acidity Functions in Perchloric Acid. Values for the H_A and H_0''' acidity functions in perchloric acids from dilute to 75% acid were obtained in the usual manner[12] using the pK values[13] in Tables I and II and the measured log I values, as described in the Experimental Section. Values of each acidity function are listed for closely spaced intervals of acidity in Table III. It can be seen from these values that H_0 decreases (*i.e.*, acidity increases) with acid concentration much more rapidly than H_A particularly at the higher acid concentrations. For example at 70% HClO$_4$, the acidity as measured by H_0 is about 6 logarithmic units greater than that measured by H_A. In other words the protonating ability of this acid solution is about a million times greater toward a tertiary amine than an amide.[14]

Table III. Acidity Functions in Perchloric Acid at 25°

% HClO$_4$	H_A[a]	H_0'''[a]	% HClO$_4$	H_A	H_0'''
0.166		+1.79[c]	51.7	−2.86	−5.30
0.268		+1.58	53.9	−3.03	−5.81
0.677		+1.12	55.3	−3.15	−6.13
1.38		+0.81	56.8	−3.30	−6.51
2.11		+0.55	57.4	−3.33	−6.64
2.74		+0.44	58.7	−3.43	−6.99
4.42		+0.12	59.8	−3.52	−7.29
5.47	+0.05[b]	0.0	60.8		−7.64
7.39		−0.25	60.9	−3.60	
8.47	−0.23	−0.38	62.2	−3.70	−7.98
12.1	−0.49	−0.74	63.3	−3.81	−8.36
16.3	−0.75	−1.18	64.4	−3.91	−8.70
20.3	−0.95		65.4	−3.93	−9.01
20.5		−1.51	66.3	−4.05	−9.29
25.0	−1.24	−1.92	67.4	−4.13	
28.9	−1.43	−2.29	68.2	−4.23	−9.89
32.2	−1.60	−2.63	69.1	−4.37	−10.16
36.0	−1.79	−3.04	69.8	−4.44	−10.41
38.5	−1.93	−3.34	71.0	−4.65	−10.80
40.5	−2.04	−3.58	72.0	−4.70	−11.11
44.2	−2.28	−4.10	72.9	−4.94	−11.40
46.7	−2.43	−4.43	73.5	−5.08	−11.62
48.5	−2.62	−4.63	74.4	−5.13	−11.91
50.7	−2.76	−5.04	75.4		−12.21

[a] Details of the indicators used to obtain each value can be found in ref 11. [b] The average value of the deviations in each H_A value as calculated from different indicators was 0.04 unit. [c] The average value of the deviations in each H_0''' value calculated from different indicators was 0.02 unit.

It is interesting to compare the behavior of the major acidity functions (derived from the protonation of neutral molecules) in perchloric acid, as shown graphically in Figure 1, including one of the carbonium ion functions[15] (H_R') for comparison. The order of the five acidity scales is strikingly similar in HClO$_4$ to that observed in sulfuric and other acids, namely $H_A > H_0 > H_0''' > H_I > H_R'$ at all acidities except for the very dilute region where all acidity functions converge into the pH scale. Despite the thermodynamic difficulties inherent in the acidity function approach, it is very satisfying that a number of quite different acidic media show the same order of protonating ability toward a variety of structurally different types of base. This demonstrates that acidity functions are at least semiquantitatively capable of measuring some fundamental property of acidic media in a consistent way, albeit complicated by individual activity coefficient behavior of the various cations and base molecules involved. This point will be discussed further in a later section.

Acidity Function Dependence on Water Activity. An attractive possibility of explaining acidity function medium dependence in terms of hydration effects rested upon Wyatt's observation[16] that H_0 is a unique function of the water activity of the media for different mineral acid solutions. This relationship was later confirmed and extended by Yates and Wai[7] who showed that H_0 values in H_2SO_4 and HClO$_4$ lay on exactly the same curve when plotted against a_{H_2O} over the full measurable range of acidity. However the present acidity

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(13) It should be pointed out that even if the thermodynamic validity of these pK values is open to question because of the possibility of anomalous effects[12] outside the range of measurable log I values, this would not necessarily affect the derived acidity scales. The parallelism between successive ionization curves is a sufficient condition for a thermodynamically valid scale to be established, since lateral displacement of any curve (*i.e.*, a change in pK of any one indicator) will not affect the positions of other curves or the calculated values of the acidity function.

(14) How great a value this difference would be in pure HClO$_4$ could not easily be determined, since aqueous HClO$_4$ undergoes phase changes at 25° at about 79 and 94% acid. A continuous stepwise measurement of the acidity of HClO$_4$ from 0 to 100% would therefore necessitate working at elevated temperatures, with attendant increased danger of explosions.

(15) N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *J. Amer. Chem. Soc.*, **81**, 2344 (1959).

(16) P. A. H. Wyatt, *Discuss. Faraday Soc.*, **24**, 162 (1957).

function values can be used to show that this observation probably holds only for the H_0 function, and that other acidity scales are not in general unique functions of the water activity of the medium. If the present values of H_0''' or H_A are plotted against a_{H_2O} along with similar plots based on available data in other acids, it is clear that each acidity function shows a quite different water activity dependence in each acid. It can also be demonstrated that neither is H_R (or H_R') a unique function of the water activity in different acids. Thus it appears that Wyatt's observation was fortuitous for H_0 only, and that although the water activity is an important variable in determining acidity function behavior, the medium variation of the relevant activity coefficients must depend significantly on other variables. Arnett has also shown previously[5] that acidity function differences, which are related to ratios of these activity coefficients, cannot be simply related to water activity. Although there may be a rough qualitative relationship between the hydration requirements of the cationic species and the rate of increase of acidity of a medium toward a particular type of base, it seems unlikely that the complex interplay of the various factors affecting solvation energies can be accommodated in any simple structural approach. Various authors[3b,5,17] have suggested that it is preferable to express acidity function differences (or breakdown) in terms of the activity coefficients themselves (or their ratios) which are directly measurable,[18] rather than in terms of more chemical structural approaches such as hydration numbers.[19] Such a treatment will be described in a later section.

