A Critical Test of the Hammett Acidity Function

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The applicability of the H_0 acidity function to primary aromatic amines in general has been tested by using a set of five aniline indicators bearing no nitro-substituents. Up to 45% sulfuric acid the scale generated by these bases is the same (within experimental uncertainty) as that based entirely on nitro-anilines.

La possibilité d'application de la fonction d'acidité H_0 aux amines aromatiques primaires en général a été testée en utilisant une série de cinq indicateurs aniline ne portant pas de substituants nitro jusqu'à 45% d'acide sulfurique, l'échelle produite par ces bases est la même (dans les limites de l'incertitude expérimentale) que celle fondée uniquement sur les nitro-anilines.

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It is now clear that the applicability of any acidity function is largely restricted to a particular class of organic base. In the case of the original acidity function H_0, this class is the primary aromatic amine series. However, in order to establish the H_0 scale of acidity it was necessary to employ nitro-substituents to produce indicators of progressively weaker basicity in order to extend measurements over a wide range of acidity. In fact every indicator used by Hammett and Deyrup (1), and subsequently those used by Jorgenson and Hartter (2), contained at least one such group; even the primary reference indicator used to anchor the scale to the dilute aqueous standard state was *p*-nitroaniline.

From what is currently known of the medium variation of activity coefficients for typical organic bases and their cations (3), it is evident that substituent groups such as nitro- can produce as marked variations in individual f_B and f_{BH^+} values as changing the nature of the basic group itself (4). Thus, if the contributions to the ratio f_{BH^+}/f_B (which determines different acidity function behavior) by nitro-substituents were atypical of substituents in general, the H_0 function would not be generally applicable even to primary amine bases. It is therefore very important to test this possibility, since it is a necessary condition for the establishment of any acidity function that the medium variation of the ratio f_{BH^+}/f_B be the same (or very similar) for each member of the particular class of base which defines it, *i.e.*, that it be independent of the nature of the other substituent groups.

We have therefore investigated a set of primary anilines of differing basicity, which contain no nitro groups, to determine whether the H_0 function generated by these bases coincides with that reported for nitroanilines.[1]

Results and Discussion

Nitro groups are strongly electron withdrawing oxygen-containing groups which would be expected to interact strongly and specifically with the solvent through formation of strong O^-—H—O type hydrogen bonds. This is particularly true of the free base forms, since the nitro- and amino- group are directly conjugated in *o*- and *p*-substituted nitroanilines. We have therefore chosen anilines substituted only by such groups as —F, —Cl, —Br, $—CF_3$; which although electron withdrawing, would be expected to produce weaker and less specific solute–solvent interactions. The set of indicators chosen and their pK_{BH^+} values are listed in Table 1. The pK_{BH^+} values of the primary

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[1] Note that it is not a sufficient test merely to plot ionization curves for individual non-nitro-substituted anilines against H_0. This would only investigate their approximate obedience to this function in terms of an indicator slope near unity.

TABLE 1. pK_{BH^+} values of substituted aniline indicators

Substituted aniline	pK_{BH^+}	% H_2SO_4 at $\frac{1}{2}$ ionization
2-Chloro-5-trifluoromethyl-	$+1.195 \pm 0.004$	0.4
2,5-Bis(trifluoromethyl)-	$+0.38 \pm 0.005$	2.4
Pentafluoro-	-0.36 ± 0.016	9.3
4-Bromo-2,3,5,6-tetrafluoro-	-0.93 ± 0.020	18.4
2,4-Dichloro-3,5,6-trifluoro-	-1.28 ± 0.028	25.2

indicator 2-chloro-5-trifluoromethylaniline was determined spectrophotometrically in dilute hydrochloric acid and values of $K = C_B C_{H^+}/C_{BH^+}$ extrapolated to infinite dilution (see Fig. 1) in the usual procedure (5), so that the pK_{BH^+} reported in Table 1 is a thermodynamic pK value. This is important since any subsequently derived H_0 scale depends strongly on both the nature and the pK of the first indicator. The remaining pK values were obtained by the standard overlap method (6) using spectrophotometrically determined log I values (I = ionization ratio = $[BH^+]/[B]$).[2] The overlap and parallelism between successive indicator curves was excellent.

