Kinetic Acidity Function $H_c^{\ddagger}$. 1. Definition of the Function in Aqueous Sulfuric Acid and Its Applicability to Acid-Catalyzed Hydrogen Exchange of the Ring Protons of Aromatic Molecules, and Protonation of Carbon–Carbon Double and Triple Bonds[1]

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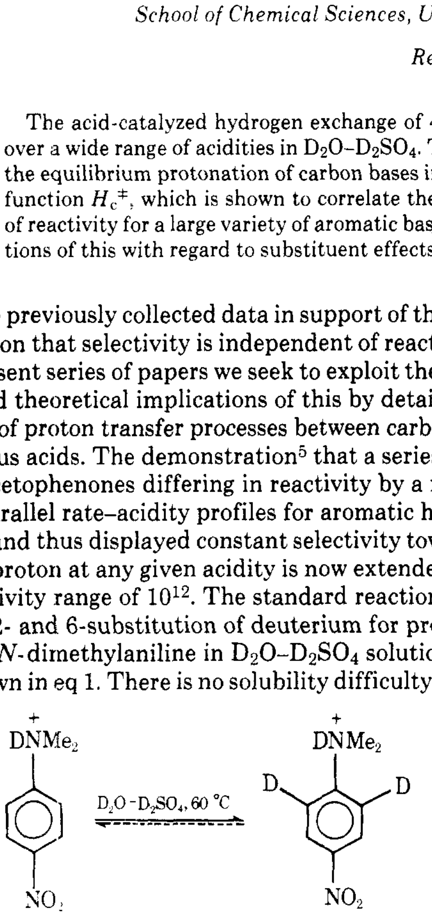
The acid-catalyzed hydrogen exchange of 4-nitro-*N*,*N*-dimethylaniline in the 2,6 positions has been measured over a wide range of acidities in D_2O–D_2SO_4. This enables the extension of the H_c acidity function, which describes the equilibrium protonation of carbon bases into the high acidity region, and also the definition of a kinetic acidity function $H_c^{\ddagger}$, which is shown to correlate the selectivity of proton-transfer reactions to carbon over a wide range of reactivity for a large variety of aromatic bases, as well as for carbon–carbon double and triple bonds. The implications of this with regard to substituent effects and Marcus theory are examined.

We have previously collected data in support of the general contention that selectivity is independent of reactivity.[3–5] In this present series of papers we seek to exploit the experimental and theoretical implications of this by detailed consideration of proton transfer processes between carbon bases and aqueous acids. The demonstration[5] that a series of substituted acetophenones differing in reactivity by a factor of 10^3 had parallel rate–acidity profiles for aromatic hydrogen exchange and thus displayed constant selectivity toward the hydrated proton at any given acidity is now extended over a total reactivity range of 10^{12}. The standard reaction chosen is that of 2- and 6-substitution of deuterium for protium in 4-nitro-*N*,*N*-dimethylaniline in D_2O–D_2SO_4 solutions at 60 °C, as shown in eq 1. There is no solubility difficulty down to about 20% acid, despite the relatively high concentrations required for the NMR determinations, and the observed rate variation is small over the 20–100% acidity range covered, since the increase in rate due to acid catalysis is largely compensated by the concomitant decrease in concentration of reactive free base. The aromatic hydrogen exchange of 4-methoxy-, 4-methyl-, 4-hydroxybenzaldehyde, and 2,4-dinitroaniline has also been studied. These data, together with appropriate literature data, enable us to demonstrate the validity of the standard reaction in determining the selectivity pattern for exchanges in aromatic and heteroaromatic rings bearing a wide range of different substituent types, as well as in carbon–carbon double- and triple-bonded base systems.



(1)

Consideration of the results illustrates well the incompatability of theories which demand on the one hand a connection between selectivity and reactivity, and thus nonlinear free energy relationships, with the resultant picture of a progressively more reactant like transition state as rate increases, and on the other selectivity independent of reactivity, linear free energy relationships, and transition state structure *apparently* invariant with reaction rate.[3,4]

Experimental Section[6]

Materials. Sulfuric acid, sulfuric acid-d_2, water-d_2, 4-methoxy-, 4-methyl-, and 4-hydroxybenzaldehyde, 2,4-dinitroaniline, 1,1-diphenylethylene, 1,3-dimethoxybenzene, and 2,5-dimethoxytoluene were available commercially, and the latter compounds were recrystallized or distilled under reduced pressure. Melting points or boiling points agreed with literature values.

pK_a and Rate Determinations. The pK_a values of the benzaldehydinium ions were evaluated by both UV[5] and NMR[5,6] techniques in H_2O–H_2SO_4 solutions. In the latter case the chemical shift differences of the aromatic resonances were monitored. The results of the pK_a determinations are shown in Table I. The two methods show reasonable agreement, but the UV results are undoubtedly more accurate and are thus used in the subsequent calculations.

The determination of the equilibrium protonation patterns of 1,1-diphenylethylene, 1,3-dimethoxybenzene, and 2,6-dimethoxytoluene was also attempted, to check and extend the upper acidity reaches of the H_c acidity function,[7] but sulfonation[8] and decomposition occurred rapidly at high acidities so that accurate optical densities corresponding solely to the absorption of BH^+ in this region were impossible to obtain.

Rate measurements were carried out in D_2O–D_2SO_4 at 9% concentrations of substrate, as previously described.[5,6] The NMR exchange pattern for the 6-position of 2,4-dinitroaniline is shown in Figure 1. The positions for substitution for 4-nitro-*N*,*N*-dimethylaniline were established as 2,6 by reacting the molecule in D_2O–D_2SO_4, extracting the base after neutralizing, and measuring its NMR spectrum in deuteriochloroform when the high-field aromatic protons were found to have disappeared. The results for 4-methoxyacetophenone in 9% concentration at 60 °C previously reported[5] were supplemented with additional measurements. The conversion of k observed (k_{obsd}) to k free base (k_{fb}) was carried out as follows: we have

$$k_{\text{fb}}[B] = k_{\text{obsd}}([BH^+] + [B]) \tag{2}$$

so that

$$\log k_{\text{fb}} = \log k_{\text{obsd}} + \log ([BH^+]/[B] + 1) \tag{3}$$

Since the correlation between $[BH^+]/[B]$ and acidity is known for the benzaldehydes (Table I) in the acidity region where kinetic exchange was carried out, eq 3 could be used directly for these compounds. 4-Nitro-*N*,*N*-dimethylaniline follows the H_0''' acidity function[9] and has a pK_a value of 0.65.[9] Therefore, for the region of kinetic measurement of this base, $[BH^+] \gg [B]$, and eq 3 becomes

$$\log k_{\text{fb}} = \log k_{\text{obsd}} + \log [BH^+]/[B] = \log k_{\text{obsd}} - H_0''' + 0.65 \tag{4}$$

while for 2,4-dinitroaniline[10] the appropriate expression is

$$\log k_{\text{fb}} = \log k_{\text{obsd}} - H_0 - 4.27 \tag{5}$$

The correlation coefficients of the first-order plots for the kinetic runs were generally better than 0.990, but a few were lower than this. In no case, however, was there any evidence for systematic deviation from linearity up to at least three half-lives, and no evidence for decomposition from the NMR spectra.