Linear Relationships between Acidity Functions. Using the presently determined values of H_A and H_0''' it is possible to test for perchloric acid in the previously reported observation,[20] that acidity functions in sulfuric acid are remarkably linear functions of H_0 over a wide acidity range (*ca.* 8 log units). This is shown in Figure 2, where interpolated values of H_R, H_I, H_0''', and H_A are plotted against values of H_0 at equivalent acid concentrations in perchloric acid. It can be seen that for nondilute acid solutions (*i.e.*, negative acidity values) the same kind of extensive linearity is obtained for $HClO_4$ as for H_2SO_4. Thus empirically the relation $H_X = mH_0 +$ constant appears to hold to a good degree of approximation. This can be shown to be an approximate linear free energy relationship, in a similar sense to the ϕ-parameter treatment of Bunnett and Olsen.[9] However this empirical relationship must clearly break down in dilute solutions, as all acidity functions approach a common pH scale. It can be shown that similar, if more limited, relationships hold for HCl, H_3PO_4, and HNO_3 solutions.

The importance of these linear relationships is not in generating useful empirical parameters such as m or ϕ but in demonstrating the remarkable similarity in acidity function variation for each different category of base, from acid to acid. Table IV shows calculated values of dH_X/dH_0 based on these linear plots. The similar values for each function of dH_X/dH_0 show that over wide ranges of acid concentration the activity coefficient ratios, which quantitatively determine individual acidity function behavior, show very similar responses to concentration changes in different acid media. This suggests that activity coefficient ratios such as f_{BH^+}/f_B and f_{XH^+}/f_B may be directly related in very useful ways. This possibility is tested and explored in a subsequent section.

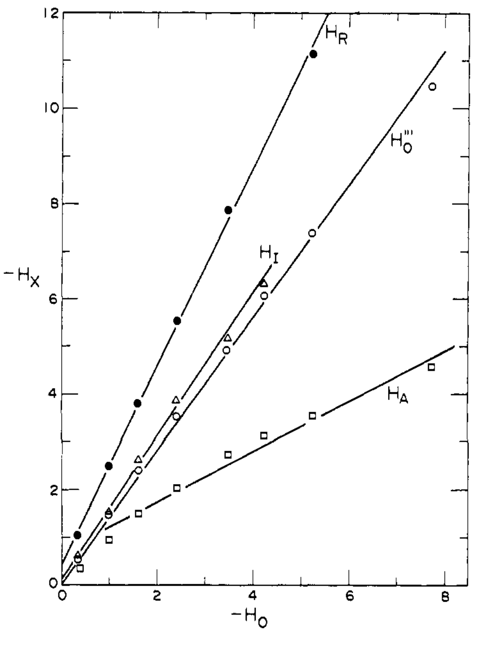

Figure 2. Plots of H_X *vs.* H_0 taken at equivalent acid concentrations in perchloric acid solutions. (Data for $H_X = H_R'$, H_I from ref 4 and 26.)

Table IV. Approximate Linear Interdependence of Acidity Functions in Aqueous Mineral Acids at 25°

Rate of change[a] dH_X/dH_0	Acid[b] $HClO_4$	H_2SO_4	HCl	HNO_3	H_3PO_4
dH_R/dH_0	2.1[c]	2.0	2.0	2.3	2.25
dH_I/dH_0	1.5	1.3			
dH_0'''/dH_0	1.35	1.3	1.3	1.3	
dH_A/dH_0	0.6	0.6	0.8		

[a] Based on plots of H_X *vs.* H_0 at equivalent % acid in the range 0–70% using interpolated values taken at 10% intervals. [b] Approximate linearity of H_X in H_0 begins at 10% acid ($HClO_4$, H_2SO_4, HNO_3), 5% acid (HCl), and 20% (H_3PO_4), *i.e.*, essentially for all negative values of acidity scales. [c] Least-squares correlation coefficients generally 0.999 or better, except for the H_A correlations.

Activity Coefficient Behavior of Typical Indicator Species in $HClO_4$. The activity coefficient behavior of four typical neutral indicators and four pentacyanopropenide (PCP^-) salts of typical indicators was determined in perchloric acid by the solubility method developed originally by Boyd.[18] The solubilities of the neutral bases give values of f_B (or log f_B) directly, whereas those of the pentacyanopropanide salts give $\log f^*_{BH^+}$ values (relative to tetraethylammonium ion as standard reference ion) according to the Boyd approximation

$$f^*_{BH^+} = [f_{\pm(BH^+PCP^-)}]^2/[f_{\pm(TEA^+PCP^-)}]^2 = \frac{f_{BH^+}f_{PCP^-}}{f_{TEA^+}f_{PCP^-}} \simeq \frac{f_{BH^+}}{f_{TEA^+}}$$

The reasons for the selection of tetraethylammonium

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(17) N. C. Deno and C. Perrizzolo, *J. Amer. Chem. Soc.*, **79**, 1345 (1957).