Acidity function values were calculated from the equation $H_0 = pK_{BH^+} - \log I$ using all pK and log I data available for any given acid, using the method given by Katritzky (7). These are listed in Table 2, with two sets of reported values for H_2SO_4 at 25° based on nitroaniline indicators, for comparison. It can be seen that the present H_0 values, entirely based on non-nitro-substituted anilines, are in very good agreement with the previously reported values. The maximum difference, at the highest acidity available for comparison, is only of the order of 0.1 logarithmic unit.[3] This demonstrates that the H_0 scale is independent of the number and type of non-basic substituents, at least up to 45% acid. It seems unlikely that extension of the scale by the present approach would produce variations significantly outside the normally accepted range of uncertainty of acidity function values in more concentrated acids. In any

TABLE 2. Comparison of H_0 values generated by non-nitro- and nitro-substituted anilines for aqueous H_2SO_4 at 25 °C

	H_0 values		
% H_2SO_4	This work	Reference 7	Reference 2*
2	0.51	0.53	0.55
4	0.15	0.20	0.23
6	−0.07	−0.02	0.03
8	−0.27	−0.20	−0.14
10	−0.44	−0.35	−0.31
12	−0.59	−0.50	−0.45
14	−0.72	−0.65	−0.60
16	−0.83	−0.78	−0.72
18	−0.94	−0.92	−0.86
20	−1.06	−1.06	−1.01
22	−1.16	−1.20	−1.15
24	−1.28	−1.34	−1.30
26	−1.39	−1.47	−1.44
28	−1.52	−1.60	−1.58
30	−1.64	−1.73	−1.72
32	−1.76	−1.85	−1.85
34	−1.90	−1.99	−1.99
36	−2.05	−2.12	−2.12
38	−2.20	−2.27	−2.27
40	−2.35	−2.42	−2.41
42	−2.50	−2.60	−2.53
44	−2.63	−2.77	−2.73

*Taken from values reported by Hammett and Deyrup (1) and incorporated into Jorgenson and Harter's revised H_0 scale.

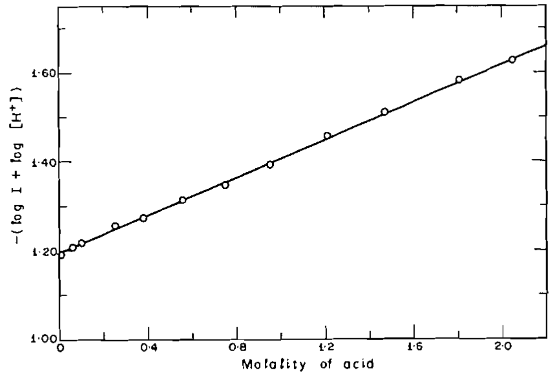

FIG. 1. Extrapolation of ionization data for primary reference indicator (2-chloro-5-trifluoromethylaniline) to obtain pK_a value at infinite dilution.

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[2] Tabulated values can be obtained from the authors on request.

[3] It is noteworthy that differences of this magnitude arise between independently determined H_0 scales even using essentially the same indicator set of nitro-substituted anilines. See, for example, the data of Ryabova and coworkers (8).

event, further extension would be difficult to accomplish experimentally since there are few suitable substituent groups which could achieve the necessary diminutions in base strength comparable with those of dinitro- or trinitroanilines.

It is very reassuring that the H_0 function meets the above test adequately, since if it had not, the damage to the Hammett acidity function concept (even with its presently recognized limited generality) would have been irreparable. It would be of interest to determine whether other acidity functions meet the same critical test as adequately as H_0.

Experimental

2-Chloro-5-trifluoromethylaniline and pentafluoroaniline were commercial samples and were purified by repeated distillation.

2,5-Bis(trifluoromethyl)aniline

1,4-Bis(trifluoromethyl)benzene was nitrated by the method of Ross (9) to yield 2,5-bis(trifluoromethyl)nitrobenzene. The nitro compound was dissolved in ethanol and reduced with hydrogen using Raney nickel as a catalyst. The amine was purified by distillation. Boiling point 50–51 °C (5 mm). Melting point of acetyl derivative, 143–145 °C; literature (9): b.p., 70.5 °C (145 mm). Melting point of acetyl derivative 146.5–147 °C.

4-Bromo-2,3,5,6-tetrafluoroaniline

This compound was obtained by the bromination of 2,3,5,6-tetrafluoroaniline according to the method of Castellano and co-workers (10), and purified by recrystallization and sublimation. Melting point, 60–61 °C; literature (11): 60–61 °C.

2,4-Dichloro-3,5,6-trifluoroaniline

1,3-Dichlorotetrafluorobenzene (supplied by I.C.I. of England) and a slight excess of concentrated aqueous ammonia were added to ethanol to give a homogeneous solution. This was then heated in a sealed autoclave at 140 °C for 24 h. The solution was diluted with water and extracted with methylene chloride. The methylene chloride extract was treated with 60% sulfuric acid and the acid layer diluted with water yielding a white solid. After washing well and drying, the solid was purified by repeated sublimation: m.p. 73–74 °C.

Anal. Calcd. for $C_6H_2Cl_2F_3N$: C, 33.37; H, 0.93; N, 6.48; Cl, 32.83. Found: C, 33.39; H, 0.96; N, 6.29; Cl, 32.68.

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