Aromatic Protonation. VIII. The Equilibrium Protonation of Hydroxy- and Alkoxybenzenes[1]

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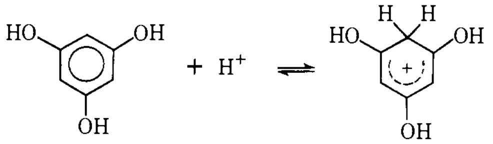
Abstract: The position of equilibrium between a series of hydroxy- and alkoxybenzenes (1,3,5-trihydroxybenzene and its methyl and ethyl ethers, 1,3-dihydroxybenzene and 1,3-dihydroxy-2-methylbenzene and their methyl ethers, 1,3-dihydroxy-5-methylbenzene, and the 3,5-dimethyl derivatives of phenol and anisole) and their benzenonium ion conjugate acids was measured as a function of acid strength in concentrated aqueous perchloric and sulfuric acids. No single acidity function serves to correlate the acidity dependence of all of these reactions, but H_c (and not H_0) does give linear log I ($I = C_{\mathrm{BH^+}}/C_{\mathrm{B}}$) plots whose nonunit slopes depend on the number of hydroxy (and alkoxy) groups a substrate possesses. The data show both hydroxy and alkoxy groups to be strongly base strengthening but the situation is complicated by the fact that hydroxy is superior to alkoxy in the less concentrated acids, whereas the opposite is true in more concentrated solutions. Extrapolation of the log I *vs.* H_c plots down to dilute solution affords a set of pK_a's, and substituent effects on these suggest that p$K_a = -23$ for the conjuate acid of benzene itself.

In the preceding paper of this series,[1b] we demonstrated that hydroxy- and alkoxy-substituted benzenes related to phloroglucinol, resorcinol, and phenol are reversibly protonated by concentrated aqueous acids to give the corresponding benzenonium ions, *e.g.*, eq 1. This reaction is accompanied by gross changes in the uv spectrum, which makes it very well suited for quantitative study by the indicator method. In this paper we present the results of such an investigation.



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Our original purpose in carrying out this work was to evaluate the basic strength of hydroxy- and alkoxybenzenes, and also to measure the acidity dependence of the position of equilibrium of these protonation reactions for the purpose of comparison with the acidity dependence of the corresponding kinetic processes, reported in the following paper.[3] The results obtained, however, have proved also to provide considerable insight into the nature of concentrated acids and especially the acidity function concept.[4]

Results

Positions of equilibrium of the reaction between free aromatic bases, HAr, and their benzenonium ion conjugate acids, HArH$^+$ (eq 1), were measured at a number of different acid concentrations by using the absorbance at λ_{max} of the long-wavelength bands of the benzenonium ions to estimate indicator (conjugate acid to free-base concentration) ratios, $I = C_{\mathrm{HArH^+}}/C_{\mathrm{HAr}}$. For all of the substrates examined, these intense benzenonium ion bands occur in a region (315–350 nm) in which the absorption of unprotonated aromatics is negligible; thus, these systems constitute a most favorable situation for obtaining precise values of I.[5] Measurements were made at constant total substrate concentrations (10^{-4} M or less), and indicator ratios were evaluated using eq 2, in which $A_{\mathrm{HArH^+}}$ is the absorbance of a solution sufficiently acidic to convert the substrate completely into its benzenonium ion and A is the absorbance of a less acidic solution containing both the free aromatic base and its conjugate acid.

$$I = C_{\mathrm{HArH^+}}/C_{\mathrm{HAr}} = A/(A_{\mathrm{HArH^+}} - A) \qquad (2)$$

Medium effects on $A_{\mathrm{HArH^+}}$ were found to be negligible as is usually the case with arenonium ions,[6] but absorbances measured in the more concentrated acid solutions did sometimes change with time. These disturbances could be ascribed to hydrolysis[7] and sulfonation[8] reactions which are known to occur in these media with these substrates; in all cases the changes were sufficiently slow to allow corrections to be made easily by measuring absorbance as a function of time and extrapolating back to the instant of solution preparation.

The substrates examined may be grouped into three categories based on the number of hydroxyl and/or alkoxyl groups they contain. The parent substances of the monosubstituted class, phenol and anisole, proved to be insufficiently basic to be completely protonated in the strongest aqueous acids available, and evaluation of I according to eq 2 was thus impossible. Introduction of two meta methyl substituents, however, raised the basicity to the point where direct measurements of $A_{\mathrm{HArH^+}}$ could be made, and 3,5-dimethylphenol and 3,5-dimethylanisole were therefore used as representatives of this class. The dioxy-substituted series included 1,3-dihydroxybenzene and its mono- and dimethyl ethers in addition to the 2- and 5-methyl derivatives and the dimethyl ether of the former, and the trisubstituted series consisted of 1,3,5-trihydroxy-

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(1) (a) This research was supported by the Petroleum Research Fund of the American Chemical Society and by the U. S. Atomic Energy Commission through grants (No. 1180-A1,4 and AT(11-1)-1025, respectively) to the Illinois Institute of Technology. Taken in part from the Ph.D. Thesis submitted by L. E. Hakka to the Illinois Institute of Technology, June 1966. (b) Part VII: A. J. Kresge, Y. Chiang, and L. E. Hakka, *J. Amer. Chem. Soc.*, **93**, 6167 (1971).

(2) Petroleum Research Fund Fellow.

(3) See accompanying paper, A. J. Kresge, S. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **93**, 6181 (1971).

(4) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 9.

(5) A. J. Kresge and H. J. Chen, *Anal. Chem.*, **41**, 74 (1969).

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

(7) W. M. Schubert and R. H. Quacchia, *ibid.*, **85**, 1284 (1963).

(8) B. G. Ramsey, *ibid.*, **88**, 5358 (1966).