(18) In the sense that Boyd has demonstrated: R. H. Boyd, *ibid.*, **85**, 1555 (1963).

(19) R. W. Taft, *ibid.*, **82**, 2965 (1960).

(20) K. Yates and R. A. McClelland, *ibid.*, **89**, 2686 (1967).

Table V. Activity Coefficients of Typical Indicators in $HClO_4$ at 25°

(a) Neutral Bases

	Log f_B[a]			
% $HClO_4$	2,6-Dichloro-4-nitroaniline[b]	2,4-Dichloro-6-nitroaniline[c]	2,4-Dinitroaniline[d]	4-Chloro-*N*-tricyanovinylaniline[d]
0.00	0	0	0	
0.50				0[e]
5.47	−0.181			−0.258
8.47		−0.234	−0.337	
12.11	−0.321			−0.519
16.29		−0.420	−0.588 (−0.586)[f]	
20.25	−0.487			−0.737
24.95		−0.632	−0.824	
28.89	−0.696			−0.919
32.18		−0.765	−1.002 (−1.030)[f]	
36.02				−1.036
38.52	−0.838			
40.50		−0.905	−1.198	
44.17			(−1.339)[d]	−1.101
48.46	−1.005	−1.044	−1.423	
50.66				−1.188
55.31		−1.164	−1.636	−1.278
58.71	−1.197			
60.86		−1.314	−1.802 (−1.740)[f]	−1.382
64.39			−1.814[e]	
69.05			−1.826[e]	

(b) Pentacyanopropenide Salts

% $HClO_4$	TEA^+PCP^-		Anilinium PCP^-		*p*-Nitroanilinium PCP^-		Pyridinium PCP^-	
	Log $f_\pm$	Log f_{PCP^-}[g]	Log $f_\pm$	Log $f^*_{BH^+}$[h]	Log $f_\pm$	Log $f^*_{BH^+}$	Log $f_\pm$	Log $f^*_{BH^+}$
0	0	0	0	0	0	0	0	0
0.68			0.066[i]				−0.015[e]	
1.38			−0.099				−0.061	
5.47	−0.393	−0.786	−0.149	0.488			−0.284	0.217
8.47					−0.207[j]			
12.11	−0.524	−1.048	−0.263	0.523	−0.221	0.606	−0.527	−0.007
20.25	−0.976	−1.952	−0.361	1.230	−0.338	1.276	−0.783	0.385
28.89	−1.308	−2.616	−0.420	1.775	−0.410	1.795	−0.987	0.641
36.02	−1.537	−3.074	−0.461	2.152	−0.424	2.226	−1.142	0.789
44.17	−1.836	−3.672	−0.666	2.341	−0.422	2.827	−1.359	0.955
50.66	−2.117	−4.234	−0.692	2.850	−0.433	3.367	−1.427	1.379
55.31	−2.301	−4.602	−0.698	3.205	−0.488	3.625	−1.505	1.591
60.86	−2.652	−5.304			−0.755	3.794		

[a] The activity coefficient is obtained from the ratio of the absorbance in pure water to that in acid. [b] Determined at 367 mμ. [c] Determined at 420 μ. [d] Determined at 348 mμ. [e] The neutral base is protonated significantly in these acids and the values of log f_B are probably less reliable than the rest. [f] Obtained by the distribution method. [g] $f_{PCP^-} = f_{TEA^+}f_{PCP^-} = [f_{\pm(TEA^+PCP^-)}]^2$. [h] $f^*_{BH^+} = [f_{\pm(BH^+PCP^-)}/f_{\pm(TEA^+PCP^-)}]^2$. [i] Estimated from the Debye–Hückel expression as described in Experimental Section. [j] Estimated by comparison with anilinium$^+$ PCP^-.

(TEA^+) and pentacyanopropenide (PCP^-) as reference ions have been discussed previously.[21] The activity coefficients of all eight species are listed in Table V at different acid concentrations. The medium variation of these activity coefficients is similar to the behavior already observed for this type of base in sulfuric acid solutions; namely the cations are very strongly salted out with increasing acid concentration, while the free bases are generally salted in, but show less marked variation with medium than the cations. However there are several differences in $HClO_4$. Firstly, the neutral bases do not show the initial weak salting out in dilute solutions as found for H_2SO_4.[21] This parallels the effects found by Long and McDevit[22] in various electrolyte solutions. They found that benzene was salted out initially by most electrolytes, except perchloric acid and salts with large ions such as tetraethylammonium bromide. Another significant difference from H_2SO_4 solutions is that not only are neutral bases of similar structure salted in more strongly (log f_B more negative) in $HClO_4$, but also similar cations are salted out more strongly (log f_{BH^+} more positive) with increasing acid concentration. From the definition of H_0 (for example)

$$H_0 = -\log \frac{a_{H^+}f_B}{f_{BH^+}} = -\log a_{H^+} - \log f_B + \log f_{BH^+}$$

it can be seen that each of these differences would tend to work in favor of H_2SO_4 as the more acidic medium (*i.e.*, more negative H_0 values). Despite this it is clear that acidity functions in $HClO_4$ are always considerably more negative[2] than the corresponding function in H_2SO_4 (except for the very dilute regions). Thus the proton activities in moderate to concentrated $HClO_4$ must be even greater relative to those in H_2SO_4 than the difference their H_X values would imply. Again[7] it appears that "intrinsically," $HClO_4$ is a much more strongly acidic medium than H_2SO_4 over most of the aqueous concentration range.

