

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

The Acidity Dependence of the Carbon Protonation of Phloroglucinol and its Methyl Ethers

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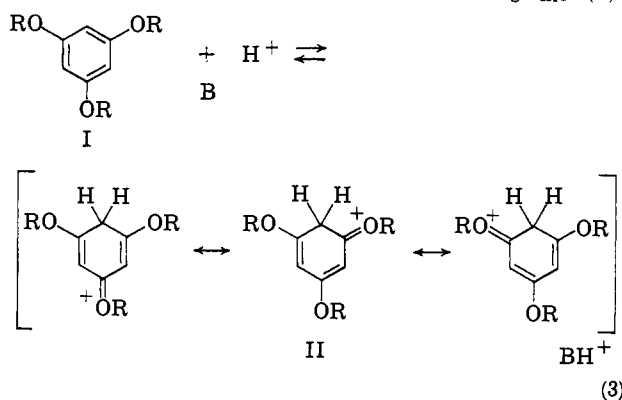
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The equilibrium carbon protonation of phloroglucinol and its methyl ethers in 40–65% perchloric acid has been studied by the usual ultraviolet spectrophotometric methods. An acidity dependence lying between H_0 and H'_R is shown by the protonation of the triether, $-\log ([BH^+]/[B])/dH_0$ having the value 1.26. The protonations of phloroglucinol and its mono- and dimethyl ethers are much more closely dependent on H_0 than on H'_R . The quantity $-\log ([BH^+]/[B])/dH_0$ declines as methoxyl substituents are successively replaced by hydroxyl, reaching the minimum value of 0.85 for phloroglucinol. It is concluded that the function H'_R does not always apply to carbon protonation; further, that neither H_0 nor H'_R are unique functions for the reversible protonation of neutral bases. The decline in $-\log ([BH^+]/[B])/dH_0$ as methoxyl substituents are replaced by hydroxyl, due to a decline in $-\log (f_B/f_{BH^+})/dH_0$, is rationalized in terms of hydrogen-bonding solvation of the positive hydroxyl hydrogens of the conjugate acid. An Area Method of determining $[BH^+]/[B]$, in which integrated intensities in a region of the spectrum are used, has been successfully applied here.

For many years it was more or less assumed that the equilibrium protonation of weak neutral bases should be dependent on the Hammett acidity function.¹ However, Deno, Groves and Saines recently concluded that the carbon protonation of diarylolefins is dependent on the H'_R acidity function rather than on H_0 .^{2,3} A number of diarylolefin-diaryllalkyl cation equilibria were studied in from 42 to 92% sulfuric acid, with from three to four values of $[BH^+]/[B]$ being measured for each olefin base. In general, the data fit eq. 2 better than eq. 1, which has been extensively applied to the reversible protonation of weak nitrogen and oxygen bases.⁶ Later, Kresge and Chiang reported that the equilibrium carbon protonation of 1,3,5-trimethoxybenzene, eq. 3 ($R = CH_3$), follows H'_R .⁵

$$pK_{BH^+} = H_0 + \log ([BH^+]/[B]) \quad (1)$$

$$pK'_{BH^+} = H'_R + \log ([BH^+]/[B]); H'_R = H_R - \log a_{H_2O} \quad (2)$$



Agreement of the protonation of the carbon bases with eq. 2 would imply that the activity coefficient ratio f_B/f_{BH^+} varies in the same way with medium as does f_{ROH}/f_R^+ for the indicator arylmethanols used to determine H_R .^{2,3} Agreement with eq. 1 would imply that f_B/f_{BH^+} varies as the corresponding ratio for the neutral bases used to determine H_0 .^{1,6}

A possible implication of the results of references 2 and 5 is that equilibrium protonation on carbon may in general not be dependent on the same acidity func-

tion as protonation on nitrogen or oxygen; further, that carbon protonation may in general be specifically dependent on H'_R . However, in preliminary communications on independent work, both Schubert and Quacchia⁷ and Kresge and Chiang⁸ reported that the equilibrium protonation of phloroglucinol and its ethers (methyl⁷ and ethyl⁸) is not uniquely described by either H_0 or H'_R . That is, the quantities $-\log ([BH^+]/[B])/dH_0$ or $-\log ([BH^+]/[B])/dH'_R$ varied according to the specific compound.

The present paper describes the details of the results reported in the Communication.⁷ At the time of appearance of references 2 and 5, the study of the equilibrium protonation of the mono-, di- and trimethyl ethers of phloroglucinol was being carried out in these laboratories as a necessary adjunct to a kinetic study of the acid-catalyzed hydrolysis reaction of these ethers.⁹ The work then was extended to an examination of the equilibrium protonation of phloroglucinol itself.

Experimental

Preparation of Materials.—Phloroglucinol was purified by recrystallization from water and drying; m.p. 195–205° dec. Treatment of phloroglucinol with dimethyl sulfate and sodium hydroxide yielded 1,3,5-trimethoxybenzene,¹⁰ which was distilled, b.p. 130–133° at 10 mm., recrystallized from ligroin, then ethanol, and sublimed; m.p. 52–53°. Phloroglucinol monomethyl ether was prepared in a similar manner; m.p. 77–78°. Phloroglucinol dimethyl ether, m.p. 42.5–43.5°, was prepared by hydrolysis of the diazonium salt of 3,5-dimethoxyaniline.

Perchloric acid solutions were prepared by dilution of concentrated reagent grade perchloric acid (Merck), and their strength determined by titration against standard base.

