Solvent Effects in Organic Chemistry. IV. The Failure of Tertiary Aromatic Amines as Hammett Bases

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The applicability of the H_0 function to the protonation behavior of a series of fourteen tertiary amine indicators is tested in aqueous sulfuric acid solutions. Despite the structural similarity of the primary and tertiary amines, it is found that the latter generate their own acidity function (H_0''') falling midway between that for primary anilinium ions (H_0') and that for arylcarbonium ions (H_R'). Apparent average hydration numbers for the primary and tertiary anilinium ions are estimated by Taft's treatment and the difference between them is found to vary considerably with acid strength. A rough accounting for the difference between H_0' and H_0''' is given using Boyd's activity coefficients and some drastic assumptions. Attention is called to the fact that the present H_0 functions may only be used with rigor for nitrated anilines in view of the specific influence of the nature of the basic group and other substituents (especially the nitro group) on activity coefficients of the free and protonated base. Furthermore, the fact that activity coefficient behavior *may be explained* in terms of specific hydration of the weak base cations by no means requires that this is actually the sole or even the main factor. Since the behavior of even rather similar ions and molecules cannot be predicted at present, it is doubtful that a simple solvation theory for widely differing types of Brønsted bases and their ions will be possible. This *caveat* applies with even greater force against the interpretation of transition state behavior. It is suggested, however, that an exact treatment of acid-catalyzed reactions may soon be possible in terms of the activity coefficients of model ions, molecules, and activated complexes.

For over 30 years the main basis for discussion of organic processes in strongly acid solutions has been the H_0 acidity function, invented and developed by Hammett and his students.[2] The H_0 function provides an operational means for estimating how the degree of protonation of a Brønsted base changes as a function of acidity in acidic media of sufficient strength to preclude the use of a pH meter. This is obviously of tremendous value for the quantitative treatment of acid catalysis in strong acids[3-7] and detailed but controversial procedures[6,7] have been developed using correlation of reaction rates with H_0 as a criterion for reaction mechanism. If all Brønsted bases show similar dependence of the activity coefficients of their free base (f_B) and conjugate acid (f_{BH^+}) forms through a given region of acidity, then it is possible to use the H_0 function as a thermodynamically rigorous scale for referring an equilibrium constant measured for the indicator in acid of strength H_0 back to the pK_a that its conjugate acid would have in pure water (the standard state). This is so because H_0 is defined operationally and theoretically as

$$H_0 = pK_a - \log Q = -\log (a_H \cdot f_B / f_{BH^+}) \quad (1)$$

where $Q = (BH^+)/(B)$ is the measured indicator ratio. The test of this assumption is whether the difference between $\log Q$ values for indicators of comparable basicity remains constant through a given range of acidity since it is easily seen from eq. 1 that

$$pK_a^1 - pK_a^2 = \log Q^1 - \log Q^2 \quad (2)$$

for any given value of H_0. For the nitrated anilines used by Hammett and Deyrup[2] this requirement was met quite well for sulfuric acid solutions up to about 65 wt. %. At that point a tertiary aniline was employed in contrast to the primary ones which had

been used (but for one secondary amine and an azo compound) for building the scale through dilute sulfuric acid solutions. The rest of the H_0 scale in strong acid was mostly developed with ketones and it was noted that eq. 2 was not followed so well. This was attributed to the influence of serious medium effects on the spectra rather than to a failure of the fundamental assumption that the activity coefficient ratio f_B/f_{BH^+} was independent of the base involved. Paul and Long,[4] however, suggested that the discrepancy might be due to a breakdown of the activity coefficient postulate and that Brønsted bases of widely different size or structure might follow different acidity functions even though they were of the same charge type. More recently Taft[8] has focused attention on differences between the acidity function behavior of this same tertiary amine and a secondary aniline in contrast to the primary members of the Hammett indicator series. Also, Boyd's[9] direct measurements of the activity coefficients of anilines of different degree and their ions in acid of varying strength leave little doubt that tertiary amines may be expected to follow a somewhat different acidity function than that for the primary anilines.

There are by now numerous cases[10-19] where the protonation equilibria for various kinds of Brønsted bases do not follow the traditional H_0 function[4] exactly, in the sense that a plot of $\log Q$ vs. H_0 does not have the unit slope[20] required by eq. 1. Most of these cases

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(20) Since this is a log–log plot it is not surprising that straight lines are almost invariably obtained. In fact, there are probably few areas of physical organic chemistry where there are so many fortuitous and probably meaningless linear relationships as that of acidity function phenomena.

Compound	Name of compound	Reference for preparation	M.p., °C. Lit.	M.p., °C. Obsd.	λ_{max}, mμ[a]	pK_a[b]
1	N,N-Dimethyl-4-nitroaniline	24	163	164–165	423	+0.66
2	N,N-Diethyl-2,4-dinitroaniline	25	80	79–80	393	+0.21
3	N-(2,4-Dinitrophenyl)piperidine	26	92	93–94	395	−0.38
4	N,N-Dimethyl-2,6-dinitro-4-methylaniline	27	95	96–97	445	−1.66
5	N,N-Dimethyl-2,4-dinitro-1-naphthylamine	28	88	87–88	430	−2.59
6	N,N-Dimethyl-4-chloro-2,6-dinitroaniline	29	111	111–112	452	−3.12
7	N-Methyl-4-nitrodiphenylamine	30	68.5	69–70	420	−3.42
8	N-Methyl-4'-bromo-4-nitrodiphenylamine	31	113.5	114–115	417.5	−4.21
9	N,N-Diethyl-2,4,6-trinitroaniline	32	163	165–166	402	−5.71
10	N-Methyl-2,4-dinitrodiphenylamine	33	167	169.5	397	−6.19
11	N,N-Dimethyl-2,4,6-trinitroaniline	34		140–141	385	−6.55
12	N-Methyl-4-bromo-2',4'-dinitrodiphenylamine	31	140	140	400	−6.93
13	N-Methyl-x',4'-dibromo-2,4-dinitrodiphenylamine	35		162–163	382	−8.17
14	N-Methyl-2,4,2',4'-tetranitrodiphenylamine	36	210	210	410	−10.56