One final point is that differences between individual log f_B or log $f^*_{BH^+}$ values for indicators of similar structure are smaller but not negligible in $HClO_4$ (as found

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(21) R. H. Boyd in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3.

(22) F. A. Long and W. F. McDevit, *Chem. Rev.*, 51, 119 (1952).

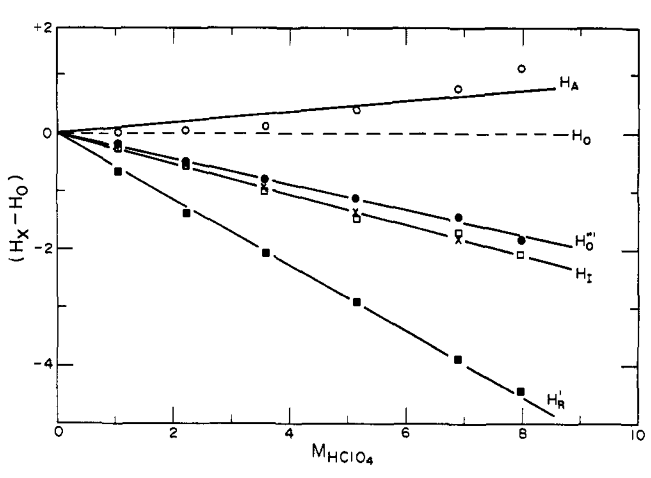

Figure 3. Plots of observed values of $(H_X - H_0)$ *vs.* molarity of acid, based on different acidity functions in perchloric acid solutions. (Points × estimated from log $(f_B f_{XH^+}/f_{BH^+} f_X)$ values as described in text.)

for H_2SO_4), and that changing the number of nitro substituents again seems to be primarily responsible for these differences.

Semiquantitative Treatment of Acidity Function Breakdown. Acidity function breakdown is most easily expressed as the difference between any given acidity function H_X in a particular medium and the value of H_0 for that medium. From the definition of acidity functions, this difference should simply be equal to a (logarithmic) ratio of activity coefficients

$$(H_X - H_0) = -\log \frac{a_{H^+} f_X}{f_{XH^+}} + \log \frac{a_{H^+} f_B}{f_{BH^+}} = \log \frac{f_B f_{XH^+}}{f_{BH^+} f_X} \quad (1)$$

since the a_{H^+} term should cancel because all indicator species are at very low concentrations. Arnett has shown that when these differences (which he calls "failure ratios")[5] are plotted against acid molarity, good linear plots can be obtained over a wide range of acid concentration. This linearity corresponds to a complex type of Setschenow behavior,[23] and the slope of such a plot gives a combined Setschenow constant (A) for the total medium effect on the four activity coefficients

$$H_0 - H_X = AM_{\text{acid}} = \log f_B f_{XH^+}/f_{BH^+} f_X$$

Using the present data for H_0''' and H_A and reported data for H_0, H_R', and H_I it is shown in Figure 3 that such relationships are also found for $HClO_4$ solutions. Data available for H_2SO_4 solutions are plotted in Figure 4a for the same four functions. This shows very similar behavior. Thus relationships of the type expressed by the above Setschenow type equation appear to be fairly general.

The question is, are these linear relationships fortuitous or can they be accounted for quantitatively in terms of observed activity coefficient behavior? If acidity functions are fundamentally sound measures of the proton activity of a medium (complicated by other activity coefficient terms), then it should be possible to account quantitatively for the linear relationships in Figure 4a, and their slopes, in terms of independently measured activity coefficient ratios of the form log $(f_B f_{XH^+}/f_{BH^+} f_X)$. This can be tested using available data based on solubility measurements.[21] The most extensive data have been obtained for H_2SO_4, and values of f_B, f_X, f_{BH^+}, and f_{XH^+} can be selected for suitable model indicator species for each of the five acidity functions, as listed in Table VI.[24] Using interpolated values at equivalent acidities for the various log f contributions (based on smooth curves through experimental points, taking average values where more than one model species is available), the plots of log $(f_B f_{XH^+}/f_{BH^+} f_X)$ *vs.* M_{acid} which result are shown in Figure 4b. The similarity between the curves in Figures 4a and 4b is truly remarkable.[25] More limited data for $HClO_4$ can be used to calculate log $(f_B f_{XH^+}/f_{BH^+} f_X)$ (for indole models), which is also linear in M_{HClO_4} (as shown in Figure 3). The slopes of these plots, whether obtained directly from observed $(H_X - H_0)$ values *vs.* M_{acid} or indirectly from estimated log $(f_B f_{XH^+}/f_{BH^+} f_X)$ values are