Table I. Indicator Ratios Measured in Aqueous Perchloric Acid at 25°

Wt % acid	Log I	Wt % acid	Log I	Wt % acid	Log I	Wt % acid	Log I
1,3,5-Trihydroxybenzene		1-Hydroxy-3,5-diethoxybenzene		1,3,5-Trimethoxybenzene		1,3-Dihydroxy-2-methylbenzene	
36.69	−1.587	37.71	−1.458	41.21	−1.599	60.61	−1.220
37.71	−1.562	42.23	−0.833	43.42	−1.309	61.69	−0.970
40.16	−1.244	45.83	−0.354	44.31	−1.211	63.46	−0.528
41.37	−1.108	47.81	−0.024	44.66	−1.100	65.22	−0.173
42.23	−1.100	50.03	+0.322	45.83	−0.905	66.26	+0.102
42.36	−1.034	52.74	0.793	45.91	−0.859	68.02	0.568
44.36	−0.837	53.90	1.048	46.77	−0.727	69.41	0.987
46.17	−0.605			47.81	−0.488		
46.59	−0.560	1,3,5-Triethoxybenzene		47.88	−0.458	1,3-Dimethoxy-2-methylbenzene	
46.77	−0.569	42.23	−1.014	47.98	−0.435	61.69	−1.268
48.88	−0.309	44.31	−0.668	49.48	−0.135	63.46	−0.743
49.36	−0.196	45.83	−0.413	50.03	−0.081	66.02	+0.038
50.03	−0.173	47.81	−0.022	50.53	+0.077	69.41	0.962
51.11	−0.021	50.03	+0.378	50.68	0.040		
52.04	+0.063	52.74	0.900	50.96	0.222	1,3-Dihydroxy-5-methylbenzene	
53.15	0.245	53.90	1.114	51.37	0.300	53.90	−1.304
53.90	0.317			52.70	0.598	56.09	−0.922
54.00	0.338	1,3-Dihydroxybenzene		52.74	0.465	57.05	−0.740
54.46	0.464	63.46	−1.192	52.95	0.699	58.83	−0.404
56.09	0.600	65.22	−0.872	53.90	0.714	60.61	−0.054
56.21	0.646	66.75	−0.468	55.01	1.031	61.69	+0.172
56.84	0.738	68.02	−0.219	56.09	1.126	63.47	0.560
57.04	0.707	69.01	+0.080			65.22	0.887
58.83	0.947	70.31	0.436	1,3-Dihydroxy-5-ethoxybenzene		66.26	1.128
59.99	1.205	71.20	0.662	37.71	−1.423	66.75	1.260
61.37	1.383			42.23	−0.932		
				44.31	−0.670	1-Hydroxy-3,5-dimethylbenzene	
1,3-Dihydroxy-5-methoxybenzene		1-Hydroxy-3-methoxybenzene		46.77	−0.352	65.22	−1.188
42.23	−1.125	62.42	−1.118	50.03	+0.106	66.26	−0.897
45.83	−0.616	63.46	−0.863	53.90	0.660	66.75	−0.695
47.87	−0.333	65.22	−0.459	57.05	1.130	68.02	−0.391
50.03	−0.034	66.75	−0.011			69.01	−0.030
50.68	+0.056	68.06	+0.366			70.31	+0.388
52.74	0.330	69.01	0.592			71.20	0.689
53.90	0.505	70.31	0.935			72.37	0.984
57.05	0.923	71.20	1.150			72.60	1.080
61.69	1.454					73.70	1.368
		1,3-Dimethoxybenzene					
1-Hydroxy-3,5-dimethoxybenzene		61.69	−1.094			1-Methoxy-3,5-dimethylbenzene	
42.23	−1.204	62.28	−0.899			65.22	−1.052
44.31	−0.905	63.46	−0.598			66.26	−0.651
45.83	−0.647	65.22	−0.117			67.08	−0.435
46.77	−0.498	66.75	+0.381			68.02	−0.167
47.81	−0.308	68.06	0.683			69.01	+0.255
50.03	+0.052	69.01	1.064			70.31	0.721
50.68	0.156	70.31	1.442			71.20	1.192
52.74	0.500						
53.90	0.701						
56.09	1.002						

benzene and all of its methyl and ethyl ethers. Measurements were made for the most part in perchloric acid, but some substrates were examined in sulfuric acid as well. The results for perchloric acid are summarized in Table I and those for sulfuric acid in Table II.

Indicator ratios for 1,3,5-trihydroxybenzene and its methyl ethers in perchloric acid solution have also been measured in another laboratory,[9] and agreement between that study and the results obtained here is, on the whole, very good. A convenient way to compare the two sets of data is in terms of the H_c acidity function,[10] which provides the best linear correlation of these log I values (*vide infra*). The present results, when fitted to relationships of the form $\log I = a + bH_c$, give standard deviations in log I of 0.027, 0.024, 0.017, and 0.050 for trihydroxybenzene and its mono-, di-, and trimethyl ethers, respectively, whereas the standard deviations of the previously reported[9] data from the same lines are 0.030, 0.056, 0.104, and 0.086 for the compounds taken in the same order. There is a material difference between the two investigations in only one case, the dimethyl ether (which is the most readily hydrolyzed of these substrates), and even here the discrepancy amounts to no more than 0.1 log unit.

Discussion

Acidity Dependence. The position of equilibrium of acid–base reactions in dilute aqueous solution is usually governed by hydrogen ion concentration in the sense of eq 3, but this is seldom if ever true in concentrated acids. This situation has led to the invention of acidity functions, h ($H = -\log h$), which preserve the

$$\log \frac{C_{\mathrm{BH^+}}}{C_{\mathrm{B}}} = \log I = \mathrm{p}K_{\mathrm{BH^+}} + \log C_{\mathrm{H^+}} \qquad (3)$$

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[9] W. M. Schubert and R. H. Quacchia, *J. Amer. Chem. Soc.*, **85**, 1278 (1963).

[10] M. T. Reagan, *ibid.*, **91**, 5506 (1969).