[a] This value is that observed in the pK_a region of acidity. For most compounds it scarcely differs from that in water. [b] Assuming that H_0''' is a thermodynamically exact acidity function.

however involve molecules of quite different size or groups of quite different structure from the anilines used by Hammett. In view of the fact that the primary aniline scale has recently been subjected to a careful re-examination[21] with modern instrumentation,[22] we felt that it would be valuable to develop for comparison an H_0 scale based entirely on tertiary amine indicators. Any differences between the two acidity functions should give a clear indication of how serious an error may be made by assuming that the usual H_0 scale may be used for molecules of slightly different structures. Furthermore, since the differences in activity coefficient behavior of primary, secondary, and tertiary amines have been attributed to different degrees of specific hydration of the corresponding ammonium ions,[8] the divergence of the two acidity functions might supply values which would be useful for quantitative treatments of solvation in aqueous sulfuric acid solutions.

We report here our results for fourteen carefully chosen tertiary amines. Because of the base-strengthening effect of steric inhibition of resonance, it was not possible to use N,N-dialkylated anilines as indicators in strongly acidic media; for example, N,N-dimethyl-2,4,6-trinitroaniline is half-protonated in 66% H_2SO_4. A number of ·N-methyldiphenylamines were therefore employed.

We have considerable reluctance against burdening the literature with a new acidity function. Nonetheless, as will be seen below, the fact is that tertiary amines generate one of their own and in order that it shall not be confused in this paper with the generally accepted H_0 scale[4] for primary anilines we shall name it H_0''' for use in the following discussion and call that of Jorgenson and Hartter H_0'.

Experimental

All of the compounds except indicator 13 were prepared essentially according to published descriptions. These are listed in Table I. In several cases we moderated the reaction of polynitrochlorobenzenes with anilines by dilution with alcohol. Occasionally we used different solvents for recrystallization from

those described in the original articles. Aside from these minor changes the methods were quite straightforward.

N-Methyl-x',4'-dibromo-2,4-dinitrodiphenylamine (Indicator 13).—To a stirred suspension of 10.9 g. (0.040 mole) of N-methyl-2,4-dinitrodiphenylamine in 100 ml. of glacial acetic acid was added 6.4 g. (0.040 mole) of bromine. The solid dissolved to give a clear red solution from which material soon precipitated and another 6.4 g. of bromine was added. The mixture was brought to reflux over the period of an hour and was refluxed for another hour. Upon cooling, 11.0 g. of mixed yellow and reddish orange crystals was obtained. After six recrystallizations from acetic acid and two from ethanol, 3.0 g., a 17% yield, of yellow prisms melting at 162–163° was obtained. Anal. Calcd. for $C_{13}H_9N_3Br_2O_4$: C, 36.22; H, 2.10; Br, 37.08. Found: C, 36.25, 36.45; H, 2.16, 2.04; Br, 36.96, 37.28.

Spectrophotometric Measurements.—Standardized sulfuric acid solutions were prepared and handled according to methods described by Arnett and Wu[23] and indicator solutions were also prepared in the way described there with the exceptions of the following small details. Firstly, indicator stock solutions were prepared in anhydrous methanol or glacial acetic acid and introduced into the aqueous sulfuric acid solution with a 0.25-ml. Hamilton microsyringe (No. 725) equipped with a Chaney adapter to deliver 0.200 ml. An independent experiment showed that an optical density of 0.671 ± 0.001 could be obtained with this instrument for three replica measurements.

As is usual in this field, insolubility of some of the indicators was a problem. To deal with low solubilities, 10-cm. cells were used routinely in the Cary-14 spectrophotometer, the long path length and large molar absorptivity indices of most of the compounds allowing the use of highly dilute solutions (10^{-5}–10^{-6} M). The long path-length cells, however, required preparation of 50-ml. samples with considerable consumption of standard acid. Often it was necessary to warm the acid after the indicator had been added to it and agitate vigorously in order to effect complete solution as shown by a Tyndall beam. In these cases there was no indication of reprecipitation after cooling to room temperature (26 ± 2°) at which all measurements were made. Several other indicators not mentioned here were rejected because of insolubility. Instability was not a problem as was shown by repeated scans of the acid solutions of the indicators.

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TABLE II
Spectral Data for Different Indicators at Different Acidities

1. N,N-Dimethyl-4-nitroaniline
M of HCl   D at 423 mμ   log Q

	D at 423 mμ	log Q
H_2O	0.994	
0.0100	.951	−1.35
.0400	.832	−0.71
.0600	.761	− .51
.1000	.670	− .32
.2000	.482	+ .03
.400	.286	+ .39
.600	.187	+ .64
1.000	.097	+ .97
6.0	.000	

% H_2SO_4		
H_2O	0.996	
1.02	.602	−0.18
1.51	.500	.00
2.60	.343	+ .28
3.35	.256	+ .46
4.92	.178	+ .66
8.01	.092	+ .99
8.99	.074	+1.10
9.93	.066	+1.15
13.51	.029	+1.52
30.09	.000	