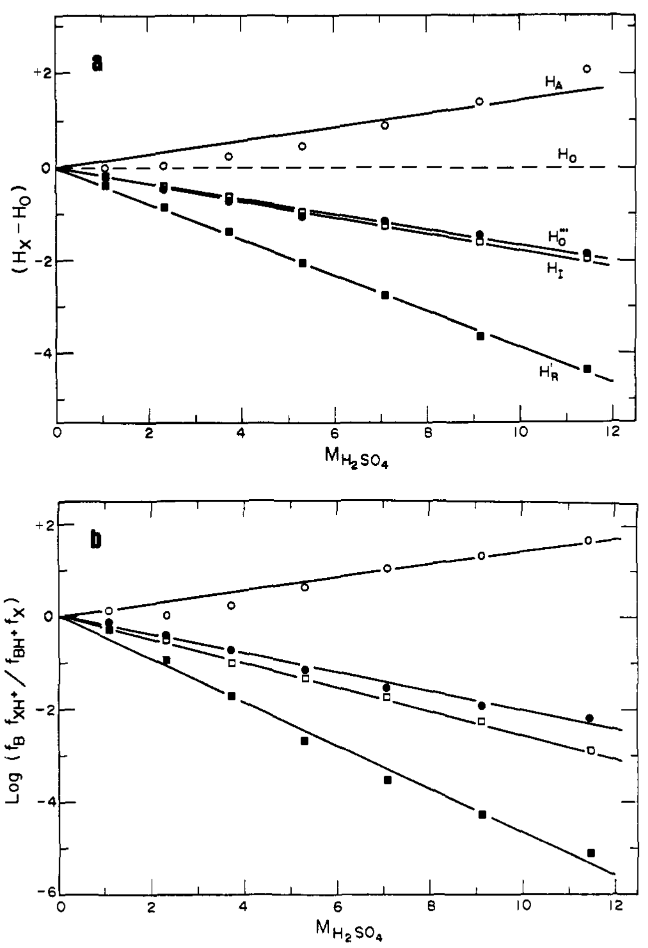

Figure 4. (a) Plots of observed values of $(H_X - H_0)$ *vs.* molarity of acid for different acidity functions in sulfuric acid solutions. (b) Plots of estimated values of log$(f_B f_{XH^+}/f_{BH^+} f_X)$ *vs.* molarity of acid in sulfuric acid solutions for the same four functions as in Figure 4a. (See text and Table VI for methods of estimation of activity coefficient ratios.)

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[23] F. A. Long and J. Schulze, *J. Amer. Chem. Soc.*, 86, 327 (1964).

[24] Note that although the observed activity coefficients for the ionic species are all necessarily of the form log $f_{XH^+}/f_{\text{ref}^+}$, the term for the reference ion (always TEA$^+$) will cancel in the overall ratio.

[25] Attempts to obtain similar correspondence considering only cation activity coefficients are unsuccessful, *i.e.*, log f_{XH^+}/f_{BH^+} does not give linear Setschenow relationships *vs.* M_{acid}. This is not surprising in view of the significant variations in log f_B or log f_X terms noted earlier, despite frequent assumptions that terms for neutral species are relatively unimportant in determining acidity function behavior.

Table VI. Model Compounds Used to Calculate Values of log $(f_Bf_{XH^+}/f_{BH^+}f_X)$

H_x type	Indicator type	Activity coefficient	In H_2SO_4[a]	In $HClO_4$
H_0	Substituted anilines	f_B	Ten substituted anilines	2,6-Dichloro-4-nitro-, 2,4-dichloro-6-nitro-, and 2,4-dinitroaniline
		f_{BH^+}[b]	Anilinium, *p*-chloro-, *p*-nitro-, and *m*-nitroanilinium ion	Anilinium and *p*-nitroanilinium ion
H_0'''	Substituted *N*,*N*-dialkylanilines and diphenylamines	$f_{B'''}$	*N*,*N*-Dimethyl-2,4-dinitroaniline,[c] *N*,*N*-dimethyl-2,4,6-trinitroaniline,[c] and diphenylamine	
		$f_{B'''H^+}$	*N*,*N*-Dimethylanilinium ion	
H_I	Substituted indoles	f_I	3-Methylindole,[c] *p*-chloro-*N*-tricyanovinylaniline	*p*-Chloro-*N*-tricyanovinylaniline
		f_{IH^+}[b]	Quinolinium and pyridinium ion	Pyridinium ion
H_A	Substituted amides	f_A	Nine substituted benzamides	
		f_{AH^+}[b]	Benzamidonium ion	
H_R'	Substituted triarylcarbinols	f_{ROH}	Triphenylcarbinol, diphenylcarbinol, and *p*-nitrophenyldiphenylcarbinol[d]	
		f_{R^+}[b]	Tris(*p*-methoxyphenyl)carbonium ion	

[a] Data for H_2SO_4 taken from the compilation in ref 21 except where noted. [b] All values for cationic species based on pentacyanopropenide (PCP^-) salts and are referred to tetraethylammonium ion (TEA^+) using the Boyd approximation. [c] K. Yates and R. A. McClelland, unpublished results. [d] K. G. Harbison, Ph.D. Thesis, M.I.T., 1966.

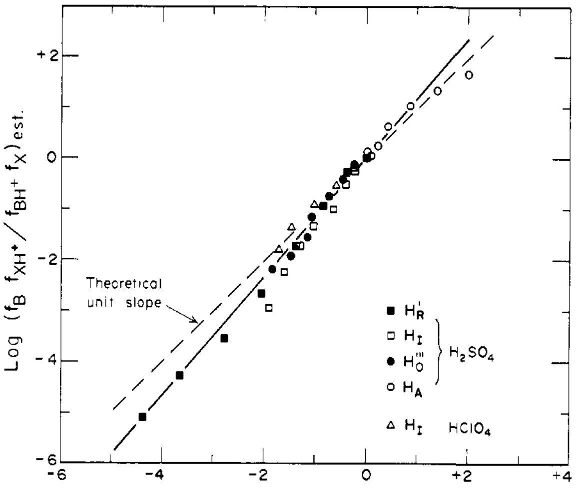

Figure 5. Plot of log $(f_Bf_{XH^+}/f_{BH^+}f_X)_{\text{estimated}}$ *vs.* $(H_X - H_0)_{\text{observed}}$ for all available data in sulfuric and perchloric acid solutions.

in remarkably good agreement considering the nature of the approximations involved in the latter and the necessity of having to choose from a limited selection of model indicators. The semiquantitative agreement which results is shown in Table VII, where the values of the combined Setschenow constants obtained by each method are listed. This demonstrates that to a good approximation the various acidity functions, when corrected for individual indicator behavior, are capable of measuring some common property of the medium, namely the proton activity variation. This can be shown more clearly by plotting $(H_X - H_0)$ for all the functions against the corresponding values of the logarithmic *f* ratio directly. Theoretically a linear relationship with unit slope is required by eq 1. In fact the majority of points on such a plot fall very close to the theoretical line, as shown in Figure 5. The fact that the points are mostly within 0.5 log unit of the line is striking, when it is considered that the sum of the individual terms that contribute to each function vary over a range of about 8 logarithmic units.