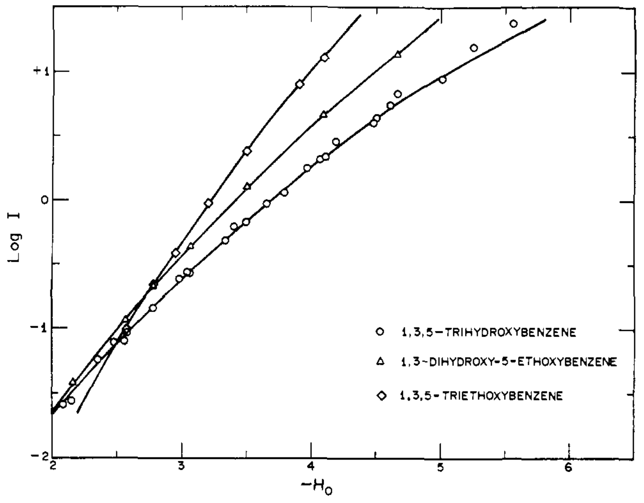

Figure 1. The relationship between H_0 and log I (indicator ratio) for 1,3,5-trihydroxybenzene and its mono- and triethyl ethers.

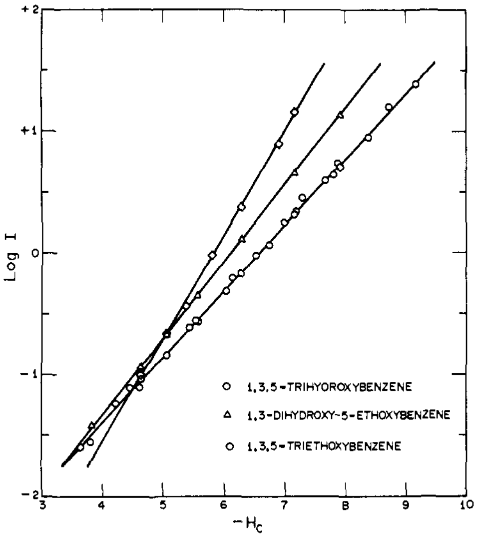

Figure 2. The relationship between H_c and log I (indicator ratio) for 1,3,5-trihydroxybenzene and its mono- and triethyl ethers.

Table II. Indicator Ratios Measured in Aqueous Sulfuric Acid at 25°

Wt % acid	Log *I*	Wt % acid	Log *I*
1,3,5-Trihydroxybenzene		1-Hydroxy-3-methoxybenzene	
39.86	−1.412	70.62	−1.000
41.70	−1.160	71.82	−0.709
44.06	−0.912	72.24	−0.600
44.94	−0.849	72.24	−0.623
47.02	−0.611	74.73	−0.180
48.63	−0.445	74.73	−0.185
48.73	−0.423	75.70	−0.002
50.71	−0.227	75.89	+0.042
52.40	−0.046	75.89	0.054
54.42	+0.178	77.12	0.305
55.99	0.356	77.12	0.320
56.60	0.423	78.23	0.619
58.03	0.631	78.23	0.649
58.59	0.720	78.73	0.762
59.66	0.785	78.73	0.780
59.89	0.881	80.83	1.183
61.61	1.078	80.83	1.197
63.34	1.221	81.24	1.491
64.92	1.372	81.24	1.449
62.90	1.298		
1,3,5-Trimethoxybenzene		1,3-Dimethoxybenzene	
44.22	−1.521	68.60	−1.198
46.84	−1.136	71.01	−0.848
48.23	−0.887	73.31	−0.391
49.26	−0.721	73.67	−0.312
50.76	−0.468	74.80	−0.056
51.87	−0.302	75.96	+0.205
52.97	−0.130	77.07	0.454
54.79	+0.181	78.62	0.719
55.34	0.259	80.93	1.379
56.62	0.450		
58.41	0.791	1,3-Dihydroxy-2-methylbenzene	
60.29	1.068	65.21	−1.565
61.71	1.404	67.78	−1.022
		69.18	−0.739
1,3-Dihydroxybenzene		72.24	−0.193
70.43	−1.161	73.28	−0.044
71.84	−0.923	74.73	+0.217
72.98	−0.723	75.89	0.432
74.44	−0.488	78.23	1.028
75.64	−0.257	78.73	1.209
76.83	−0.064		
77.90	+0.144	1,3-Dimethoxy-2-methylbenzene	
79.25	0.375	69.18	−1.411
80.41	0.568	71.82	−0.801
81.32	0.724	73.28	−0.526
82.65	0.928	74.73	−0.210
83.67	1.063	77.12	+0.286
		80.32	0.962

simple acidity dependence of eq 3 as expressed in eq 4. No single acidity function which makes eq 4 universally

$$\log I = \mathrm{p}K_{\mathrm{BH}^+} + \log h \qquad (4)$$

true exists, but experience has shown that weak bases can usually be grouped into a relatively small number of categories, to each of which a single acidity function applies.[11]

Bases are usually placed into one or another of these categories because of their structure; substances of similar structure tend to have similar protonation acidity dependence. Phenols and phenol ethers are certainly structurally similar, and yet, as we have pointed out in preliminary accounts of this research,[12] no single acidity function serves to correlate the protonation behavior of these bases. This is illustrated in Figures 1 and 2 where values of log *I* for three of the bases studied here are plotted against two typical acidity functions, H_0[13] and H_c.[10] According to eq 4, plots of this kind should be linear and of unit slope, if the acidity function employed is to govern the particular protonation reaction being examined. The relationships between log I and H_0 shown in Figure 1, however, are decidedly not linear, and those between log *I* and H_c (Figure 2), while linear, are not of unit slope; the lines in Figure 2 have slopes, as determined by weighted linear least-squares analysis (*vide infra*), of 0.55 ± 0.01, 0.63 ± 0.01, and 0.85 ± 0.01 for 1,3,5-trihydroxybenzene and its mono- and triethyl ethers, respectively. Moreover, since these different slopes pertain to solutions of the same acid composition, no single acidity scale which is a physically realistic, *i.e.*, single-valued and continuous, func-

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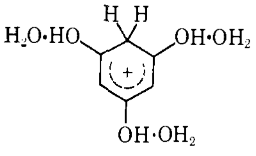
[11] For recent reviews, see: (a) R. H. Boyd in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel-Dekker, New York, N. Y., 1969, Chapter III, and (b) C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

[12] (a) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961); (b) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Amer. Chem. Soc.*, **84**, 4343 (1962); (c) A. J. Kresge, R. A. More O'Ferrall, L. E. Hakka, and V. P. Vitullo, *Chem. Commun.*, 46 (1965).