2. N,N-Diethyl-2,4-dinitroaniline
% H_2SO_4 D at 393 mμ   log Q

% H_2SO_4	D at 393 mμ	log Q
H_2O	0.990	
2.60	.570	−0.13
3.35	.496	− .00
4.92	.386	+ .19
8.01	.216	+ .55
9.93	.145	+ .71
13.51	.080	+1.06
16.76	.055	+1.23
19.12	.030	+1.51
52.35	.000	

3. N-(2,4-dinitrophenyl)-piperidine
% H_2SO_4 D at 395 mμ   log Q

% H_2SO_4	D at 395 mμ	log Q
H_2O	0.764	
2.60	.660	−0.80
3.35	.627	− .66
4.92	.568	− .46
8.01	.395	− .03
9.93	.309	+ .17
13.51	.182	+ .51
15.77	.132	+ .69
19.12	.068	+1.02
20.79	.058	+1.10
23.15	.032	+1.39
52.07	.002	

4. N,N-Dimethyl-2,6-dinitro-4-methylaniline
% H_2SO_4 D at 445 mμ   log Q

% H_2SO_4	D at 445 mμ	log Q
H_2O	0.837	
9.93	.795	−1.28
13.51	.725	−0.81
16.76	.635	− .50
19.12	.535	− .25
20.76	.452	− .07
23.15	.355	+ .13
26.85	.205	+ .49
30.06	.125	+ .76
34.98	.035	+1.36
52.07	.000	

5. N,N-Dimethyl-2,4-dinitro-1-naphthylamine
% H_2SO_4 D at 430 mμ   log Q

% H_2SO_4	D at 430 mμ	log Q
H_2O	0.903	
19.12	.834	−1.07
22.75	.789	−0.83
26.85	.660	− .42
30.09	.548	− .17
32.23	.460	+ .00
34.98	.298	+ .33
36.59	.236	+ .49
37.85	.211	+ .56
39.94	.138	+ .80
41.56	.106	+ .96
45.15	.061	+1.29
47.87	.042	+1.55
52.35	.023	+2.25
67.47	.018	

6. N,N-Dimethyl-4-chloro-2,6-dinitroaniline
% H_2SO_4 D at 452 mμ   log Q

% H_2SO_4	D at 452 mμ	log Q
H_2O	0.765	
26.85	.683	−0.92
30.06	.651	− .76
32.23	.590	− .53
34.98	.476	− .22
37.85	.315	+ .16
39.94	.241	+ .34
41.56	.199	+ .45
44.19	.105	+ .80
47.26	.052	+1.14
51.89	.015	+1.70
67.47	.000	

7. N-Methyl-4-nitrodiphenylamine
% H_2SO_4 D at max.   log Q

% H_2SO_4	D at max.	log Q
H_2O	0.950	
29.62	.854	−0.95
32.23	.820	− .80
34.98	.711	− .47
36.49	.640	− .31
37.85	.568	− .17
38.71	.529	− .10
39.98	.458	+ .04
41.56	.371	+ .20
45.15	.186	+ .63
47.26	.126	+ .83
49.76	.067	+1.15
52.35	.029	+1.58
63.33	.005	

8. N-Methyl-4′-bromo-4-nitrodiphenylamine
% H_2SO_4 D at max.   log Q

% H_2SO_4	D at max.	log Q
H_2O	0.965	
38.71	.855	−0.89
41.56	.795	− .67
45.55	.553	− .13
47.26	.466	+ .03
47.87	.440	+ .08
49.76	.308	+ .33
52.35	.203	+ .57
55.19	.114	+ .87
57.33	.061	+1.17
59.25	.037	+1.40
68.31	.000	

9. N,N-Diethyl-2,4,6-trinitroaniline
% H_2SO_4 D at 402 mμ   log Q

% H_2SO_4	D at 402 mμ	log Q
33.96	0.974	
52.35	.864	−0.90
53.84	.848	− .83
55.19	.757	− .54
57.33	.620	− .24
58.08	.569	− .15
59.54	.402	+ .15
61.92	.231	+ .51
64.81	.097	+ .96
67.47	.034	+1.44
71.34	.008	+2.08
82.42	.000	

10. N-Methyl-2,4-dinitrodiphenylamine
% H_2SO_4 D at max.   log Q

% H_2SO_4	D at max.	log Q
34.98	0.833	
52.35	.805	−1.46
53.84	.790	−1.26
56.04	.751	−0.96
57.33	.685	− .66
59.54	.591	− .39
61.92	.419	.00
63.33	.315	+ .22
64.81	.209	+ .48
67.47	.080	+ .99
71.34	.025	+1.56
96	.003	

11. N,N-Dimethyl-2,4,6-trinitroaniline
% H_2SO_4 D at 385 mμ   log Q

% H_2SO_4	D at 385 mμ	log Q
38.71	0.956	
58.08	.875	−1.03
59.54	.821	−0.78
62.17	.635	− .29
63.33	.558	− .14
64.81	.421	+ .12
67.47	.208	+ .58
68.31	.148	+ .78
71.34	.055	+1.33
72.86	.038	+1.56
96	.013	

12. N-Methyl-4′-bromo-2,4-dinitrodiphenylamine
% H_2SO_4 D at max.   log Q

% H_2SO_4	D at max.	log Q
41.56	0.907	
59.54	.854	−1.20
61.92	.787	−0.81
63.33	.708	− .55
64.81	.591	− .27
67.47	.346	+ .22
68.05	.290	+ .34
71.34	.098	+ .94
72.86	.048	+1.31
73.88	.033	+1.51
75.65	.021	+1.77
96	.006	