Table VII. Combined Setschenow Constants in H_2SO_4 and $HClO_4$

Indicator type	Acid	A_H[a]	A_f[b]
Amides	H_2SO_4	+0.18 (0.966)[c]	+0.16 (0.979)
	$HClO_4$	+0.14 (0.937)	
Tertiary amines	H_2SO_4	−0.16 (0.994)	−0.21 (0.995)
	$HClO_4$	−0.22 (0.997)	
Indoles	H_2SO_4	−0.17 (0.998)	−0.25 (0.999)
	$HClO_4$	−0.26 (0.996)	−0.26 (0.996)
Arylcarbonium ions[d]	H_2SO_4	−0.39 (0.999)	−0.47 (0.996)
	$HClO_4$	−0.54 (0.998)	

[a] Obtained from plots of $(H_x - H_0)$ *vs.* M_{acid} using acidity function data in ref 2, 3a, and 4. [b] Obtained from plots of log $(f_Bf_{XH^+}/f_{BH^+}f_X)$ *vs.* M_{acid} using data for model indicators in Table VI. [c] Figures in parentheses are least-squares correlation coefficients. [d] Based on H_R', not H_R.

Thus by correcting individual acidity function values (including H_0) by the appropriate terms as in

$$\log a^*_{H^+} = \log f^*_{XH^+} - \log f_X - H_X$$

it should be possible to calculate values of log $a^*_{H^+}$ which are reasonably independent of the particular acidity function used to obtain them. That this is the case is shown by the calculated values in Table VIII, where five independent estimates of the proton activity in H_2SO_4 and two in $HClO_4$ are listed. The agreement within each set of values is surprisingly good up to about 60% acid. Individual values are generally within ±0.5 log unit of the average. Such a deviation would introduce an error of less than 1 kcal at 25° in any solvation energies estimated from these values.

The utility of such a set of calculated proton activities does not lie in establishing any intrinsic scale of acidity, since, as pointed out earlier, for all practical purposes

Table VIII. Hydronium Ion Activities[a] Estimated from Different Acidity Functions

% acid	Log $a^*_{\mathrm{H}^+}$[b] (aq H_2SO_4) estimated[c] from						Log $a^*_{\mathrm{H}^+}$[b] (aq $HClO_4$) estimated[c] from		
	H_0	H_0'''	H_A	H_-	H_R'	Mean[d]	H_0	H_-	Mean
10	0.43	0.53	0.56	0.54	0.54	0.5	1.20	0.86	1.0
20	1.55	1.59	1.54	1.61	1.46	1.6	2.66	2.28	2.5
30	2.84	2.82	2.86	2.86	2.63	2.8	4.10	3.71	3.9
40	4.34	4.24	4.53	4.23	3.80	4.2	5.77	5.36	5.6
50	6.13	5.74	6.27	5.76	5.35	5.9	7.75	7.38	7.6
55							9.00	8.54	8.8
60	8.05	7.58	8.00	7.39	7.43	7.7			
70	10.08	9.74	9.69	9.43	9.34	9.7			

[a] Relative to tetraethylammonium ion (TEA^+). [b] $\log a^*_{\mathrm{H}^+} = \log a_{\mathrm{H}^+}/f_{\mathrm{TEA}^+}$. [c] Using relationships $\log a^*_{\mathrm{H}^+} = -H_X - \log f_X + \log f^*_{\mathrm{XH}^+}$ and available activity coefficient data from ref 21 and present study. [d] Standard deviation from the mean for all points = 0.22.

acidity depends on the particular bases involved. However the value of such a scale in combination with other data is potentially very great. For example, by combining the values of Table VIII with measured values of $\log f$ for model bases and ions it should be possible to derive quantitative information on free energies (or their differences) for the solvation of various cations and transition states. In the latter case this would be very valuable data, since suitable alternative models for transition states of acid-catalyzed reactions could then be compared with these. Clearly what is needed to test and extend the applicability of the above relationships is much more experimental data on suitably and carefully chosen model systems. Work is at present in progress in this laboratory along these lines.

Experimental Section

Acid Solutions. Perchloric acid solutions less concentrated than 70% (w/w) were prepared by diluting Baker and Adamson Reagent acid (70% min) with doubly distilled water. More concentrated acids were prepared by dissolving perchloric acid monohydrate (84.8%; G. Frederick Smith Co.) in the 70% acid. Acid solutions were transparent above the 220-nm region. Concentrations were determined by standard titration against sodium hydroxide. Restandardization at the conclusion of the work showed no significant changes in concentration with time.

Indicators. The set of amides used in the establishment of the H_A scale was identical with the set previously used to establish similar scales in sulfuric[3] and hydrochloric acids.[26] These are listed in Table I. The set of tertiary anilines, used to establish H_0''', was very generously supplied by Professor E. M. Arnett and is essentially the same as the set used by his group to establish H_0''' in sulfuric acid.[2a] These are listed in Table II.