[13] (a) A. J. Kresge and H. J. Chen, to be published; (b) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

tion of acid concentration can correlate all three sets of data in the sense of eq 4.

Such diverse behavior can nevertheless be understood in terms of hydrogen-bonding interactions of the kind first proposed to account for differences in protonation behavior between primary, secondary, and tertiary anilines.[14] As we[12b] and others[7,15] have pointed out, conjugate acids of phenols can hydrogen bond with the solvent in the manner illustrated in **1** for 1,3,5-trihydroxybenzene; this interaction will offset some of the solvation lost when the proton adds to trihydroxybenzene, and the result will be a characteristic water balance in the protonation reaction (eq 5) and a certain dependence



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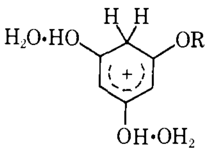

2

$$H^+(H_2O)_n + HAr \overset{K_5}{\rightleftharpoons} HArH^+(H_2O)_m + (n - m)H_2O \quad (5)$$

of its position of equilibrium on water activity (eq 6).

$$K_5 = \frac{[HArH^+(H_2O)_m][H_2O]^{n-m}}{[HAr][H^+(H_2O)_n]} = I\frac{[H_2O]^{n-m}}{[H^+(H_2O)_n]} \quad (6)$$

$$\log I = \log K_5 + \log [H^+(H_2O)_n] - (n - m) \log [H_2O]$$

In the case of phenol ethers, however, this kind of hydrogen-bonding interaction is blocked (**2**), and the water balance of eq 5 is altered. The direction of the change is to greater $(n - m)$ or a stronger inverse dependence of log I on water activity; since the water activity of concentrated acids decreases with increasing acid concentration, this is equivalent to a steeper acidity dependence. This, of course, is the direction of the change illustrated by Figures 1 and 2.

It follows from this explanation that the acidity dependence of the protonation of phenols and phenol ethers might be classified according to the number of free hydroxyl groups they possess, and it is of interest to see whether this is in fact the case. It is perhaps most convenient to do this by examining the slopes of plots of log I *vs.* some acidity function, preferably a scale which gives linear relationships. If, as has been suggested,[16] all acidity functions are linear in one another, and therefore in the premier[17] scale H_0 (eq 7),

$$H_x = c + mH_0 \quad (7)$$

the choice of function is of course immaterial. The contrast between the curved relationships of Figure 1 and the straight lines of Figure 2 suggests, however, that eq 7 may not be universally applicable. Since this is itself a matter of considerable interest, it was investigated in some detail before the individual acidity dependences of phenols and phenol ethers were examined.

To this end, the method of least squares was used to fit the log I values of Tables I and II to linear, quadratic, and cubic expressions in three acidity functions, H_0, H_R', and H_c.[18] In the event that eq 7 holds, the quality of the fits to all three acidity scales would be expected to be the same. If, on the other hand, eq 7 were to be inapplicable in the present situation, some acidity functions should provide better linear correlations than others; furthermore, the quality of these poorer correlations should be improved in going over to quadratic or cubic correlations. In this analysis, account was taken of the fact that the inherent reliability of log I values varies with the magnitude of I, being greatest when I is near unity and least when I is either very large or very small.[5] This was done by weighting log I values in proportion to the reciprocals of their expected uncertainties squared;[19] uncertainties in log I, $\sigma_{\log I}$, were estimated using the recently derived[5] error function shown as eq 8.

$$\sigma_{\log I} \propto (1 + 1/I)(2 + 2I + I^2)^{1/2} \quad (8)$$

The results of this analysis showed, first of all, that cubic expressions are not needed to represent the data, for in virtually no case did the standard deviation in log I, $\sigma_{\log I}$, decrease substantially in going from a quadratic fit to a cubic fit. Quadratic expressions, however, were sometimes a significant improvement over linear relationships, especially in the correlations using H_0 for the trioxy series of substrates in perchloric acid solution: the average value of $\sigma_{\log I}$ for these seven bases dropped from 0.041 for linear fits to 0.018 for quadratic fits. The change was not quite so marked when H_R' was used to correlate these same data: $\sigma_{\log I}$ averaged 0.028 (linear) and 0.019 (quadratic), and with H_c the improvement was hardly significant, $\sigma_{\log I}$ (average) = 0.023 (linear) and 0.020 (quadratic). This demonstrates analytically what Figures 1 and 2 suggest visually, namely that H_c provides respectable linear correlations of these data whereas the relationships between log I and H_0 are decidedly curved. The superiority of H_c is not quite so marked for substrates other than those in the trioxy series, nor is it as strong for these bases in sulfuric acid as it is in perchloric acid. Where substantial differences do exist, however, it seems to be generally true that H_c is better than H_R' and that both are superior to H_0 in providing linear correlations of log I values.

These results imply that H_c is sometimes not a linear function of H_0, and close examination of these scales reveals that this is indeed the case. Figure 3 shows that the gradient of H_c against perchloric acid molarity is nearly constant over its entire measured range, but that H_0 changes direction in the vicinity of 6–7 M. There are in fact approximately linear relationships between H_0 and H_c above and below this region, but not within it. (The derivative dH_c/dH_0 is approximately constant at 1.9 from 2 to 6 M perchloric acid, and at 1.4 above 7 M acid.) Since trihydroxybenzene and its ethers undergo protonation both above and below this region, log I for these bases cannot be a linear function of one of these acidity functions if it is a linear function of the other. The remaining substrates, on the other

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(14) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **82**, 2965 (1960); E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964); **88**, 1177 (1966).

(15) W. M. Schubert and R. H. Quacchia, *ibid.*, **84**, 3778 (1962).

(16) (a) K. Yates and R. A. McClelland, *ibid.*, **89**, 2686 (1967); (b) ref 4, p 275.

(17) Premier in point of time and very probably also in respect to the accuracy with which its values are known.

(18) H_0 was chosen because it is the most widely used and probably most accurately known acidity function, and H_R' and H_c, because they would seem to be the most appropriate functions for carbon protonations such as the present reactions.

(19) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," Wiley, New York, N. Y., 1954, p 244.