13. N-Methyl-x′,4′-dibromo-2,4-dinitrodiphenylamine
% H_2SO_4 D at max.   log Q

% H_2SO_4	D at max.	log Q
57.33	0.946	
64.81	.916	−1.48
65.63	.889	−1.19
68.31	.788	−0.69
70.09	.698	− .44
71.34	.631	− .30
73.55	.462	+ .03
73.88	.408	+ .13
75.91	.225	+ .52
77.46	.154	+ .73
79.44	.057	+1.25
96	.007	

14. N-Methyl-2,4,2′,4′-tetra-nitrodiphenylamine
% H_2SO_4 D at max.   log Q

% H_2SO_4	D at max.	log Q
68.31	0.965	
75.65	.958	−2.13
79.44	.890	−1.07
82.42	.828	−0.78
85.16	.604	− .22
86.25	.511	− .04
87.72	.389	+ .18
88.00	.340	+ .27
91.87	.132	+ .83
93.30	.088	+1.04
94.85	.050	+1.34
100	.008	

Results

Calculations.—Values for the ionization ratio Q were obtained from the optical density D of the solution where partial ionization is occurring and optical density values D_B and D_{BH^+} for solutions of the same stoichiometric concentration of indicator in dilute acid (at least two H_0 units more positive than the pK_a of the indicator) and concentrated acid (at least two H_0 units more negative than the pK_a of the indicator).

$$Q = (BH^+)/(B) = (D_B − D)/(D − D_{BH^+}) \quad (3)$$

For all of the compounds described here the absorption peaks listed in Table I were very broad and almost free of wave length shifts due to medium effects in the pK_a
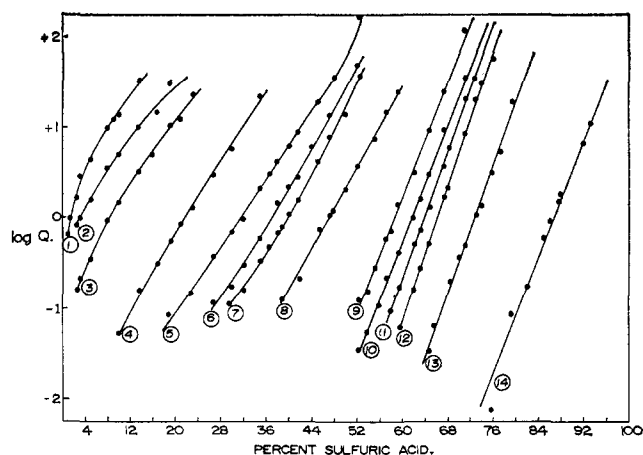
Figure 1.

region. This is most important since it means that none of the measurements was changed by more than 0.10 pK_a unit by the use of the corrections for shifts which have recently been discussed by Noyce and Jorgenson.[37] They are therefore practically free of interpretive ambiguities although we have used both treatments for different indicators. The acidity function scale for the tertiary indicators was anchored to the standard state in water by means of a plot of log $(BH^+)/(B)$ — log (H^+) vs. (HCl) to give the thermodynamic pK_a of N,N-dimethyl-4-nitroaniline. This was then used with the indicator ratios of the various indicators in acid of increasing strength to calculate their pK_a's by means of eq. 2. As may be seen from Fig. 1 the overlap principle holds well for these compounds.

The H_0 scale for tertiary indicators (H_0''', Table III) was set up by calculation of values at different weight per cent sulfuric acid solutions from plots of log Q vs. per cent sulfuric acid for each indicator and then application of eq. 1 to the smoothed values of log Q for integral values of the percentage. In regions of overlap

TABLE III

HAMMETT ACIDITY SCALE (H_0''') FOR TERTIARY ANILINES

% H_2SO_4	H_0'''	% H_2SO_4	H_0'''	% H_2SO_4	H_0'''
1.00	+0.84	30.00	−2.44	62.00	−6.22
1.50	+ .66	32.00	−2.63	64.00	−6.54
2.60	+ .36	34.00	−2.83	66.00	−6.91
4.00	+ .14	36.00	−3.04	68.00	−7.28
6.00	− .11	38.00	−3.25	70.00	−7.65
8.00	− .34	40.00	−3.46	72.00	−8.01
10.00	− .53	42.00	−3.67	74.00	−8.35
12.00	− .69	44.00	−3.89	76.00	−8.71
14.00	− .88	46.00	−4.12	78.00	−9.07
16.00	−1.09	48.00	−4.33	80.00	−9.44
18.00	−1.28	50.00	−4.54	82.00	−9.80
20.00	−1.47	52.00	−4.75	84.00	−10.13
22.00	−1.66	54.00	−4.97	86.00	−10.47
24.00	−1.86	56.00	−5.24	88.00	−10.81
26.00	−2.06	58.00	−5.58	90.00	−11.14
28.00	−2.25	60.00	−5.91	92.00	−11.44
				94.00	−11.74

where there were H_0 values derived from several indicators for a given strength of acid they were weighted in proportion to how close the acidity was to the pK_a of each indicator and the average was taken. In no case

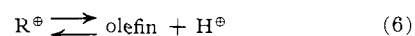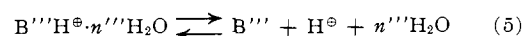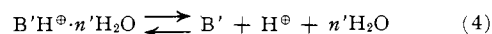(37) D. S. Noyce and M. J. Jorgenson, J. Am. Chem. Soc., **84**, 4312 (1962).

was the range of differences greater than 0.10 H_0 unit.