Compounds Used for Activity Coefficient Measurements. 2,6-Dichloro-4-nitroaniline, 2,4-dichloro-6-nitroaniline, and 2,4-dinitroaniline were commercially available (Aldrich). The first two were recrystallized (ethanol) and further purified by zone refining, mp 189-190° (lit.[27] 189-190°) and 102-103.5° (lit.[28] 101-102°), respectively. 2,4-Dinitroaniline tended to explode when it was zone refined. It was recrystallized (ethanol) to constant mp 187-188° (lit.[29] 180, 188°).

Pyridinium pentacyanopropenide (PCP^-) was prepared by the method of Middleton, *et al.*,[30] by allowing pyridine to react with tetracyanoethylene (Aldrich). The salt was recrystallized (water) to give yellow flakes, mp 166-167° (lit.[30] 167-168°). Tetraethylammonium pentacyanopropenide was prepared by mixing equimolar aqueous solutions of tetraethylammonium bromide and pyridinium pentacyanopropenide. The precipitated yellow needles were recrystallized (water) and gave mp 222-230.5° (lit.[30] 220-221°). Attempts to prepare anilinium and 4-nitroanilinium pentacyanopropenide by a similar metathesis were unsuccessful. These were prepared *via* the sodium pentacyanopropenide salt. The preparation of this salt is very difficult, and the yield is highly sensitive to the reaction conditions. The sodium pentacyanopropenide showed the pentacyanopropenide anion absorption at 412 nm and did not melt when heated to 300°. To prepare anilinium pentacyanopropenide, equimolar amounts of aniline and sodium pentacyanopropenide were dissolved in the minimum volumes of 10% $HClO_4$ and mixed. A yellow compound precipitated on cooling, which was shown to be the desired salt by (i) the appearance of the aniline absorption peak at 280 nm when the solution was made slightly basic with $NaHCO_3$, (ii) the formation of a red coupled product with β-naphthol after diazotization, and (iii) the PCP^- absorption peak at 412 nm. Recrystallization (water) gave bright yellow crystals, mp 144.5-146° (lit.[30] 145-146°). *Anal.* Calcd for $C_{14}H_8N_6$: C, 64.61; H, 2.07; N, 32.30. Found: C, 65.04; H, 4.14; N, 31.37. The high percentages of carbon and hydrogen suggest that some hydrolysis to give aniline occurred during recrystallization. However, this would be protonated to give anilinium ion during the solubility measurements.

4-Nitroanilinium pentacyanopropenide was prepared similarly, using 25% $HClO_4$ as solvent. This was also characterized by its uv spectrum and by the formation of a red coupled product with β-naphthol. The crude salt (mp 162-168°) was recrystallized twice (20% $HClO_4$) giving a brown product (mp 169-171°). *Anal.* Calcd for $C_{14}H_7NO_2$: C, 55.08; H, 2.29; N, 32.13. Found: C, 52.35; H, 3.09; N, 30.15. The poor analytical results showed that the salt was not very pure. Further purification of the salt was not possible due to its sparing solubility in organic solvents and its hydrolysis in aqueous solvents. The analysis suggests the major contaminant is the free 4-nitroaniline, which would not interfere seriously with the solubility measurements.

4-Chloro-*N*-tricyanovinylaniline was prepared from 4-chloroaniline and tetracyanoethylene by the method of McKusick, *et al.*,[31] and was recrystallized to a mp of 158-159° (lit.[31] 160°) *Anal.* Calcd for $C_{11}H_5N_4Cl$: C, 57.77; H, 2.19; N, 24.51; Cl, 15.54. Found: C, 57.41; H, 2.32; N, 24.01; Cl, 15.96.

Ionization Ratio Measurements. Preparation of indicator solutions and spectrophotometric measurements (at 25 ± 0.5°) were carried out essentially as previously described.[7] Ionization ratios (I) for each indicator were obtained from the standard relationship

$$I = [BH^+]/[B] = (\epsilon_B - \epsilon)/(\epsilon - \epsilon_{BH^+})$$

where ϵ_B, ϵ_{BH^+}, and ϵ_B are respectively the molar extinctions at a certain fixed wavelength of the free base, its conjugate acid, and a test solution containing both species. Values of ϵ_B and ϵ_{BH^+} were obtained from smooth sigmoid curves of total absorbance *vs.* acid concentration. Instead of choosing these values at some arbitrary acidity on either side of the inflection point, as is usual, ϵ_B and ϵ_{BH^+} were taken from the beginning of the linear portions at the extremities of each sigmoid curve. For the amide series, absorbance values near λ_{max} of the conjugate acid form were used to calculate ionization ratios. It has been shown[32] that this is equivalent to the isobestic point method[33] of correcting for medium effects on the spectra.

Treatment of Data. The pK_a values of the amide indicators were

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(26) K. Yates and J. C. Riordan, *Can. J. Chem.*, **43**, 2329 (1965).

(27) G. Goldschmidt and L. Strohmenger, *Ber.*, **55**, 2457 (1922).

(28) A. F. Holleman and F. E. van Haeften, *Recl. Trav. Chim. Pays-Bas*, 40, 72 (1921).

(29) "Dictionary of Organic Compounds," 4th ed, Eyre and Spottiswoode Publishers Ltd., London, 1965.

(30) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **80**, 2795 (1958).

(31) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *ibid.*, **80**, 2806 (1958).

(32) D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962).