Table III. Slopes and Intercepts of Linear Correlations of Log I with H_c

Substrate	Slope ($-$d log $I/\mathrm{d}H_c$) HClO$_4$ Obsd	Slope HClO$_4$ Calcd[a]	Slope H$_2$SO$_4$ Obsd	Slope H$_2$SO$_4$ Calcd[b]	Intercept HClO$_4$	Intercept H$_2$SO$_4$
1,3,5-Trihydroxybenzene	0.55 ± 0.01	0.48	0.63 ± 0.01	0.67	−3.59 ± 0.04	−3.74 ± 0.03
1,3-Dihydroxy-5-methoxybenzene	0.61 ± 0.01	0.61			−3.87 ± 0.08	
1-Hydroxy-3,5-dimethoxybenzene	0.74 ± 0.01	0.75			−4.61 ± 0.05	
1,3,5-Trimethoxybenzene	0.92 ± 0.02	0.88	0.90 ± 0.01	0.91	−5.80 ± 0.14	−5.57 ± 0.05
1,3-Dihydroxy-5-ethoxybenzene	0.63 ± 0.01	0.61			−3.84 ± 0.01	
1-Hydroxy-3,5-diethoxybenzene	0.72 ± 0.01	0.75			−4.21 ± 0.08	
1,3,5-Triethoxybenzene	0.85 ± 0.01	0.88			−4.94 ± 0.06	
1,3-Dihydroxybenzene	0.70 ± 0.02	0.65	0.76 ± 0.01	0.78	−8.13 ± 0.25	−8.29 ± 0.11
1-Hydroxy-3-methoxybenzene	0.78 ± 0.02	0.79	0.92 ± 0.02	0.92	−8.58 ± 0.22	−9.62 ± 0.24
1,3-Dimethoxybenzene	0.87 ± 0.02	0.92	0.95 ± 0.02	0.94	−9.13 ± 0.22	−9.81 ± 0.23
1,3-Dihydroxy-2-methylbenzene	0.73 ± 0.02	0.65	0.84 ± 0.03	0.78	−7.77 ± 0.20	−8.40 ± 0.26
1,3-Dimethoxy-2-methylbenzene	0.88 ± 0.05	0.92	0.93 ± 0.02	0.94	−9.40 ± 0.50	−9.73 ± 0.19
1,3-Dihydroxy-5-methylbenzene	0.67 ± 0.01	0.65			−6.08 ± 0.05	
1-Hydroxy-3,5-dimethylbenzene	0.86 ± 0.02	0.83			−10.15 ± 0.29	
1-Methoxy-3,5-dimethylbenzene	0.97 ± 0.04	0.96			−11.14 ± 0.46	

[a] Based on 0.17 and 0.04 as the slope-lowering parameters per hydroxy and alkoxy group, respectively. [b] Based on 0.11 and 0.03 as the slope-lowering parameters per hydroxy and alkoxy group, respectively.

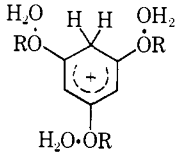
hand, are weaker bases and protonate largely above 7 M acid where these two acidity functions, being linearly related, are equally capable of providing linear correlations. Sulfuric acid is different from perchloric in that H_0 and H_c are approximately linear functions of one another throughout the entire measured range; thus, here also these two scales can provide linear correlations of similar quality. It seems, therefore, to have been a fortuitous accident that eq 7 was first proposed (and used successfully)[16a] on the basis of data obtained in sulfuric acid; it does appear to be approximately valid in this medium in spite of its breakdown in regions of perchloric acid.

Table IV. Values of H_c for Perchloric Acid in the Region above 60 Wt % at 25° [a]

Wt % HClO$_4$	M HClO$_4$	$-H_c$
61.60	9.50	9.25
63.67	10.00	9.88
65.70	10.50	10.53
67.68	11.00	11.19
69.63	11.50	11.91
71.56	12.00	12.73

[a] These and the values published in ref 10 are represented to within 0.02 unit by the following polynominals: 0.5–7.0 M HClO$_4$, $-H_c = -0.3672 + 5.099(M/10) + 59.36(M/10)^2 - 321.4\cdot(M/10)^3 + 757.2(M/10)^4 - 801.7(M/10)^5 + 316.1(M/10)^6$; 7.0–12.0 M HClO$_4$, $-H_c = -99.971 + 551.11(M/10) - 1128.7(M/10)^2 + 1074.3(M/10)^3 - 378.27(M/10)^4 - 60.907(M/10)^5 + 52.333(M/10)^6$.

Since the H_c acidity function provides good linear correlations of the present log I data, it was chosen as the basis against which to examine the acidity dependence of these protonation reactions, and, in particular, to determine whether acidity dependence is related to the number of free hydroxyl groups which a substrate possesses in positions able to take on positive charge. The results, presented in Table III, show that slopes, $-\mathrm{d}\log I/\mathrm{d}H_c$, do increase regularly as hydroxyl groups are converted into alkoxyl functions. In fact, least-squares analysis of the data obtained in sulfuric acid gives a relationship, $-\mathrm{d}\log I/\mathrm{d}H_c = 0.95 - 0.09n$, where n is the number of hydroxyl groups, which reproduces the slopes with an average deviation of 0.04. The H_c acidity function, however, is based principally on hydrocarbon indicators whose conjugate acids presumably do not undergo specific interaction with the solvent;[10] the constant term of this relationship might therefore be expected to be unity, *i.e.*, those substrates without free hydroxyl groups should show protonation behavior exactly parallel to H_c. The fact that they do not suggests that there may be another interaction mechanism, perhaps electrostatic stabilization of positively charged oxygen as in **3**, in addition to the hydrogen-bonding effect shown above in structures **1** and **2**. The correlation between slopes and structure is in fact improved if a second effect, specific to alkoxyl groups, is introduced; the average deviation in d log $I/\mathrm{d}H_c$ drops to 0.02, very nearly the same as its experimental uncertainty, when slope-lowering parameters of 0.11 and 0.03 (least-squares values) for hydroxyl and alkoxyl, respectively, are used to reproduce the data.