Discussion

Plainly the protonation of our series of tertiary amines is not exactly expressable in terms of the H_0' function. A plot of H_0''' vs. H_0' as abscissa gives a nearly linear curve with a gentle upward sweep whose average tangent is about 1.3. The failure of the Hammett activity coefficient postulate in this case although not large is surely sufficient to raise serious questions about the precise application of the traditional H_0 function[4] to molecules other than nitrated primary aromatic amines. If tertiary aromatic amines do not follow the H_0 function exactly, why should Brønsted bases of other classes be expected to? The H_0 function has served as a useful first-order approximation for Brønsted bases in general. Closer examination suggests that each functional class has its own acidity function as has been seen here for the tertiary amines and elsewhere for the azulenes,[13] pyrroles,[18] amides,[16,17] and aliphatic ethers.[19] Within these classes it is likely that ultimately each compound has its own acidity function which in turn depends on the solvent system.

Hydration Treatment.—Several workers[38-41] have considered possibilities for expressing the traditional H_0 function in terms of the hydration of the proton. The most ambitious of these treatments is a computer calculation of the varying degrees of proton hydration over the entire aqueous sulfuric acid range.[40] It is expected that the hydration factors for adjacent indicators and their ions are so similar in a series of well matched indicators *that they may be ignored as long as one is not really concerned with the actual hydration number of the proton* (a useful but elusive notion). An exact solution of the problem, however, requires knowledge of the hydration numbers of the indicator species themselves through the acid range under study. Although this limitation has been noted by most of the above authors, it has usually been ignored in practice because it was felt that little error would be introduced by neglecting it. Our results show that these calculations may be sensitive to the choice of indicator type so that different apparent hydration factors for the proton in acid of given strength will result because the $f_B f_{H(OH_2)_n^+}/f_{BH^+}$ term[40] may vary with the indicator structure.

The hydration approach can be used with more rigor for explaining differences between the protonation behavior of different classes of weak neutral bases if it is assumed that all of the activity coefficient differences between the classes are due to hydration factors. At present there is no way of testing this assumption. Although we doubt that it is entirely true, we will now examine the consequence of applying it to the case in point. Following Taft's lead,[8] let us consider the disparity between H_0' and H_0''' in terms of the equations

$$B'H^{\oplus} \cdot n'H_2O \rightleftharpoons B' + H^{\oplus} + n'H_2O \qquad (4)$$

$$B'''H^{\oplus} \cdot n'''H_2O \rightleftharpoons B''' + H^{\oplus} + n'''H_2O \qquad (5)$$

$$R^{\oplus} \rightleftharpoons \text{olefin} + H^{\oplus} \qquad (6)$$

(38) (a) R. P. Bell and K. N. Bascombe, Discussions Faraday Soc., **24**, 158 (1957); (b) P. A. H. Wyatt, ibid., **24**, 162 (1957).

(39) C. Perrin, J. Am. Chem. Soc., **86**, 256 (1964).

(40) H. B. Dunford, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.

(41) E. Högfeldt, Acta Chem. Scand., **14**, 1627 (1960); **16**, 1054 (1962).

TABLE IV

ACIDITY FUNCTIONS, ACTIVITY COEFFICIENTS, AND HYDRATION FACTORS

% H₂SO₄	$H_0'{}^a$	H_0'''	$H_R'{}^b$	log^c a_{H_2O}	$n'{}^d$	$n'''{}^e$	$n' - n'''{}^f$	log $f_{BH}+'$	log $f_{BH}+'''$	log f_R+	\multicolumn{2}{c}{$-H_0' - H_0'''$—}	\multicolumn{2}{c}{$-H_R' - H_0'''$—}
											Exptl.	Calcd.^{g}	Exptl.	Calcd.
10	−0.31	−0.53	−0.70	−0.02	13.4	6.8	9.5	−0.28	−0.34	−0.40	0.22	0.06	−0.17	−0.06
20	−1.02	−1.47	−1.86	− .06	12.8	5.4	5.4	− .04	− .30	− .48	.45	.26	− .39	− .18
30	−1.70	−2.44	−3.10	− .12	8.2	4.4	3.2	+ .22	− .32	− .82	.74	.54	− .66	− .50
40	−2.43	−3.46	−4.55	− .24	4.1	2.7	1.6	+ .28	− .50	−1.16	1.03	.78	−1.09	− .66
50	−3.37	−4.54	−6.15	− .44	2.6	2.7	0	+ .10	−1.04	−2.46	1.17	1.14	−1.61	−1.42
60	−4.46	−5.91	−8.13	− .76	1.9	0.9	1.1	− .56	−1.70	−3.56	1.45	2.26	−2.22	−1.86
70	−5.80	−7.65	−10.18	−1.37	0.6	0.2	0.41				1.85		−2.53	
80	−7.34	−9.44	−11.84	−2.28			.24				2.10		−2.40	
90	−8.93	−11.14	−13.23	−3.49			.06				2.21		−2.19	

^{a} Ref. 21. ^{b} Ref. 9. ^{c} V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951). ^{d} Calculated from eq. 11 by plotting $H_R - H_0'$ *vs.* log a_{H_2O}. ^{e} Calculated from eq. 11 by plotting $H_R - H_0'''$ *vs.* log a_{H_2O}. ^{f} Calculated from eq. 13 by plotting $H_0' - H_0'''$ *vs.* log a_{H_2O}. ^{g} Calculated from eq. 13.