(33) L. P. Hammett and R. P. Chapman, *ibid.*, 56, 1282 (1934).

referred to that of 2-nitroaniline as primary reference for reasons discussed previously. The pK_a of this base has been measured in several mineral acids, and the reported "best" value[34] of -0.29 was used. The primary reference pK_a for the tertiary anine series, namely for *N,N*-dimethyl-4-nitroaniline, was obtained by linear extrapolation of ($\log I - \log [HClO_4]$) *vs.* $[HClO_4]$ to $[HClO_4] = 0$ by the method of least squares. Subsequent pK values in each series were obtained by the usual stepwise procedure using consecutive indicators. Each pair of indicators gave several values for the pK of the second indicator, which were averaged.

The functions of H_0''' and H_A were calculated from the equations

$$H_0''' = pK_{B'''H^+} - \log I_{B'''}$$

$$H_A = pK_{AH^+} - \log I_A$$

where B''' refers to a tertiary amine and A to an amide. The average value of the acidity in a given solution was determined from the pK and log I values of all indicators which had been studied in that solution.

Activity Coefficient Measurements. Solubilities in aqueous perchloric acids were measured in a thermostatically controlled (25 ± 0.1°) glove box to provide a measure of protection against possible explosion of the concentrated acid when saturated with organic substances. However no explosions occurred even with the most highly saturated solutions in the most concentrated perchloric acids used (*ca.* 80%). Activity coefficients were obtained from solubilities as described by Boyd.[18] Solubilities of the neutral bases were obtained from the absorbance of the free base peak in the ultraviolet spectrum, and for the salts the pentacyanopropenide peak at 412 nm was used. It was necessary to dilute the latter solutions, before measuring the spectra, using a perchloric acid solution of sufficient strength to prevent reversible deprotonation of the anilinium ions. Hence it was impossible to measure solubilities of some of the salts directly in water. The activity coefficients of these salts in the least concentrated acids possible for measurements were estimated from the Debye–Hückel theory, using the equation[35]

$$-\log f_i = \frac{Z_i^2 \alpha \sqrt{\mu}}{1 + \beta r_i \sqrt{\mu}}$$

For water at 25°, $\alpha = 0.509$ and $\beta = 0.329 \times 10^8$;[35] r_i was taken as 5×10^{-8} cm and was calculated assuming complete dissociation of both the salt and perchloric acid in the solution.

The activity coefficients for one indicator (2,4-dinitroaniline) were checked using a distribution method. Methylene chloride was found to be a suitable solvent, and the distribution ratio between this solvent and perchloric acid was measured as a function of indicator concentration at different concentrations. The concentrations of 2,4-dinitroaniline in each phase were determined spectrophotometrically, after equilibration.

Acknowledgment. The continued financial support of the National Research Council of Canada is gratefully acknowledged.

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Spiroaromaticity in Spiro[2.3]hexadienyl Anions. Kinetic Acidities in Highly Basic Media

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Abstract: Experimental tests for special stabilization (spiroaromaticity) in a spiro[2.3]hexadienyl anion compared with a series of spiro[2.3]hex-4-en-6-yl anions using polarography and kinetic acidity measurements reveal no significant stabilization. The kinetic acidity data were obtained by hydroxide ion catalyzed tritium exchange in dimethyl sulfoxide–water mixtures. The second-order rate constants were determined to be as follows: for **12**, 4.6×10^{-5}; for **13**, 24.14×10^{-5}; for **14**, 2.03×10^{-5}; for **15** (mixture of isomers), 5.70×10^{-5}. Brønsted coefficients (β) of *ca.* 0.80 for proton abstraction from the spiro[2.3]hexadiene **12** and spiro[2.3]hex-4-ene **13** suggest that the transition states from both compounds resemble the carbanionic products.

Aromatic character was used originally to describe the special stability accruing to certain combinations of electrons in monocyclic systems with a continuous periphery of p atomic orbitals.[1] Other molecular geometries can also in principle allow for continuous overlap of the kind associated with classical aromaticity, and thus particular combinations of electrons in the overlapping orbitals can lead to stabilization of the ground state. In the candidates for such "nonclassical" aromaticity, smooth overlap of the cyclic arrays of p orbitals can be perturbed by the insertion of saturated carbon atoms and by nonplanar geometries. Homoaromaticity,[2] bicycloaromaticity,[3] and spiroaromaticity[4] have been suggested as three particular examples; general rules for the π-electron combinations which provide stabilization (and destabilization) have been formulated for these and other topologies.[5]

The effects of homoaromaticity have been observed in several instances, such as the difference of $10^{4.5}$ in the rate of exchange of the allylic protons in bicyclo[3.2.1]octa-2,6-diene compared with similar exchange in bicyclo[3.2.1]oct-2-ene. The diene undergoes exchange more rapidly, presumably *via* the homoaromatic anion **1**.[6] Similarly, 3-methylbicyclo[3.2.2]nona-2,6,8-triene undergoes proton exchange 750 times faster than

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[1] For discussion of aromaticity in modern terms, see (a) D. Ginsburg, Ed., "Non-benzenoid Aromatic Compounds," Interscience, New York, N. Y., 1959; (b) "Aromaticity," *Chem. Soc. Spec. Publ.*, No. 21 (1967); (c) G. M. Badger, "Aromatic Character and Aromatic Compounds," Cambridge University Press, London, 1969.

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[5] M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, 93, 6193 (1971).

[6] (a) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); (b) J. M. Nicholson, unpublished work cited by S. Winstein in ref 1b, p 34.