The log k_{fb} values for 4-nitro-*N*,*N*-dimethylaniline were plotted against H_c[7], giving a good straight line plot of slope 0.648 (Figure 2). This line was extrapolated to $H_c = 0$, yielding a $(7 + \log k_{\text{fb}})$ value of 2.95 at this acidity (but see footnote *e* to Table V). H_c was then calculated from

$$-H_c = \frac{7 + \log k_{\text{fb}} - 2.95}{0.648} \tag{6}$$

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Table I. pK_a Data

4-X-benzaldehyde	UV					NMR			
X	λ^a	$H_0^{1/2\,b}$	m^c	$mH_0^{1/2}$	r^d	$H_0^{1/2\,b}$	m^c	$mH_0^{1/2}$	r^d
OCH_3	350	−5.55	0.71	−3.91	0.993	−5.96	0.75	−4.47	0.987
CH_3	315	−6.82	0.61	−4.16	0.998	−6.99	0.62	−4.32	0.985
OH	340	−5.95	0.58	−3.42	0.995	−6.23	0.57	−3.52	0.961

[a] Wavelength (nm) at which measurements were taken. [b] H_0 value at half-protonation. [c] Slope of plot of log $[BH^+]/[B]$ vs. $-H_0$. [d] Correlation coefficient; in all cases at least six readings of log $[BH^+]/[B]$ between ±1 were taken, and generally considerably more.

Table II. Rate Constants for Aromatic Hydrogen Exchange of 4-Nitro-*N,N*-dimethylaniline and the H_c and $H_c^{\ddagger}$ Scales

% acid	$-H_0^a$	$7 + \log k_{obsd}$	$7 + \log k_{fb}$	$-H_c^b$	$-H_c^c$	$-H_c^{\ddagger}$
23.15	1.28	1.643	3.94	1.78	1.53	1.03
26.42	1.50	1.664	4.41	2.13	2.25	1.40
30.47	1.77	1.674	4.85	2.57	2.93	1.84
36.77	2.18	1.511	5.26	3.30	3.56	2.43
38.20	2.30	1.630	5.53	3.48	3.98	2.55
38.86	2.32	1.601	5.55	3.61	4.01	2.61
42.60	2.67	1.393	5.79	4.27	4.34	2.92
44.98	2.82	1.441	6.09	4.68	4.85	3.11
48.92	3.19	1.562	6.61	5.43	5.65	3.45
49.80	3.28	1.283	6.43	5.53	5.37	3.53
54.97	3.75	1.116	6.86	6.38	6.03	4.05
56.35	3.94	1.312	7.31	6.65	6.73	4.21
56.82	3.99	1.204	7.28	6.68	6.68	4.27
60.59	4.45	1.033	7.73	7.40	7.38	4.74
63.73	4.88	0.708	7.86	7.98	7.58	5.18
65.87	5.18	0.862	8.41	8.43	8.43	5.49
68.79	5.61	0.788	8.84	9.03	9.09	5.95
69.70	5.77	0.953	9.23	9.23	9.69	6.09
72.26	6.16	0.850	9.60	9.83	10.26	6.50
77.78	7.09	0.699	10.40	11.03	11.50	7.38
78.36	7.17	0.362	10.16	11.14	11.12	7.47
82.54	7.85	0.496	11.07		12.59	8.09
87.77	8.69	0.200	11.85		13.73	8.76
93.36	9.60	−0.104	12.24		14.34	9.37
95.93	9.97	−0.177	12.57		14.85	9.63
98.55	10.61	−0.427	12.85		15.28	9.92
100.00	11.43	−0.359	13.09		15.65	10.10

[a] Reference 10. [b] Reference 7. [c] Calculated from eq 6.

Table III. The $H_c^{\ddagger}$ Kinetic Acidity Function [a] in Aqueous Sulfuric Acid

% acid	$-H_c^{\ddagger}$	% acid	$-H_c^{\ddagger}$	% acid	$-H_c^{\ddagger}$
5	−0.08	40	2.66	75	6.85
10	0.31	45	3.12	80	7.61
15	0.61	50	3.60	85	8.38
20	0.91	55	4.07	90	9.06
25	1.28	60	4.64	95	9.61
30	1.73	65	5.30	100	10.10
35	2.19	70	6.07		

[a] It may be noticed that the values of $H_c^{\ddagger}$ given here differ marginally, usually only in the second decimal place, from those given previously.[1] The original values were derived from a polynomial designed by computer to fit the ($\log k_{fb} - 2.95$) vs. percent acid curve, but even if this was taken to the tenth order, it was found more accurate (if less impressive) to fit a curve to the points by eye, from which the above values were read off.

Obviously the values of H_c obtained from eq 6 were very similar to those of Reagan's,[7] and essentially confirm them. However, the extension of the scale using eq 6 into regions of acidity above 75% appears a useful innovation, because it is doubtful if any indicators could be found stable enough in strong sulfuric acid to permit its evaluation by determination of ionization ratios.

$H_c^{\ddagger}$ values were found from the curve of $\{(7 + \log k_{fb}) - 2.95\}$ vs. percent acid, so that $H_c^{\ddagger} = H_c$ at zero, and are recorded in Tables II and III, and Figure 3.

The kinetic results for the benzaldehydes and 2,4-dinitroaniline are given in Table IV, together with literature data, as described in the Discussion.

Discussion

Applicability of the Scale to Kinetic Aromatic Ring Protonation. The deuteriodeprotonation reaction,[28,29] eq 1, proceeds via the benzenonium ion $DArH^+$, commonly known as the Wheland intermediate. It involves the scheme

$$ArH + D^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} DArH^+ \xrightarrow{k_2} H^+ + DAr \qquad (7)$$

so that

$$k_{obsd} = k_1/(1 + k_{-1}/k_2) \qquad (8)$$

The isotope effect k_{-1}/k_2 (= k_D/k_H) is essentially acid invariant, and so the acidity dependence of k_{obsd} is that of k_1.

The plot of log k_{fb} (4-nitro-*N,N*-dimethylaniline) vs. H_c[7] (Figure 2) is essentially a Brønsted plot, in that the logarithmic rate constants are plotted against a function describing the equivalent equilibrium process.

$$7 + \log k_{fb} = -0.648H_c + 2.95 \qquad (6a)$$

i.e.,

$$\Delta\Delta G^{\ddagger} = \alpha\Delta\Delta G^{\circ} + \text{constant} \qquad (9)$$

Varying the solvent while keeping the acid–base system con-

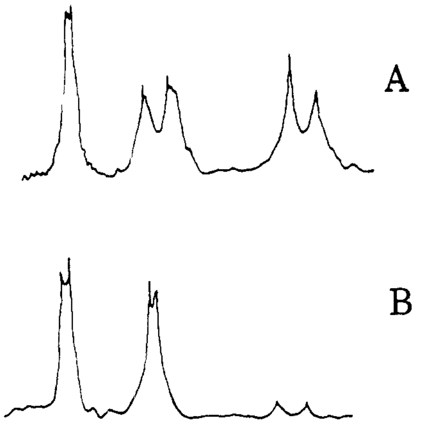


Figure 1. Exchange of 2,4-dinitroaniline at the 6-position in 70% $D_2O–D_2SO_4$ at 80 °C: A, initial spectrum of the aromatic resonances; B, after about 3 half-lives.

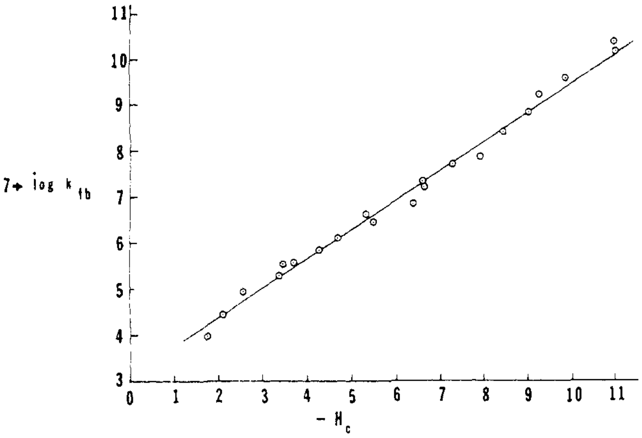


Figure 2. Plot of log k_{fb} (4-nitro-*N*,*N*-dimethylaniline) vs. $-H_c$.