for the equilibria of primary (B′) and tertiary (B‴) amines and olefins with their conjugate acids in aqueous acid in which account is taken of possible differences in degree of hydration for the two types of ammonium ions.[7,8] It is also assumed that the carbonium ion from protonation of the olefin is not hydrated at specific groups,[8,42] although it is certainly stabilized by solvation. We also neglect solvation of nonionic species here although this is an unjustified simplification.[9] From eq. 1 we arrive immediately at the three expressions for corresponding acidity functions if allowance is made for possible differences in hydration of the onium ions

$$H_0' = -\log a_{H^\oplus} - \log f_{B'} + \log f_{B'H^\oplus \cdot n'H_2O} - n' \log a_{H_2O} \quad (7)$$

$$H_0''' = -\log a_{H^\oplus} - \log f_{B'''} + \log f_{B'''H^\oplus \cdot n'''H_2O} - n''' \log a_{H_2O} \quad (8)$$

$$H_{R'} = -\log a_{H^\oplus} - \log f_{olefin} + \log f_{R^\oplus} \quad (9)$$

$$H_R = -\log a_{H^\oplus} - \log f_{ROH} + \log f_R+ + \log a_{H_2O} \quad (10)$$

One may now subtract eq. 7 or 8 from 10 and obtain generally (dropping primes)

$$H_R - H_0 = (\log f_B - \log f_{ROH}) + (\log f_{R^\oplus} - \log f_{BH^\oplus \cdot nH_2O}) + (n + 1) \log a_{H_2O} \quad (11)$$

Similarly we may subtract eq. 8 from 7 and get

$$H_0' - H_0''' = (\log f_{B'''} - \log f_{B'}) + (\log f_{B'H^\oplus \cdot n'H_2O} - \log f_{B'''H^\oplus \cdot n'''H_2O}) + (n''' - n') \log a_{H_2O} \quad (12)$$

If it is assumed in each case that the activity coefficient terms for the various bases and their ions are nearly constant over a given short range of acidity, the slope of a plot of $H_R - H_0$ or $H_0' - H_0'''$ *vs.* log a_{H_2O} will give a measure of the apparent average degree of hydration of the ammonium ion in the acid solution under consideration from eq. 11. Similarly, eq. 12 yields the apparent average differences in degrees of hydration for primary and tertiary amines in acid of the given H_0' and H_0'''. In Table IV are found typical values for n', n''', and $(n' - n''')$ from application of these expressions or alternatively by subtraction of eq. 7 or 8 from 9. It will be seen that there is the required agreement although it is rough because of the difficulty in drawing tangents to the curves.

When $(H_0' - H_0''')$ or $(H_R' - H_0''')$ are plotted against log a_{H_2O} strongly curved lines are obtained showing that by this treatment the apparent hydration numbers of tertiary ammonium ions are constantly changing with respect to those of olefin carbonium ions or primary ammonium ions as the acidity changes. In strong acid the hydration properly becomes low as "free" water becomes progressively less available, while in dilute solutions the hydration factors become indeterminate as all terms approach zero. Plots of the above functions *vs.* log molarity of water, log molarity of sulfuric acid, and log mole fraction of both solvent components are likewise strongly curved.

Boyd[9] has recently shown by direct observation that there is a considerable difference in the activity coefficient behavior between carbonium ions and the ammonium ions derived from primary and tertiary amines. He also finds that serious differences exist between the activity coefficient behaviors of free indicator bases bearing different numbers of nitro groups as the acidity of the medium changes. These variations between bases carrying different functional groups were first noted by Hammett and Chapman,[43] examined further by Deno and Perrizzolo,[44] and have been investigated widely in our laboratory.[45] We find that almost all classes of weak bases bearing an unsaturated function show the Hammett–Chapman effect. Therefore, serious errors may result from assuming that the entire difference between the acidity function behavior of different classes of weak bases can be dealt with through the activity coefficients of the cations. It is especially unfortunate that the indicators which have been used to construct the present H_0 acidity functions carry nitro groups which are known to show serious Hammett–Chapman effects. We have attempted recently to develop a series of primary aniline indicators using strongly negative groups other than nitro to reduce basicity, but have failed so far because of poor solubility, anomalous spectra, or inability of the groups to depress basicity far enough. It is highly possible that the nitroanilines are such weak bases partly because of the ability of the nitro group to be strongly solvated in medium strength acid. If this is the case they are a poor model for comparison to unnitrated molecules.

Boyd[9] used his activity coefficient data to account fairly well for the difference between H_0, H_-, and H_R'. In order to apply his treatment to the H_0' and H_0''' scales through eq. 11 and 12 we should have activity

(42) E. M. Arnett and R. D. Bushick, *J. Am. Chem. Soc.*, **86**, 1564 (1964).

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

(44) N. Deno and C. Perrizzolo, *ibid.*, **79**, 1345 (1957).

(45) J. N. Anderson, unpublished work.

coefficient data for a primary and tertiary nitrated aniline, a triarylcarbinol, and the corresponding anilinium and carbonium ions. Unfortunately, Boyd did not report the needed data for a tertiary nitrated aniline or the corresponding ion. The best that we can do at present is to make the following substitution: for $B'H^\oplus$ the anilinium ion, for $B'''H^\oplus$, the N,N-dimethylanilinium ion, and for $R^\oplus$ the trianisylcarbonium ion. Secondly, we will assume that the terms involving activity coefficients of the free bases are negligible and that they are hydrated to the same degree. On the average, the tertiary amine indicators carry one more nitro group than the corresponding primary one used over the same acidity range and this may cause serious drift of the $(\log f_{B'''} - \log f_{B'})$ term. However, a careful examination of Fig. 1 in this paper and Fig. 1 in that of Jorgenson and Hartter[21] shows no sharp variation in slope between adjacent indicators carrying different numbers of nitro groups. This suggests that the effect of a nitro group to decrease the activity coefficient of a free amine base is nearly compensated in dilute acid by an increase in activity coefficient of the conjugate acid ion, a phenomenon which has been noted by Boyd[9] for several cases.