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A similar analysis of acidity dependence in perchloric acid solution must at first be limited to substrates in the trihydroxybenzene series, for the original determination of H_c[10] did not provide values above 60 wt % acid, where the other bases examined here are protonated. The data for these seven most basic substrates yield 0.17 and 0.04 as the best values of slope-lowering parameters for hydroxyl and alkoxyl groups, respectively, and these reproduce the observed values with an average difference of 0.03.

With these slope-lowering parameters for perchloric acid solution in hand, it is now possible to extend the H_c scale into the region above 60 wt % acid. Log I values for 1,3-dimethoxybenzene, 1,3-dimethoxy-2-methylbenzene, and 1-methoxy-3,5-dimethylbenzene (Table I) were used for this purpose, since these are the bases which should provide the least interaction with the solvent and thus approach true H_c indicators most closely; what differences do remain were corrected for by using 0.04 as the slope-lowering effect of a methoxyl group.[20] Values of this extended H_c scale are presented in Table IV.

Table V. Basic Strengths of Phenols and Phenol Ethers Referred to Dilute Aqueous Solution at 25°

	pK_a	
Substrate	$HClO_4$	H_2SO_4
1,3,5-Trihydroxybenzene	−3.13 ± 0.04	−3.37 ± 0.03
1,3-Dihydroxy-5-methoxybenzene	−3.48 ± 0.08	
1-Hydroxy-3,5-dimethoxybenzene	−4.35 ± 0.06	
1,3,5-Trimethoxybenzene	−5.72 ± 0.14	−5.46 ± 0.05
1,3-Dihydroxy-5-ethoxybenzene	−3.47 ± 0.02	
1-Hydroxy-3,5-diethoxybenzene	−3.93 ± 0.09	
1,3,5-Triethoxybenzene	−4.78 ± 0.06	
1,3-Dihydroxybenzene	−7.83 ± 0.25	−8.05 ± 0.11
1-Hydroxy-3-methoxybenzene	−8.37 ± 0.22	−9.54 ± 0.24
1,3-Dimethoxybenzene	−8.99 ± 0.22	−9.75 ± 0.23
1,3-Dihydroxy-2-methylbenzene	−7.51 ± 0.20	−8.24 ± 0.26
1,3-Dimethoxy-2-methylbenzene	−9.29 ± 0.50	−9.66 ± 0.19
1,3-Dihydroxy-5-methylbenzene	−5.75 ± 0.05	
1-Hydroxy-3,5-dimethylbenzene	−10.01 ± 0.29	
1-Methoxy-3,5-dimethylbenzene	−11.11 ± 0.46	

These new H_c values were then used to calculate the remaining slopes presented in Table III; these, too, are well reproduced by the slope-lowering parameters obtained from the trihydroxybenzene series; the average deviation between observed and calculated slopes is again 0.03. Thus, the acidity dependence of the protonation of all of the bases examined here can be explained in considerable detail in terms of specific interactions between benzenonium ion conjugate acids and the solvent.

Basic Strength. The variety in acidity dependence shown by the phenols and phenol ethers examined here prevents their being put on a common basicity scale applicable in concentrated acid solutions; it also makes quantitative evaluation of their basic strength difficult, and it even eliminates a unique ordering of basicity in qualitative terms. For example, as Figures 1 and 2 show, 1,3,5-trihydroxybenzene is more basic (has the greater I value) than 1,3,5-triethoxybenzene in solutions of low acidity, but in more concentrated acids this order is reversed. Such behavior is general for substrates of the trihydroxybenzene series; all of the log I plots intersect someplace within the measured range ($-H_c$ = 4–8, 40–60 wt % $HClO_4$). As a result, in solutions more dilute than 40% acid, conversion of hydroxyl substituents to alkoxyl groups lowers basic strength, whereas in solutions more concentrated than 60% acid, the opposite is true. This behavior persists in substrates of the mono- and dihydroxybenzene series, for, although these ethers generally appear more basic than the corresponding phenols in the regions where measurement was made, extrapolation of log I plots down to lower acidities implies that crossovers will occur before dilute solution is reached.

Such inversion of basic strength suggests that two opposing mechanisms by which substituents interact with the system are in operation. The two mechanisms which can be identified in the present case are (1) stabilization of positive charge in the benzenonium ion through direct electron release from the substituent, at which alkoxy groups are more effective than hydroxy, and (2) distribution of this charge into the solvent *via* hydrogen bonding, at which hydroxy groups are more effective than alkoxy. The hydrogen-bonding effect predominates at low acidities where the concentration of water molecules, which are fairly basic and therefore good hydrogen bond acceptors, is high, and the other effect takes over at higher acidities where water molecules are replaced by more acidic solvent species. Thus, the basic strength of phenols and phenol ethers depends not only on the structure of the molecules themselves, but also on the medium in which they are placed. Since no greater fundamental significance may be attached to any one medium over another, there can be no unique order of intrinsic basic strength. Relative basicities in any given perchloric or sulfuric acid solution can, on the other hand, be evaluated by calculating and comparing the appropriate indicator ratios using the relationships of Table III.

From a practical point of view, there is one medium, dilute aqueous solution, which is more important, if not more fundamental, than others simply because it has been used more often than any other for measurements of acid–base properties. Dilute solution pK_a's cannot, of course, be obtained directly from measurements conducted in concentrated acids; some kind of extrapolation of data from the concentrated into the dilute region must be performed. It has been suggested[21] that this can be done by extending the quantity [(log I) + H_0] as a linear function of the difference between $-H_0$ and log C_{H^+} down to the point where H_0 + log C_{H^+} becomes equal to zero; this of course occurs in dilute solution where (log I) + H_0 = (log I) − log C_{H^+} = pK_a. This procedure, however, requires that log I be a linear function of H_0, which is certainly not true in the present case. This method was therefore not used, and pK_a's were estimated simply by extrapolating the linear log I *vs.* H_c relationships of Table III down to H_c = +1.00 and then adding 1.00 to the values so obtained. These extrapolations were terminated at H_c = +1.00 because this is where H_0 is known to become effectively equal to −log C_{H^+},[13a] and the same is likely to be true also for other acidity scales based on uncharged indicators.

The results obtained in this way are listed in Table V, together with uncertainties estimated by propagating errors (standard deviations) in the slope and intercept parameters of individual (log I) − H_c relationships.