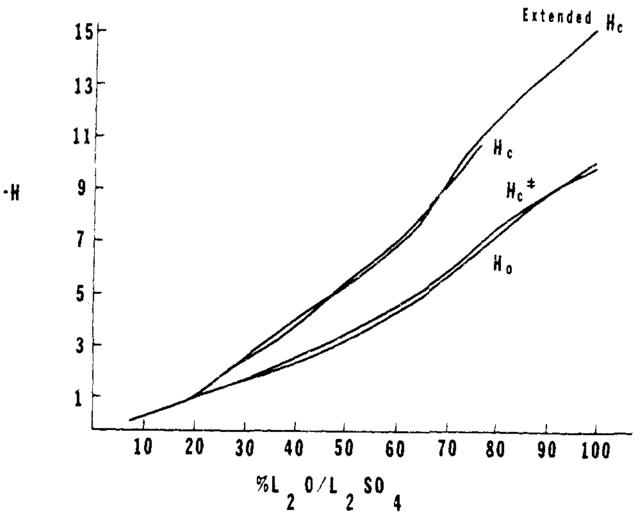


Figure 3. Comparison of the H_0, H_c, and $H_c^{\ddagger}$ acidity functions.

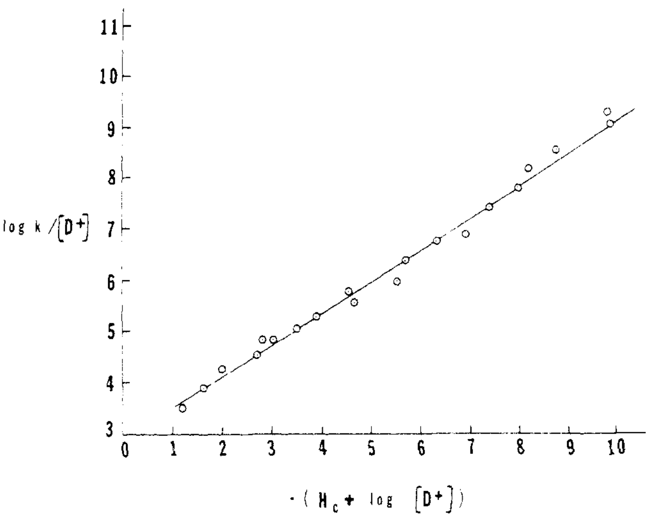


Figure 4. Plot of log $k_{fb}/[D^+]$ vs. $-(H_c + \log [D^+])$.

stant is considered by Bell[30] to provide a reliable method for systematically varying the acidity of a solution in order to obtain Brønsted α or β values, and this technique has been employed in both acid[5,29,31] and basic media.[30,32,33]

In this case the slope of the plot (Figure 2) is 0.65; slopes of Brønsted plots are widely accepted as indicative of transition state structure,[34–38] and thus the transition state structure appears here to be constant over a rate range of 10^7. This is emphasized by the plot shown in Figure 4, where the slope gives a value of $\alpha_A = 0.62$ from the expression[5]

$$\log (k/[L^+]) = \alpha_A(-H_c - \log [L^+]) + \text{constant} \qquad (10)$$

where

$$f^{\ddagger} = (f_{HAr}/f_{L^+})^{1-\alpha_A}(f_{HArL^+})^{\alpha_A} \qquad (11)$$

and L denotes H, D, or T. The translation of the activity coefficient expression eq 11 into eq 10 has been fully detailed previously,[5,29,39] and the role of α_A in thus describing the extent or proton transfer in the transition state is widely accepted.[29,30,36–38,40,41]

The good linearity of both eq 9 (Figure 2) and eq 10 (Figure 4) and similarity of their slopes may be rationalized by writing eq 10 in the form

$$\log k = \alpha_A(-H_c) + (1 - \alpha_A) \log [L^+] + \text{constant} \qquad (12)$$

and evaluating the term $(1 - \alpha_A) \log [L^+]$, which is found to have a total variation of but 0.26 over the acidity range covered.

The Bunnett–Olsen eq 13[42] may also be written in a form analogous to eq 12:

$$\log k - \log [L+] = (1 - \phi)(-H_0 - \log [L^+]) + \text{constant}$$
$$\log k = (\phi - 1)H_0 + \phi \log [L^+] + \text{constant} \qquad (13)$$

This gives a value of $(\phi - 1)$ of -0.92 (see Figure 5); the relative size and variation of $\phi \log [L^+]$ is similarly negligibly small. All these results are summarized in Table V. Note that the Bunnett–Olsen plot and also log k_{fb} vs. $-H_0$ give slight but definite curvature; this indicates that as expected the H_c acidity scale is a more appropriate extra-thermodynamic[43] function to describe the kinetic protonation of unsaturated carbon–carbon bonds than H_0.

It would have been interesting and informative to calculate log f_s^* for 4-nitro-*N*,*N*-dimethylaniline as explained by McClelland and coworkers,[44] but unfortunately one requires not only measurements of log f_s but also for a slow proton transfer the reaction must proceed on the majority species, if all dependence on an acidity function is to be removed.

This picture of an apparently constant transition state even though the activity of the solvated proton is increased by many orders of magnitude is extended to consideration of other aromatic substrates. Figure 6 shows the constant selectivity displayed by D_3O^+ for nuclear substitution in three of the aromatic substrates we have measured, differing in reactivity by a factor of 10^9 overall.

The idea that we have here a constant selectivity relationship can be summarized by the following argument. For the protonation step

Table IV. Applicability of the $H_c^‡$ Kinetic Acidity Function to Rate-Determining Carbon Protonations in Aqueous Sulfuric Acid