Our equation for calculating the difference between the two amine acidity functions then will be

$$H_0' - H_0''' = (\log f_{B'H^\oplus} - \log f_{B'''H^\oplus}) \quad (13)$$

The activity coefficients listed by Boyd for the pentacyanopropenide salts of the anilinium and carbonium ions are mean ionic values so that

$$f(BH^\oplus, PCP^\ominus) = f_\pm = \sqrt{f_{BH^\oplus} \cdot f_{PCP}} \quad (14)$$

and

$$\log f_{BH^\oplus} + \log f_{PCP^\ominus} = 2 \log f(BH^\oplus, PCP^\ominus) \quad (15)$$

Since the $\log f_{PCP^\ominus}$ term accompanies both $\log f_{B/H^\oplus}$ and $\log f_{B'''H^\oplus}$, it drops out of their difference and $\log f_{BH^\oplus}$ can be obtained from Boyd's tabulation merely by doubling his value for $\log f(BH^\oplus, PCP^\ominus)$. Furthermore, since his activity coefficients refer to the hydrated ions, there is no way of telling how much of the activity coefficient change is due to the hydration factor and how much to other contributions related to their sizes, shapes, and degrees of dielectric solvation.[42] It is seen from Table IV that agreement between $H_0' - H_0'''$ as observed and that which is calculated in this way is at best only qualitative which is not surprising in view of the approximations we have used. Considerably better agreement is found if Boyd's data for p-nitroaniline are used for f_{BH^+}.[46]

General Comments on Acidity Functions.—The use of acidity functions to calculate hydration factors, while interesting, is not at present of immediate value for the main use to which they have been put—as thermodynamic standards for interpreting equilibria and kinetics involving the protonation of weak bases. It is now recognized by most workers in the field that such interpretations may be dangerous if the traditional H_0 function cannot be generally used with confidence for all classes of Brønsted bases. The importance of the results presented here is to show how sensitive the H_0 scale may be to the structure of the base. There seems

to be no way of predicting at the moment in terms of hydration factors whether a given class of weak bases will follow the H_0 scale or how seriously its members will depart from it. Further research in this area should soon begin to clarify the problem. It is now plain that the traditional H_0 function, in the last analysis, can only be applied with confidence to nitrated primary anilines. Each Brønsted base acidity function depends on the type of group being protonated and the presence or absence of other specifically solvated groups in the basic molecule. The specific interactions of these groups with the acidic medium will influence the activity coefficients of both the free base and its cation. It is worth noting that the difference between acidity functions for anilines of different degrees carrys over into completely nonaqueous solvents.[47] Not only must the mode of ion solvation depart considerably from hydration under such conditions but often the protonated species exists primarily in a tight ion pair.[48-50] Oddly enough, it seems that acidity functions in nonaqueous media are often a good deal better than might be expected just as those in aqueous media are probably not as good as has generally been supposed.

In view of the complications involving the nitrated aniline indicators, we prefer at present to follow Taft's suggestion that the H_R carbonium ion acidity functions are a safer standard of reference than the H_0 ones. This suggestion is based in the first instance on the fine overlap obtained for the latter by Deno and his co-workers[51] and later by Arnett and Bushick.[42] It has just received powerful support from Taft's ability[52] to obtain direct free energies of ionization for triarylcarbinols using a carbonium ion cell with acetonitrile as solvent. The $\Delta F°$ values obtained in this way agree remarkably well with those obtained by Deno[51] in aqueous acid using the overlap method. This success is a strong argument against Högfeldt's recent criticism[41] of the H_R function on the grounds that it does not conform to a hydration equation used by him. The unnitrated triarylcarbonium ions are of nearly uniform size and are probably almost free of specific solvation to functional groups. Long[53] has suggested that an even better carbonium ion acidity function derived from azulene bases is preferable.

At this time it seems unlikely to us that a simple structural theory of solvation for ions, molecules, and transition states may be developed. It is seen from Table IV that the integral differences in degrees of hydration observed by Taft[8] for secondary and tertiary amines in moderately concentrated acid are an artifact resulting from the strength of acid for which the scanty data used by him were available. The apparent average hydration numbers which we get from the Taft treatment of our data for the different kinds of ammonium ions vary greatly and in different ways with the strength of acid employed. If the behavior of ac-

(46) We are grateful to Professor Taft for pointing this out.

(47) N. F. Hall and W. F. Spengeman, *J. Am. Chem. Soc.*, **62**, 2487 (1940). It is interesting that in acetic acid–sulfuric acid mixtures studied by these authors the slope of log Q for N,N-dimethyl-2,4,6-trinitroaniline *vs. H₀* for the primary anilines used by them is the same (1.5) within experimental error as that found by us in aqueous sulfuric acid.

(48) L. C. Smith and L. P. Hammett, *ibid.*, **67**, 23 (1945).

(49) H. Van Looy and L. P. Hammett, *ibid.*, **81**, 3872 (1959).

(50) E. M. Arnett and C. F. Douty, *ibid.*, **86**, 409 (1964).

(51) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

(52) E. D. Jenson and R. W. Taft, *ibid.*, **86**, 116 (1964).

(53) F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964).

tivity coefficients for quite similar ions and molecules cannot be accounted for in simple hydration terms, there is no reason why this approach should be successful when applied to activated complexes for the discrimination of mechanisms of acid catalysis.

Although recent studies on the failure of the activity coefficient postulate cannot help but undermine our confidence in many of the uses to which acidity functions have been put, the situation in the long run is far

from hopeless. As more research is done on direct measurements of activity coefficients and equilibrium constants it should be possible in suitable cases to derive exact treatments or very good estimates for the acid-catalyzed behavior of various substrates under different mechanisms. It may also be possible to find acidic media in which the activity coefficient postulate does hold. We are investigating both of these possibilities.