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(20) The original H_0 scale[10] did in fact use several methoxy-substituted benzenes as indicators without correcting for the slope-lowering effect detected here. It is unlikely, however, that this had much effect on the final results, for, whenever a methoxybenzene was used, it was closely flanked on both sides by hydrocarbon bases. Since none of the bases employed in the present study were wholly hydrocarbon, a similar masking effect could not be relied upon here.

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

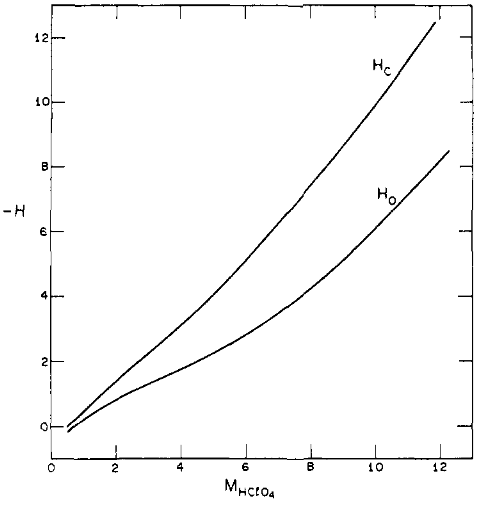

Figure 3. The H_0 and H_c acidity functions in aqueous perchloric acid.

These error limits depend only upon the precision of the measurements and do not reflect constant systematic errors inherent in the method; a more realistic assessment of the accuracy of these figures might therefore be perhaps twice the listed uncertainties, *i.e.*, ±0.1–0.2 pK unit for the strongest bases and ±1.0 unit for the most weakly basic substrates. It is of interest that these pK_a's are consistently more negative than the numbers obtained for the few cases where [(log I) + H_0] *vs.* [H_0 + log C_{H^+}] extrapolations were tried. Both the direction of this difference and its increasing magnitude from 0.2 pK unit for 1,3,5-trihydroxybenzene to 1.7 unit for 1-methoxy-3,5-dimethylbenzene are understandable in terms of the relationship between H_0 and H_c visible in Figure 3.

The pK_a's of Table V are in full accord with the idea, developed above, that hydroxyl groups are superior to alkoxyl substituents at stabilizing benzenonium ions in water-rich solvents. For example, trihydroxybenzene is a stronger base in dilute aqueous solution (has the more positive pK_a) than either trimethoxy- or triethoxybenzene, and within both sets of partial ethers as well there is a regular sequence of decreasing pK_a with increasing number of alkoxyl groups. There are, in fact, ten pairs of substrates in Table V which differ only in the replacement of one hydroxyl by one alkoxyl group, and in each case this change is accompanied by a decrease in pK_a; the average difference is 0.8 pK unit, but actual changes are slightly larger for methoxyl than for ethoxyl because ethoxyl is itself somewhat more base strengthening than methoxyl, *e.g.*, the pK_a of triethoxybenzene is one unit more positive than the pK_a of trimethoxybenzene.

The dominant feature of these pK_a data is of course the strong base-strengthening effect of oxy groups in general, whether they be hydroxy or alkoxy. Trimethoxybenzene, for example, is more basic than dimethoxybenzene by some four powers of ten, and the difference for the corresponding hydroxy compounds is greater by still another order of magnitude. These effects are 10^2–10^3 stronger than that of a methyl group situated in the same position; the difference in pK_a between 1,3-dihydroxybenzene and 1,3-dihydroxy-5-methylbenzene is only 2.1 unit. The latter, on the other hand, is considerably greater than the effect of a methyl group meta to the site of protonation; comparison of 1,3-dihydroxybenzene with 1,3-dihydroxy-2-methylbenzene (ΔpK_a = 0.3 for $HClO_4$ and 0.2 for H_2SO_4) or 1,3-dimethoxybenzene with 1,3-dimethoxy-2-methylbenzene (ΔpK_a = −0.3 for HClO and 0.1 for H_2SO_4) shows that methyl in this position has hardly any effect at all. In the presence of such strongly interacting groups as hydroxy and alkoxy, the demand for positive charge stabilization by methyl groups might be reduced, and it is significant, therefore, that each of the methyl group effects found here is considerably weaker than the corresponding effect on the basicity of purely alkyl substituted benzenes; for a series of methylbenzenes, introduction of methyl meta to the site of substitution was found to increase pK_a's by 0.7 unit and ortho (and para), by 3.0 unit.[22]

It is possible to use the data of Table V to estimate pK_a's for some molecules of interest whose basic strength could not be measured in aqueous acids directly. For example, subtracting the effect of two ortho methyl groups, estimated as twice the pK_a difference between 1,3-dihydroxybenzene and 1,3-dihydroxy-5-methylbenzene, from 1-hydroxy-3,5-dimethylbenzene, gives −14.2 ± 0.5 as the pK_a of phenol protonated on para carbon, and similar treatment of 1-methoxy-3,5-dimethylbenzene gives −15.3 ± 0.6 as the corresponding number for anisole.[23] This procedure can be extended to benzene itself after allowance is made for the increase in individual effectiveness of strongly interacting groups which attends a decrease in their number, *viz.*, the effect of hydroxyl increases from 4.5 ± 0.3 as ΔpK_a between trihydroxybenzene and dihydroxybenzene to 6.0 ± 0.5 as ΔpK_a between dihydroxybenzene and phenol, and the effect of methoxyl as measured by the corresponding methoxy compounds rises similarly from 3.1 ± 0.3 to 6.0 ± 0.7 pK units.[23,24] Saturation effects of this kind have also been observed in the ionization of triphenylcarbinol and its para methoxy derivatives in concentrated acids,[25] where the first substituent is 1.35 times as effective as the second. If the same factor is assumed to operate in the present case, extrapolation of the hydroxybenzene data to benzene gives pK_a = −23.3 and extrapolation of the methoxybenzene data, −22.3. Since these numbers are based on one position (para) in phenol and anisole, they refer to the basicity of one position in benzene. The pK_a of protonated benzene with six basic sites may be obtained by adding log 6 to these results. This gives an average value of pK_a = −22.0.