compd	registry no.	exch posn	temp (°C) and media[a]	acidity range, acid % (no. of points)	−d log k/d$H_c^‡$ (corrn coeff)	−log k		ref
						60% acid	75% acid	
1. C_6H_5T	3508-32-5	1		68–84 (6)	1.81 ± 0.14 (0.988)	9.59	5.59	11
2.		1	35	68–82 (8)	1.70 ± 0.05 (0.997)	8.87	5.11	11
3.		1	45	65–81 (7)	1.58 ± 0.05 (0.998)	7.99	4.50	11
4.		1	55	64–81 (7)	1.53 ± 0.08 (0.992)	7.50	4.13	11
5. C_6H_6	71-43-2	1	D_2O/D_2SO_4	81–87 (4)	2.03 ± 0.14 (0.995)	12.45	7.97	12
6. C_6H_6		1	T_2O/T_2SO_4	81–87 (4)	2.03 ± 0.14 (0.995)	12.64	8.17	12
7. C_6H_5D	1120-89-4	1		67–83 (6)	1.20 ± 0.04 (0.998)	7.72	5.07	13
8. C_6H_5T		1		73–84 (7)	1.76 ± 0.12 (0.990)	9.50	5.60	14
9. *o*-$CH_3C_6H_4T$	54615-78-0	1		65–75 (5)	1.29 ± 0.03 (0.999)	6.10	3.25	15
10. *m*-$CH_3C_6H_4T$	6726-72-3	1		73–81 (5)	1.60 ± 0.07 (0.997)	8.40	4.86	14
11. *p*-$CH_3C_6H_4D$	4409-83-0	1		53–73 (5)	1.27 ± 0.02 (0.999)	5.87	3.07	16
12. *p*-$CH_3C_6H_4T$	40661-90-3	1		65–75 (10)	1.30 ± 0.03 (0.998)	6.11	3.23	14, 15
13. [1-^{3}H]naphthalene	18266-06-3	1		60–69 (5)	1.33 ± 0.11 (0.989)	6.28	3.35	11
14.		1	35	52–67 (5)	1.20 ± 0.04 (0.999)	5.65	2.99	11
15.		1	45	52–67 (5)	1.21 ± 0.04 (0.998)	5.12	2.46	11
16.		1	55	50–67 (5)	1.14 ± 0.02 (0.999)	4.70	2.19	11
17. [2-^{3}H]naphthalene	26547-66-0	2	25	62–72 (9)	1.02 ± 0.06 (0.989)	7.10	4.84	11
18.		2	35	60–68 (5)	1.16 ± 0.08 (0.990)	6.57	4.01	11
19.		2	45	60–66 (3)	1.12 ± 0.25 (0.976)	5.87	3.38	11
20.		2	55	57–64 (5)	1.10 ± 0.19 (0.957)	5.51	3.08	11
21. [1-^{2}H]naphthalene	875-62-7	1	15.1	50–67 (9)	1.49 ± 0.05 (0.997)	6.41	3.10	17
22.		1		50–67 (9)	1.43 ± 0.03 (0.999)	5.81	2.65	17
23.		1	35.0	50–67 (10)	1.37 ± 0.03 (0.998)	5.24	2.21	17
24.		1	45.1	50–67 (10)	1.32 ± 0.03 (0.997)	4.74	1.82	17
25.		1	55.7	50–67 (8)	1.20 ± 0.06 (0.994)	4.29	1.64	17
26. [2-^{2}H]naphthalene	2430-34-4	2	15.1	54–67 (7)	1.53 ± 0.10 (0.989)	6.70	3.33	17
27.		2		51–67 (10)	1.48 ± 0.11 (0.980)	5.97	2.70	17
28.		2	35.0	51–67 (9)	1.46 ± 0.07 (0.993)	5.35	2.14	17
29.		2	45.1	51–67 (8)	1.42 ± 0.06 (0.995)	4.81	1.67	17
30.		2	55.7	51–67 (10)	1.34 ± 0.04 (0.996)	4.24	1.28	17
31. *p*-$CH_3C_6H_4OH$	106-44-5	2 + 6		10–45 (6)	0.96 ± 0.05 (0.995)	2.90	0.79	18
32. *p*-ClC_6H_4OH	106-48-9	2 + 6		41–64 (5)	0.85 ± 0.01 (1.000)	5.18	3.30	18
33. *p*-$NO_2C_6H_4OH$	100-02-7	2 + 6		64–98 (9)	0.73 ± 0.03 (0.992)	7.34	5.73	18
34. *p*-$CH_3OC_6H_4D$	20938-43-6	1		29–53 (5)	1.09 ± 0.03 (0.999)	3.25	0.85	19
35. *o*-$CH_3OC_6H_4D$	26351-62-2	1		39–54 (5)	1.13 ± 0.04 (0.999)	3.52	1.02	19
36. *p*-HOC_6H_4CHO	123-08-0	3 + 5	60, D_2O/D_2SO_4	63–94 (7)	0.63 ± 0.04 (0.992)	4.85	3.46	20
37. *p*-$CH_3OC_6H_4CHO$	123-11-5	3 + 5	60, D_2O/D_2SO_4	66–93 (13)	0.90 ± 0.02 (0.997)	5.33	3.33	20
38. *p*-$CH_3C_6H_4CHO$	104-87-0	3 + 5	60, D_2O/D_2SO_4	78–96 (8)	0.88 ± 0.02 (0.999)	7.85	5.90	20
39. *p*-$CH_3C_6H_4COCH_3$	122-00-9	3 + 5	60, D_2O/D_2SO_4	68–96 (9)	0.92 ± 0.03 (0.997)	7.59	5.56	4
40.		3 + 5	80, D_2O/D_2SO_4	69–99 (8)	0.93 ± 0.02 (0.998)	6.61	4.55	4
41.		3 + 5	100, D_2O/D_2SO_4	69–99 (8)	0.90 ± 0.04 (0.995)	5.63	3.64	4
42. (18% concn of substrate)		3 + 5	60, D_2O/D_2SO_4	67–95 (8)	0.86 ± 0.02 (0.999)	7.48	5.59	4
43. *p*-$C_2H_5C_6H_4COCH_3$	937-30-4	3 + 5	60, D_2O/D_2SO_4	74–96 (8)	0.95 ± 0.01 (1.000)	8.10	6.00	4
44. *p*-$(CH_3)_2CHC_6H_4COCH_3$	645-13-6	3 + 5	60, D_2O/D_2SO_4	72–97 (7)	0.95 ± 0.02 (0.999)	7.76	5.65	4
45. *p*-$(CH_3)_3CC_6H_4COCH_3$	9443-27-1	3 + 5	60, D_2O/D_2SO_4	70–96 (7)	0.89 ± 0.04 (0.995)	7.49	5.54	4
46. *p*-$CH_3OC_6H_4COCH_3$	100-06-1	3 + 5	40, D_2O/D_2SO_4	67–96 (7)	0.87 ± 0.05 (0.991)	6.12	4.20	4
47.		3 + 5	50, D_2O/D_2SO_4	67–96 (8)	0.89 ± 0.04 (0.993)	5.71	3.73	4
48.		3 + 5	60, D_2O/D_2SO_4	57–98 (16)	0.83 ± 0.03 (0.992)	5.09	3.26	4
49. (18% concn of substrate)		3 + 5	60, D_2O/D_2SO_4	66–95 (8)	0.82 ± 0.03 (0.996)	5.17	3.36	4
50. *p*-$CH_3SC_6H_4COCH_3$	1778-09-2	3 + 5	60, D_2O/D_2SO_4	69–99 (8)	0.89 ± 0.04 (0.993)	6.29	4.32	4
51. 4-$NO_2C_6H_4N(CH_3)_2$	100-23-2	2 + 6	60, D_2O/D_2SO_4	23–100 (27)	1.00 ± 0.01 (1.000)	−0.62	−2.83	20