Steric Effects of the Nitro Group on the Uncatalyzed Halogenation of Methylbenzenes[1]

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Bromination and chlorination rates of the nitro derivatives of mesitylene, isodurene, and durene have been measured in nitromethane and acetic acid solutions, respectively. In all three compounds the deactivating effect of the nitro group is very strong, i.e., in the order of 6 to 7 powers of ten. However, with the aid of free energy relationships, the reactivity of nitrodurene (p-NO$_2$) with molecular halogen is found to be higher than that predicted from the electrical effect assumed for the nitro group in electrophilic substitutions. The acceleration involves only small factors and is ascribed to steric inhibition of resonance of the nitro group. With nitromesitylene and nitroisodurene (m-NO$_2$) a slight increase in deactivation is observed instead. Here, the expectedly minor effect of steric inhibition of resonance is possibly overshadowed by increased hindrance to the approach of the reagent at the reaction center. It is believed that a precise calculation of the fractional loss of resonance for the p-NO$_2$ group is prevented by the latter effect and/or some uncertainty in the available reference parameters involved in it.

Introduction

In a previous paper[2] it was pointed out that there has been a tendency in the literature to overestimate in some cases, such as the dinitration of mesitylene, the effects of steric inhibition of resonance (hereafter indicated as s.i.r.) on chemical reactivity. Use of free energy relationships has yielded a simple tool to appraise such effects in a quantitative manner.[3,4] One of the original objectives of our studies on the reactivity of methylbenzenes was the investigation of s.i.r. effects on the rate of electrophilic substitution of nitrodurene; this was made possible by the applicability of free energy relationships in this and similar systems. In this paper we report the relative rates of uncatalyzed bromination and chlorination of the nitro derivatives of durene, mesitylene, and isodurene. It will be seen that the results are suggestive of some of the main kinds of molecular deformations to be expected from these overcrowded systems and complement the information obtained from the study of other properties.[3,5-8]

Results

Earlier attempts[9] to measure the bromination rates of nitrodurene in acetic acid showed the high inertness of this compound in this solvent. However, in nitromethane solution, all the nitropolymethylbenzenes examined could be made to react with bromine at a

measurable rate in the concentration range 0.035 to 0.055 M. Autocatalytic phenomena began to appear beyond 10% change in the case of nitromesitylene and nitroisodurene but before such a percentage was reached in the case of nitrodurene. Therefore, for the latter compound the first 5 to 6% change was considered as the portion of reaction useful to the present study and the t_{10} values were obtained by extrapolation as in the case of cyanodurene.[10] The results are reported in Table I. The probable error for the relative rate of nitrodurene is higher (15%) than for most investigated rates (4%)[11a] but sufficiently small with respect to the magnitude of the steric effect to be discussed below. Chloromesitylene was used as the compound of intermediate reactivity to assess the R and k/k_0 values as given in Table I. The results on nitrodurene were found to be in essential agreement with those obtained

TABLE I

KINETIC DATA FOR THE UNCATALYZED BROMINATION OF SOME NITROPOLYMETHYLBENZENES IN NITROMETHANE SOLUTION AT 30.0°

Aromatic compound	Substituent	Concn.,[a] M	t_{10},[b] min.	R^c	10^{7} $(k/k_0)^d$
3-Nitrodurene	p-NO$_2$	0.055	30,000	7.34×10^{-4}	14.67
2-Nitromesitylene	m-NO$_2$	.055	7,410	2.97×10^{-3}	
4-Nitroisodurene	m-NO$_2$	.035	9,000	6.67×10^{-3}	0.944[e]
		.055	3,300		
2-Chloromesitylene		.035	3.1	20.6[f]	
		.055	1.0[g]		

[a] Molarity in both reactants. [b] Time at 10% reaction. [c] Rate relative to durene (= 1000). Mean values obtained with the aid of determinations on chloromesitylene and nitroisodurene as the compounds of intermediate reactivity in either 0.035 or 0.055 M solution. [d] Reactivity relative to the parent hydrocarbon (ref. 11a). [e] Mean of the reactivity values of 2-nitromesitylene and 4-nitroisodurene. [f] For this value see ref. 11a. [g] See ref. 4.

(1) Substitution in Polymethylbenzenes, part XVII. Part XVI in ref. 10.

(2) G. Illuminati, Nature, 179, 780 (1957).

(3) R. W. Taft, Jr., and H. D. Evans, J. Chem. Phys., 27, 1427 (1957).

(4) G. Illuminati, J. Am. Chem. Soc., 80, 4945 (1958).

(5) W. G. Brown and H. Reagan, ibid., 69, 1032 (1947); J. Trotter, Can. J. Chem., 37, 1487 (1959).

(6) P. Diehl and G. Svegliardo, Helv. Chim. Acta, 46, 461 (1963); E. Bullock, Can. J. Chem., 41, 711 (1963).

(7) B. M. Wepster, Rec. trav. chim., 76, 335 (1957).

(8) (a) A. C. Littlejohn and J. W. Smith, J. Chem. Soc., 2476 (1957); (b) H. Kofod, L. E. Sutton, P. E. Verkade, and B. M. Wepster, Rec. trav. chim., 78, 790 (1959).

(9) G. Illuminati, Gazz. chim. ital., 83, 905 (1953).

(10) G. Illuminati, J. Am. Chem. Soc., 80, 4941 (1958).

(11) (a) G. Illuminati and G. Marino, ibid., 78, 4975 (1956); (b) unpublished studies.