These estimates of the basic strength of benzene agree well with the pK_a obtained by yet another comparison. Basicity constants, pK_B, for benzene and for all of its methyl derivatives have been measured in hydrogen

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[22] D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., Chapter 20.

[23] The uncertainties were estimated by propagating errors (standard deviations) in constituent quantities.

[24] These comparisons are based on pK_a's corrected for symmetry, *i.e.*, they take into account the fact that trioxybenzenes have three basic sites, dioxybenzenes, two, and monooxybenzenes, one. (The nmr spectrum of carbon-protonated anisole shows no evidence of the ortho isomer, and both the nmr spectra and rates of tritium–protium exchange of 1,3-dimethoxybenzene indicate its 2 position to be an order of magnitude less basic than the 4 or 6 position[1b,3,22].)

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

fluoride solution,[22] and, although these values cannot be compared directly with the $\mathrm{p}K_\mathrm{a}$'s evaluated here because the standard states are different, one scale can be translated into the other by virtue of the fact that the $\mathrm{p}K_\mathrm{a}$ of hexamethylbenzene has also been determined in aqueous sulfuric acid.[26] The $\mathrm{p}K_\mathrm{B}$ values of benzene and hexamethylbenzene are 9.2 and -1.4, respectively, and the $\mathrm{p}K_\mathrm{a}$ of hexamethylbenzene is -13.3; adding the $\mathrm{p}K_\mathrm{B}$ difference between benzene and hexamethylbenzene to -13.3 then gives -23.9 as the $\mathrm{p}K_\mathrm{a}$ of benzene. This, combined with the previous two values, suggests $\mathrm{p}K_\mathrm{a} = -23 \pm 1$ as the best estimate of the basic strength of benzene.

The estimates made above of $\mathrm{p}K_\mathrm{a} = -14$ and -15 for phenol and anisole protonated on carbon in the para position are of interest in relation to an earlier study of these substances whose results were interpreted in terms of protonation on oxygen.[27] These data indicated that these oxonium ions were formed in 75–80% sulfuric acid, a region somewhat below the 90–95% acid which the presently estimated $\mathrm{p}K_\mathrm{a}$'s imply to be necessary for carbon protonation. Thus, in a sense, the oxygen atom of phenol and anisole is a more basic site than ring carbon, at least in aqueous solution. As the acidity of the medium is increased, however, these first-formed oxygen-protonated species will give way to carbon-protonated conjugate acids, for protonation on oxygen will have a shallower acidity dependence (*ca.* H_0)[27] than protonation on carbon (*ca.* H_c). In very strongly acidic media, therefore, carbon will be the more basic site.

Experimental Section

Materials. The substrates used were also employed in the study described in the preceding paper;[1b] their synthesis is detailed there. Perchloric acid more concentrated than 70 wt % was prepared by mixing commercial 70% acid with perchloric acid monohydrate (85% acid) which was purchased from the G. Frederick Smith Chemical Co. All other materials were best available commercial grades and were used without further purification.

Indicator Measurements. Sample solutions were prepared by allowing 25-ml aliquots of aqueous acid to equilibrate with a constant temperature bath operating at 25.0 ± 0.1° and then adding 50 μl of *ca.* 10^{-1} *M* aqueous or methanolic stock solution of aromatic base. These 50-μl aliquots were delivered using Lang-Levy micropipets, whose precision, as determined by titration of samples of acid dispensed from them, was better than ±0.2%.

The absorbance of sample solutions was measured against references consisting of acid at the same concentration using a spectrometer (Beckman DK-2) whose cell compartment was thermostated at 25.0 ± 0.1°. (The temperature coefficient of absorbance was determined in a few cases and proved always to be less than 1% per degree.) For solutions whose absorbance changed with time, the time-scan mode of the spectrometer was employed and absorbance was extrapolated linearly back to the time of mixing aromatic base with acid. Replicate measurements on the same solution showed a reproducibility (standard deviation) better than 0.01 absorbance unit in all cases, and better than 0.003 unit for solutions whose absorbance did not change with time.

Acid concentrations were determined as weight per cent by titration with standard base, and values of acidity functions were interpolated using polynomial expressions relating the acidity function to weight per cent acid.

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[26] N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, **81**, 5790 (1959).

[27] E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 5660 (1960).

Aromatic Protonation. IX. The Kinetic Protonation of Hydroxy- and Alkoxybenzenes[1]

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Abstract: Rates of aromatic hydrogen exchange (protodetritiation) of 1,3,5-trihydroxybenzene and its trimethyl and triethyl ethers, 1,3-dimethoxybenzene, 1,3-dihydroxy-2-methylbenzene and its dimethyl ether, and anisole were measured in concentrated aqueous perchloric acid solutions. The kinetic acidity dependence of these reactions varies markedly from substrate to substrate, but the variations can be understood in terms of two factors: (1) differences in substrate structure, and (2) differences in the extent of proton transfer at transition states. Suitable treatment of these kinetic data, together with the results of equilibrium protonation of the same substrates presented in the previous paper, gives values of α_A, a parameter which measures the extent of transition state proton transfer, which range from 0.5 to 0.9. These same data provide a curved Brønsted relation whose slopes, α_B, are in excellent agreement with the α_A values. This identification of transition state as well as substrate structure as important factors governing kinetic acidity dependence in concentrated acids implies certain limitations on the use of kinetic acidity dependence as a criterion of reaction mechanism.

In the preceding paper of this series,[1b] we described a study of the equilibrium protonation of a group of hydroxy- and alkoxy-substituted benzenes related to phloroglucinol, resorcinol, and phenol. We now add to that an investigation of the kinetics of some of these protonation reactions. The results, just as those of the companion study, in addition to providing specific information about the substances examined, afford insight into the general nature of concentrated acid solu-

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[1] (a) This research was supported by the U. S. Atomic Energy Commission through a grant (No. AT(11-1)-1025) to the Illinois Institute of Technology. Taken in part from a Ph.D. Thesis submitted by V. P. Vitullo to the Illinois Institute of Technology, June 1965. (b) Part VIII: A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *J. Amer. Chem. Soc.*, **93**, 6174 (1971).

[2] Fellow of the U. S. Steel Foundation, 1962–1964.