Table IV *(continued)*

compd	registry no.	exch posn	temp (°C) and media[a]	acidity range, acid % (no. of points)	$-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ (corrn coeff)	$-\log k$ 60% acid	$-\log k$ 75% acid	ref
52. 2,4-di$NO_2C_6H_3NH_2$	97-02-9	6	80, D_2O/D_2SO_4	69–96 (6)	0.88 ± 0.04 (0.996)	4.76	2.81	20
53. [2-^{2}H]thiophene	2788-41-2	2	20	22–56 (3)	1.05 ± 0.02 (1.000)	2.54	0.20	21
54. [2-^{3}H]thiophene	1429-81-8	2	1.9	27–47 (4)	1.02 ± 0.07 (0.995)	2.74	0.48	22
55.		2		17–47 (5)	0.95 ± 0.03 (0.998)	1.77	0.33	22
56. [3-^{3}H]thiophene	1429-80-7	3	1.9	60–72 (4)	1.23 ± 0.02 (1.000)	5.52	2.81	22
57.		3		54–66 (4)	1.20 ± 0.02 (1.000)	4.27	1.62	22
58. [2-^{2}H]furan	6142-86-5	2	20	22–56 (3)	0.94 ± 0.00 (1.000)	2.89	0.81	21
59. p-$NH_3^+(CH_2)_3C_6H_4$-$(CH_2)_3{}^+NH_3$	386201-72-3	2 + 6	50, D_2O/D_2SO_4	66–96 (4)	1.09 ± 0.03 (0.999)	5.76	3.35	23
60. p-$N^+(CH_3)_3(CH_2)_3$-$C_6H_4(CH_2)_3N^+(CH_3)_3$	38441-66-6	2 + 6	50, D_2O/D_2SO_4	73–96 (3)	1.11 ± 0.02 (1.000)	5.79	3.33	23
61. p-$NH_3^+(CH_2)_2C_6H_4$-$(CH_2)_2NH_3^+$	32408-101-8	2 + 6	50, D_2O/D_2SO_4	77–96 (5)	1.14 ± 0.08 (0.994)	8.09	5.56	23
62. $C_6H_5C{\equiv}CH$	536-74-3			37–56 (7)	1.27 ± 0.05 (0.997)	0.98	−1.82	24
63.				6–48 (11)	1.16 ± 0.01 (0.999)	1.22	−1.34	25
64.			45	22–34 (6)	0.96 ± 0.01 (1.000)	0.82	−1.30	25
65.			D_2O/D_2SO_4	37–49 (7)	1.22 ± 0.04 (0.998)	1.34	−1.36	26
66. p-$ClC_6H_4C{\equiv}CH$	873-73-4			27–44 (6)	0.96 ± 0.06 (0.992)	2.04	−0.08	24
67.			D_2O/D_2SO_4	26–46 (6)	1.07 ± 0.02 (0.999)	2.09	−0.27	26
68. p-$CH_3C_6H_4C{\equiv}CH$	766-97-2			23–37 (5)	1.00 ± 0.03 (0.998)	−0.03	−2.25	24
69.			D_2O/D_2SO_4	17–39 (6)	1.05 ± 0.03 (0.999)	0.44	−1.89	26
70. p-$CH_3OC_6H_4C{\equiv}CH$	768-60-5			2–14 (8)	1.34 ± 0.04 (0.997)	−2.73	−5.70	24
71.				0–14 (10)	1.18 ± 0.03 (0.997)	−2.04	−4.66	25
72.			45	0–1 (4)	0.92 ± 0.02 (0.999)	−1.44	−3.46	25
73.			D_2O/D_2SO_4	1–14 (6)	1.22 ± 0.04 (0.998)	−1.78	−4.46	26
74. $C_6H_5C{\equiv}CD$	3240-11-7			6–49 (17)	1.16 ± 0.01 (1.000)	1.25	−1.31	26
75.			D_2O/D_2SO_4	37–48 (8)	1.17 ± 0.02 (0.999)	1.46	−1.12	26
76. p-$CH_3OC_6H_4C{\equiv}CD$	54159-16-9			0–14 (8)	1.18 ± 0.03 (0.998)	−2.00	−4.61	26
77. p-$CH_3OC_6H_4C{\equiv}CD$		45		0–6 (7)	0.98 ± 0.01 (1.000)	−1.76	−3.92	26
78. $C_6H_5CH{=}CH_2$	100-42-5			25–53 (7)	1.04 ± 0.05 (0.993)	1.43	−0.87	27
79. m-$CH_3C_6H_4CH{=}CH_2$	100-80-1			25–54 (5)	0.98 ± 0.07 (0.992)	1.23	−0.94	27
80. m-$ClC_6H_4CH{=}CH_2$	2039-85-2			42–67 (7)	1.10 ± 0.02 (0.999)	2.80	0.36	27
81. m-$BrC_6H_4CH{=}CH_2$	2039-86-3			49–67 (5)	1.08 ± 0.04 (0.998)	2.83	0.46	27
82. p-$CH_3OC_6H_4CH{=}CH_2$	637-69-4			15–32 (9)	1.07 ± 0.07 (0.987)	−1.06	−3.43	27
83. p-$CH_3C_6H_4CH{=}CH_2$	622-97-9			18–45 (7)	1.01 ± 0.01 (1.000)	0.48	−1.75	27
84. p-$ClC_6H_4CH{=}CH_2$	1073-67-2			41–60 (6)	1.24 ± 0.04 (0.998)	1.62	−1.11	27
85. p-$BrC_6H_4CH{=}CH_2$	2039-82-9			32–58 (5)	1.05 ± 0.06 (0.995)	1.93	−0.38	27
86. m-$NO_2C_6H_4CH{=}CH_2$	586-39-0			57–75 (8)	1.11 ± 0.01 (1.000)	4.11	1.67	27
87. m-$NH_3^+C_6H_4CH{=}CH_2$	68367-51-1			53–66 (4)	1.22 ± 0.04 (0.999)	3.87	1.19	27

[a] If other than 25 °C, H_2O/H_2SO_4.

$$B + D^+ \overset{k^{\ddagger}}{\rightleftharpoons} TS \xrightarrow{k^{\ddagger}} BD^+ \qquad (14)$$

for which

$$k_{\mathrm{obsd}} = K^{\ddagger}k^{\ddagger}f_B a_{H^+}/f_{\pm} \qquad (15)$$

Selectivity is proportional to log $(k_{D^+B_1}/k_{D^+B_2})$ where B_1 and B_2 are two bases of different reactivity.

Therefore from eq 15:

$$\text{selectivity } \alpha \log \frac{K^{\ddagger}k^{\ddagger}}{K^{\ddagger}k^{\ddagger}} \cdot \frac{f_{B_1}}{(f_{\pm})_1} \cdot \frac{(f_{\pm})_2}{f_{B_2}} = \text{constant} \qquad (16)$$

as shown by the parallelism of log k–acidity plots as the reactivity of the protonating species is increased by decrease of aqueous solvation.

Thus this constant selectivity is revealed by "Hammett parallelism", in the sense utilized in the demonstration that bases follow the same extra-thermodynamic acidity function from plots of log $[BH^+]/[B]$ against acidity. Thus for such an acidity function we can write

$$H_X{}^0 = -\log a_H + f_B/f_{BH^+}$$

where f_B/f_{BH^+} is constant for a family of bases; for a kinetic acidity function we have

$$H_X{}^{\ddagger} = -\log a_L + f_B/f_{\pm}$$

where $f_B/f_{\pm}$ is constant. The kinetic scale $H_c{}^{\ddagger}$, whose deri-

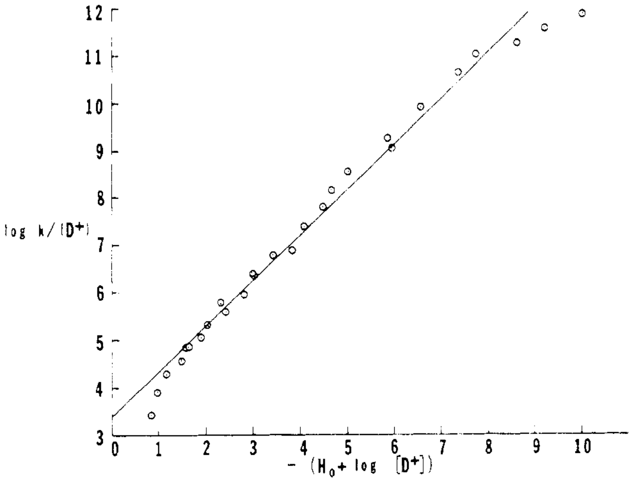


Figure 5. Plot of log $k_{fb}/[D^+]$ vs. $-(H_0 + \log [D^+])$.

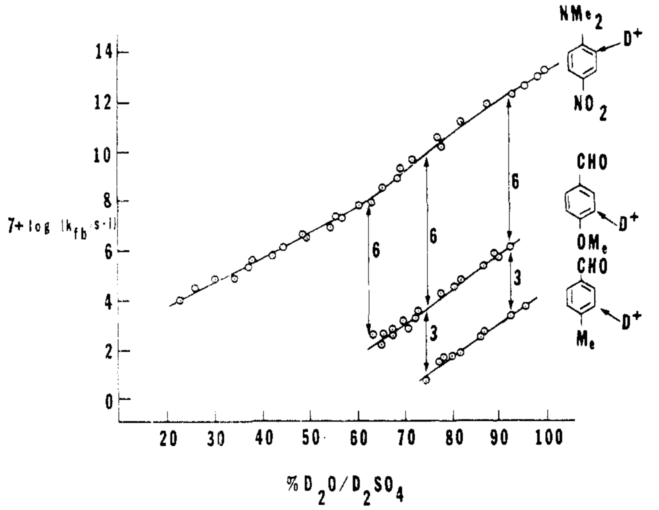


Figure 6. Constant selectivity displayed by D_3O^+ for aromatic substrates differing widely in reactivity, at 60 °C.

vation from the rate constant for nuclear exchange of 4-nitro-*N*,*N*-dimethylaniline has been described in the Experimental Section, can thus be said to govern a proton transfer process from aqueous sulfuric acid to an aromatic base if a plot of log k vs. $-H_c^{\ddagger}$ is linear with unit slope; as Figure 3 demonstrates there is fortuitously little difference between $H_c^{\ddagger}$ and H_0, although the quantitative correlation is described by curvature (see Table V).

There seems to be increasing feeling that the concept of acidity function is out dated and that it is replaceable by alternative treatments which are more significant and accurate. In our opinion, such treatments may add to the complexity of presentation and calculation without materially increasing our understanding of or ability to describe the behavior of bases in acid media. Indeed, in so far as they mask the simplicity of the Hammett approach, they may in some cases be considered to reduce ability to identify and tackle the main problems in this area. The Hammett acidity function approach recognizes "parallelism" between plots of acidity vs. ionization ratios, or in the case described here vs. rates. It contains the approximations, both fully considered in this paper and elsewhere,[5] that parallelism must be assumed exact when in fact it is often not precisely so, and second that the parallelism found extends into regions of acidity not experimentally observable for all bases; these basic difficulties and assumptions are certainly implicit (although often not explicit) in other treatments. We therefore believe that the measurement of an acidity function which describes the extra-thermodynamic or kinetic protonation behavior of a basic site not previously investigated is a legitimate exercise which can genuinely aid our understanding of reactivity and solvation effects and cannot be replaced at the present time by any other alternative which will yield more significant information or a greater depth of understanding.

The extent to which different aromatic bases follow the $H_c^{\ddagger}$ kinetic acidity function can be judged from entries 1–61 in Table IV, where the data from this work and a previous publication of ours,[5] together with all the relevant literature results of which we are aware, are assembled. The accuracy with which these aromatic bases follow $H_c^{\ddagger}$ is discussed later, but at this stage it may be noted that the parallel behavior of the benzaldehydes and acetophenones in particular removes any remaining doubt that the latter compounds are reacting via their enol form.[5]

Applicability of the Scale to Protonation of Alkenes and Alkynes. The H_c extra-thermodynamic acidity function applies equally well to olefin as well as aromatic protonation,[7] being derived using both species of indicator. It is therefore of interest in addition to test the applicability of the kinetic acidity function $H_c^{\ddagger}$ to other types of carbon protonations. Extensive and apparently very accurate data exist in the literature for both styrene[27] and phenylacetylene[25,26] hydrolyses, in aqueous sulfuric acid, for which the rate-determining step is considered to be the C-protonation stage. These have therefore been utilized as representative of the most extreme variation of carbon base structures, and the $H_c^{\ddagger}$ scale tested against them. Table IV gives the results relevant to both types of protonation (acetylenes, 62–77; styrenes, 78–87) and includes, as well as the data cited above,[25–27] results due to Scorrano and co-workers[24] who have repeated Noyce's measurements on acetylenes, but without the use of small amounts of ethanol to aid dissolution.

Table V. Acidity Function Treatments of log k_{fb} for Aromatic Hydrogen Exchange of 4-Nitro-*N*,*N*-dimethylaniline at 60 °C in the Acidity Range 23–78% Aqueous Sulfuric Acid

plotted	gradient	no. of pts	intercept	corr coeff
$(7 + \log k_{fb})$ vs. $-H_0$[a]	0.927 ± 0.022	27	3.428 ± 0.340	0.9928
$(7 + \log k_{fb})$ vs. $-(H_0 + \log [L^+])$[b]	0.917 ± 0.024	27	3.400 ± 0.335	0.9916
$(7 + \log k_{fb})$ vs. $-H_c$[c]	0.648 ± 0.014	21	3.023 ± 0.178[e]	0.9957
$(7 + \log k_{fb})$ vs. $-(H_c + \log [L^+])$[d]	0.623 ± 0.015	21	2.857 ± 0.179	0.9946

[a] Can also be represented by a smooth curve. [b] Bunnett–Olsen eq 13 can also be represented by a smooth curve. [c] Equation 6a. [d] Kresge eq 10. [e] Value of 2.95 used in the evaluation of H_c and $H_c^{\ddagger}$ scales (see Experimental Section, eq 6 and following); this value was obtained before measurement of two additional log k_{fb} values and had been employed to evaluate all the data in Table IV. Its use introduces only a very small change in estimated absolute rates and obviously none in relative rate.

Accuracy of the $H_c^{\ddagger}$ Kinetic Acidity Function. As discussed in the previous sections, there is certainly no correlation between substrate reactivity and slope parameter $-\mathrm{d} \log k/\mathrm{d}H_c^{\ddagger}$ in Table IV, shown clearly by Figure 7 in which the slopes are plotted against reactivity. Such variations as do exist are random; no trend toward decreasing selectivity can be seen as rate is increased by 10^{12}. The significance of this in terms of apparent transition state structure has been discussed above, and earlier.[3–5] *But are the variations sufficiently small to justify the designation of $H_c^{\ddagger}$ as an acidity function adequately describing the kinetic protonation of carbon bases in aqueous sulfuric acid,* remembering that *some* change must occur in the ratio $f_B/f_{\pm}$ for different bases? It would seem best to make this decision, which to a certain extent must be arbitrary, by considering variation of slopes of log I vs. H_0 plots, where I is $[BH^+]/[B]$, for acidity functions describing equilibrium protonation, which represent extra-thermodynamic relationships.[43] Obviously in these cases there are variations of the ratio f_B/f_{BH^+}, each base generating its own unique acidity function, but nevertheless the concept of general acidity functions incorporating whole families of bases has proved a useful one; much of the progress made in physical organic chemistry and, indeed, chemistry in general has been via the process of recognizing common reactivity patterns for wide ranges of molecules. For the latest determination[10] on indicators generating the H_0 acidity function, a base series which has been widely considered to be "well-behaved", there is a variation of slope parameter of 0.85 to 1.15 when the log-

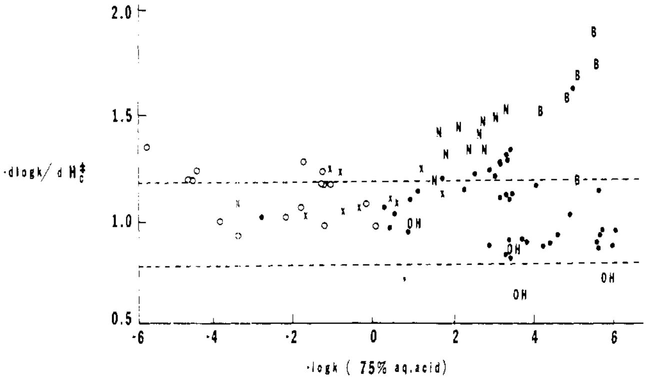


Figure 7. Variation of slope parameter $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ with reactivity $-\log k$ (75% aqueous acid) from Table IV: B, benzene (1–8); N, naphthalene[17] (21–30); OH, hydroxy compounds (31–33, 36); ●, other aromatics; X, styrenes; ○, acetylenes. The slope parameter would be 1.54 for a product-like transition state and about 0.1 for a reactant-like transition state.[3]

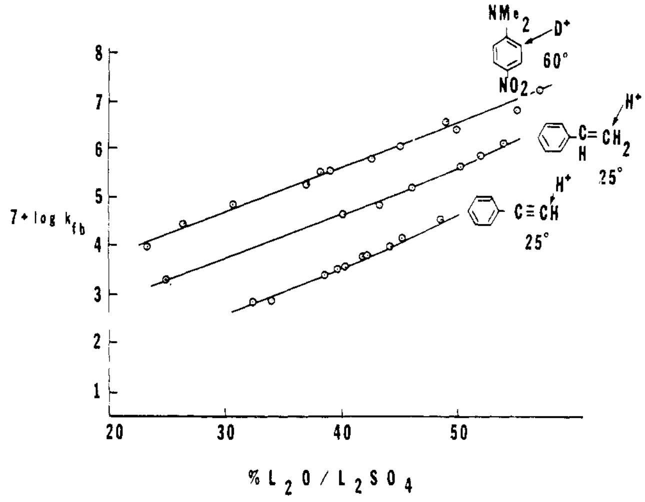


Figure 8. Constant selectivity displayed by L_3O^+ for aromatic, olefinic, and acetylenic substrates. Units of k_{fb} for the amine and acetylene are s^{-1} and for the olefin min^{-1} to avoid overlapping plots with the acetylene data.

arithmic ionization ratios for the individual bases actually defining the scale are plotted against the final "averaged" scale. For other acidity functions, plots of log I vs. $-H_0$ are excellent straight lines, but have slope variations as follows: H_0''', 1.10–1.40; H_A, 0.49–0.80; H_R, 1.64–2.36; H_I, 1.14–1.60[42] (in the latter case only the indoles actually used to define H_I being included).

Another point to be considered is the accuracy and reproducibility of results. Although clearly benzene has a slope $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ significantly greater than unity, the results by different methods (Table IV, entries 1–8) and from different laboratories show a total variation between 1.20 and 2.03. For the naphthalene exchanges, one set of results (21–30) show systematic variation with temperature and slope parameters much greater than unity, while an alternative set (13–20) obtained by a different experimental technique obey the $H_c^{\ddagger}$ scale comparatively closely, and reveal little or no variation with temperature. Even for the same compounds measured by very similar techniques, different workers obtain slopes, which may vary by 0.1 or more (cf. 62 and 63 and 70 and 71).

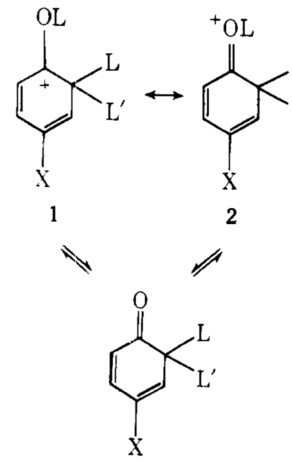
Judged within these criteria, we claim that the data for acetylenes and olefins (entries 62–87, Table IV) show that the $H_c^{\ddagger}$ scale is followed closely for all these bases, while Table IV reveals that the majority of aromatic bases also obey the scale. Figure 7 shows the variation of rate with the slope parameter. Of the total 87 compounds examined all but 29 have values of $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ falling in the range 0.80–1.20; of these 29 "errant results", 10 are for naphthalene exchange for which we have noted that an alternative set of results are within the range of agreement with $H_c^{\ddagger}$, while 7 are values for benzene and 2 for hydroxy compounds, both the subject of subsequent discussion. The results as a whole thus show a remarkable conformity to $H_c^{\ddagger}$, considering the very wide diversity of carbon bases considered, of experimental procedures, and of sources, and indicate that the scope and extent of this constant selectivity relationship may be as broad as for cation–anion combination reactions.[45]

The applicability of the scale, based on a protonation at sp^2 carbon which is thus converted to sp^3, to protonation of acetylene at sp hybridized carbon is especially surprising, but the validity of the conclusion is borne out diagramatically by Figure 8.

It is true that the measurements on the substituted aniline are chosen as the definitive ones, and they do indeed require the use of the thermodynamic acidity function H_0''' for their correction, eq 1. Thus, a cursory glance at the results reported here suggests that the kinetic acidity function $H_c^{\ddagger}$ depends for its definition on the extra-thermodynamic function H_0'''. But it is only arbitrary to say this compound occupies a primary role, once it has been shown that a number of the other bases obey the scale thus defined. Thus, if an acidity function was defined with say six indicators, and a further six bases shown to follow the scale over the same acidity range, then exactly the same picture would emerge if the latter six were chosen as the "defining" indicators, and the original six now said merely to follow it. The aniline used here does react as a minority species, but after correction for this, no significant lack of "parallelism" with the other compounds is observed, for which reaction occurs entirely or partially on the majority species. We must also consider—is the minority species reaction really a disadvantage? The observed rates cover a relatively small range which can be followed at the same temperature with the same technique. It is only when correction is carried out using the well-defined[8] H_0''' scale that the k_{fb} values are found to cover a range of 10^9. No single kinetic technique could handle this range at constant temperature. Thus we are tempted to see the H_0''' correction as a strength rather than a weakness of our results; it enables us to cover almost the entire acidity range of aqueous sulfuric acid with a single indicator.

Table IV also enforces the point made previously,[5] that temperature change has very little influence on the slopes (entries 13–16, 17–20, 39–41, 46–48, 54–57, 63, 64, 71, 72, 76, 77), and therefore that the temperature coefficient of the $H_c^{\ddagger}$ scale is small. If anything, there is a slight decrease in the slope as temperature is increased, as noted for extra-thermodynamic acidity functions.[10,46] The results for aromatic exchange of the diquaternary ions (59–61) and for m-ammoniostyrene (87) also imply that, as for extra-thermodynamic acidity scales,[47] $H_c^{+\ddagger}$ at least parallels and is probably the same as $H_c^{\ddagger}$.

In the aromatic series there are, aside from the discrepancy between one set of results for naphthalene exchange and the other (13–20 and 21–30), two obvious deviations. One is for benzene exchange which appears from the latest results[11] to have a slope of about unity against the extra-thermodynamic acidity function H_c, implying a transition state coincident with the Wheland intermediate. We can offer no explanation for this at the moment, but note that preliminary results indicate that the slope for ethylene protonation is also unity,[48] although whether the latter can go via rate-determining ethyl carbonium ion formation is debatable. The other discrepancy arises in the case of hydroxy-substituted aromatics (31, 32, 33,



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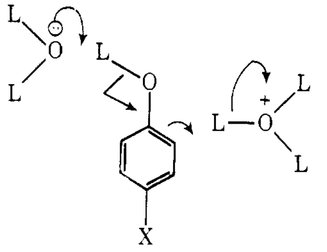

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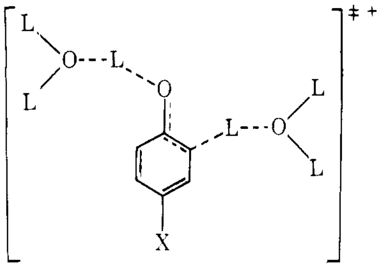

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and 36) which have slopes often, but not invariably, significantly less than unity. Such a phenomenon has been noted previously for the behavior of hydroxy compounds in acidity function treatments.[29,49] This is probably due to the fact that the Wheland intermediate is one canonical form 1 of the resonance hybrid for a protonated conjugated ketone 2. Such ketones 3 are very weak bases,[50] and thus approach of the electrophile toward the aromatic nucleus could be considered to proceed with concomitant release of the hydroxy proton 4, an increasing tendency with decrease in acidity, and leading to a transition state of the form 5. This possibility has also been envisaged by McClelland.[43]

Substituent Effects. A necessary corollary of our results is that for a series of bases whose protonation rates in aqueous sulfuric acid are correlated by σ^+, the substituent constant ρ will be sensibly independent of acidity over the entire acidity range. This is diametrically opposite to the conclusions of Modena et al.[24] who propose for example that the ρ value variation for hydration of styrenes[27] will be given by eq 17.

$$\rho = -3.0(\pm 0.1) + 0.3(\pm 0.008)(H_0 + \log [\mathrm{H}^+]) \qquad (17)$$

Equation 17 leads to ρ values of −3.20, −3.90, and −4.66 at sulfuric acid acidities of 20, 60, and 75%, respectively, a wide variation well outside experimental error. From the parameters given for compounds 78–86 in Table IV we calculate ρ values of −3.53 ± 0.14, −3.44 ± 0.13, and −3.33 ± 0.22 for the corresponding acid variation. These are all within experimental error of one another.

This discrepancy illustrates the essential difference between the two sets of results. Here we suggest that the ratio $f_B/f_\ddagger$ is essentially constant for the series of bases studied and that such variations as do exist are generally small and random. On the other hand, Modena[24] contends that systematic changes in transition state solvation and thus in the $f_B/f_\ddagger$ ratio can be detected. This discrepancy is under discussion.

In turn, the necessary connection between adherence to the $H_c{}^{\ddagger}$ acidity scale and constancy of ρ values for acid-catalyzed hydration rates in σ^+ correlations leads us to propose that the extensive correlation reported for this type of reactivity by Tidwell and his co-workers[48,51] demonstrates that $H_c{}^{\ddagger}$ is valid for at least the reactivity range covered by this σ^+ correlation, i.e., $\sim 10^{22}$, assuming that diffusion control does not intercede at the higher acidities for the most basic molecules.

Application of Marcus Theory. The constant selectivity implicit in the establishment of the $H_c{}^{\ddagger}$ acidity function has consequences for the question of validity of Marcus theory for proton-transfer reactions.[37,38,52] Marcus theory may be formalized in terms of

$$\Delta G^{\ddagger} = W^{\mathrm{r}} + (\lambda/4)(1 + \Delta G^{\circ}/\lambda)^2 \qquad (18)$$

where $\Delta G^{\ddagger}$ is the free energy of activation, W^{r} is the free energy required to bring the reactants into the encounter complex with the correct orientation of reacting bonds and solvation shell, and $\lambda/4 = \Delta G_0{}^{\ddagger}$, the intrinsic free energy barrier, which is the free energy of activation for the proton transfer step when $\Delta G^{\circ} = 0$.

The Brønsted slope $\alpha = \mathrm{d}\Delta G^{\ddagger}/\mathrm{d}\Delta G^{\circ}$, i.e.,

$$\alpha = \tfrac{1}{2}(1 + \Delta G^{\circ}/\lambda) = \tfrac{1}{2}(4\Delta G^{\ddagger}/\lambda)^{1/2} \qquad (19)$$

assuming W^{r} is small, so that the activation energy arises predominantly from the actual proton transfer step.

$$\therefore \alpha^2\lambda = \Delta G^{\ddagger} \qquad (20)$$

The change in $\Delta G^{\ddagger}$ required for α to vary from 0.5 to 0.7 is thus

$$(0.7^2 - 0.5^2)\lambda = 0.24\lambda = \Delta\Delta G^{\ddagger} \qquad (21)$$

If α_s and $\Delta G_s{}^{\ddagger}$ are calculated for a standard reaction, they can be used to define λ from

$$\Delta\Delta G^{\ddagger} = (0.24\Delta G_s{}^{\ddagger}/\alpha_s{}^2) = -RT\Delta \ln k \qquad (22)$$

For 4-nitro-*N*,*N*-dimethylaniline α is 0.648. Its bimolecular rate constant can be calculated by plotting $\log k_{\mathrm{fb}}$ against H_0 and extrapolating to $H_0 = 0$;[29] at this point $[\mathrm{H}^+] = 1$ and thus k_{fb} is equal to the bimolecular rate constant k_2. The value obtained by this method for the amine is −3.57 (see Table V). From transition state theory

$$\Delta G^{\ddagger} = -RT[\ln k_2 + \ln (h/kT)] \qquad (23)$$

where h is Planck's constant, k is Boltzmann's constant, and T is the temperature.

Substituting into eq 22 from eq 23 we obtain

$$0.24/(0.648)^2[-3.57 + \log (6.626 \times 10^{-34}/1.3805 \times 10^{-23} \times 333)] = \Delta \log k \qquad (24)$$

whence the value of $\Delta \log k$ is found to be −9.4, a logarithmic rate change which according to Marcus theory should produce a change in α of 0.5 to 0.7. We have been able to cover a rate change of 10^{12} by acid variation, 10^9 by direct observation on 4-nitro-*N*,*N*-dimethylaniline, and the remainder via utilization of the Hammett overlap principle; no change in α has been detected of the order of 0.2. The value of $10^{9.4}$ is a maximum, since if the work term W^{r} is not zero, the activation energy of the proton transfer step is smaller than that predicted, and curvature is greater.[53] Similarly Koeppl and

Kresge's modified treatment[54] using variable force constants predicts a sharper change of α than that of simple Marcus theory; this theory in general thus has no accord with our experimental observations.

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% H_2O–H_2SO_4	10^4k_{obsd}, s^{-1}
60.35	0.036
66.10	0.30
68.80	1.01
71.50	3.38

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Kinetic Acidity Function $H_c^{\ddagger}$. 2. The Scale in Perchloric Acid

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The acidity function $H_c^{\ddagger}$ defines the selectivity of proton transfer to carbon bases. Previously established for aqueous sulfuric acid media, it has now been extended to aqueous perchloric acid. The influence of substituents, temperature, ipso substitution, and base type on the scale are considered, and further general remarks on the reactivity–selectivity principle are made.

In the previous paper in this series we showed that selectivity of the hydrated proton toward aromatic, alkene, and alkyne bases in aqueous sulfuric acid was independent of reactivity. It was suggested that in consequence the rates could be correlated with a kinetic acidity function $H_c^{\ddagger}$ to a degree of accuracy similar to that involved in definition of extrathermodynamic acidity functions; $-\mathrm{d}\log k/\mathrm{d}H_c^{\ddagger}$ for reactions involving rate-limiting carbon protonation appeared generally to be about unity irrespective of base structure and reactivity for a total free energy change of about 68 kJ mol^{-1} (a rate change of 10^{12}). This result is now extended to aqueous perchloric acid. The available data are less profuse than for sulfuric acid, but are entirely adequate, covering a range of different bases, evaluated using a variety of kinetic techniques,

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