Spectral Measurements.—The Cary model 14 spectrophotometer was used to make spectral measurements at $22 \pm 2^\circ$ of perchloric acid solutions about 10^{-4} molar in substrate. Spectra were taken as soon as possible after preparation, since slow decomposition of the substrate occurs. In higher acid percentages, readings at the wave lengths of interest were made within 45 sec. of preparation of the solutions; n.m.r. spectra were determined by Mr. B. J. Nist using a Varian HR-60 spectrometer.

Results

The spectrum of 1,3,5-trimethoxybenzene at room temperature in 95% ethanol and in various percentages of perchloric acid starting with 40% is shown in Fig. 1. Owing to the insolubility of the ether, the spectrum was not measured in lower strengths of perchloric acid. Readings at the wave lengths of interest on the solutions of highest acid strength were made within 45 seconds of mixing. Cleavage of the ether was negligible in this length of time, and such readings agreed well with readings extrapolated to zero time from

(7) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **84**, 3778 (1962).

(8) A. J. Kresge, G. W. Barry, K. R. Charles and Y. Chiang, *ibid.*, **84**, 4343 (1962).

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

(10) H. Bredereck, I. Hennig and W. Rau, *Chem. Ber.*, **86**, 1085 (1953).

(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. 9.

(2) N. C. Deno, P. T. Groves and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).

(3) $H'_R = H_R - \log a_{H_2O}$, where H_R is the acidity function for the complex ionization of arylmethanols to the corresponding arylmethyl cations.⁴ The function $H_R - \log a_{H_2O}$ was first defined by Deno, Groves and Saines² and conveniently labeled H'_R by Kresge and Chiang.⁵

(4) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

(5) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, **81** (1961).

(6) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

measurements made over longer periods of time.^{11,12} The spectrum of free base in 95% ethanol has a weakly absorbing peak at a λ_{\max} of 266 $m\mu$ (ϵ 576) and a much stronger band below 230 $m\mu$. In perchloric acid of increasing strength these peaks are replaced by strong peaks of the conjugate acid at 247 $m\mu$ (ϵ 20,300) and 347 $m\mu$ (ϵ 12,300). Protonation in 63.5% perchloric acid is essentially complete, as verified by the pK values obtained. Spectral data pertinent to the calculation of pK values are given in Table I.

TABLE I
VALUES OF $\epsilon \times 10^{-3}$ FOR 1,3,5-TRIMETHOXYBENZENE^a

HClO ₄ , %	λ , $m\mu$					
	252	335	340	345	350	355
0 ^b	0.37	0	0	0	0	0
44.7	1.89	0.78	0.91	0.98	0.95	0.85
47.8	4.77	2.17	2.56	2.76	2.76	2.44
48.0	5.54	2.52	2.96	3.18	3.14	2.78
50.0	9.55	4.45	5.11	5.58	5.48	4.87
50.2	9.45	4.48	5.21	5.62	5.59	4.89
52.4	14.08	6.62	7.86	8.49	8.30	7.40
54.2	16.72	7.93	9.34	9.96	9.92	8.76
55.7	18.97	8.88	10.40	11.30	11.22	10.05
63.5	20.31 ^c	9.73 ^c	11.42 ^c	12.29 ^c	12.16 ^c	10.78 ^c
^d	23.67	11.08	12.95	14.05	14.02	12.53

^a Measured at $22 \pm 2^\circ$, quickly after solution prepared.

^b Spectrum in 95% ethanol, taken as that of the free base, ϵ_B .

^c Measured within 45 sec. and taken as ϵ_{BH^+} . ^d Value of ϵ_{BH^+} calculated, using eq. 5 ($h = h_0$) for acids through 55.7%.

Phloroglucinol and its mono- and dimethyl ethers show changes of spectrum with increasing perchloric acid strength that are very similar to those observed for the trimethyl ether. Pertinent spectral results are given in Tables II, III and IV. Solutions of phloro-

TABLE II
VALUES OF $\epsilon \times 10^{-3}$ FOR PHLOROGLUCINOL^a

HClO ₄ , %	λ , $m\mu$				
	242	335	340	345	350
0 ^b	0.40	0	0	0	0
44.8	...	1.09	1.18	1.18	1.06
47.8	4.43	2.38	2.48	2.54	2.31
50.0	6.57	3.52	3.76	3.73	3.36
52.2	9.02	4.91	5.28	5.25	4.76
54.0	10.76	5.87	6.33	6.28	5.68
55.7	12.21	6.74	7.28	7.23	6.57
63.5	14.73	8.31	8.99	8.95	8.09
67.0 ^c	15.29	8.73	9.39	9.30	8.35
^d	14.03	7.66	8.36	8.21	7.48

^a Measured at $22 \pm 2^\circ$. ^b Spectrum in 20% ethanol, taken as ϵ_B .

^c Taken as ϵ_{BH^+} . ^d Values of ϵ_{BH^+} calculated using eq. 5 ($h = h_0$) for acids through 55.7%.

glucinol in strong perchloric acid are relatively stable, so that no special precautions were necessary other than that the solutions not be allowed to stand for long periods of time before spectral readings were made. As in the case of the triether, the ether cleavage reactions of the mono- and diethers were sufficiently fast in the stronger perchloric acid solutions to make mandatory the fairly rapid measurement of the pertinent spectral data. Readings were made within 45 seconds after mixing. Values of ϵ at zero time, determined by an extrapolation procedure at two wave lengths for the monoether in 60.0% perchloric acid,¹² closely checked the values obtained by direct rapid measurement.¹³ The hydrolysis of diether, about

(11) The half-life for hydrolysis of 1,3,5-trimethoxybenzene in 63.5% perchloric acid at 22° is estimated to be greater than 150 minutes.⁹

(12) An extrapolation procedure at constant temperature requires ideally that the system be at temperature equilibrium the instant the substrate is dissolved.

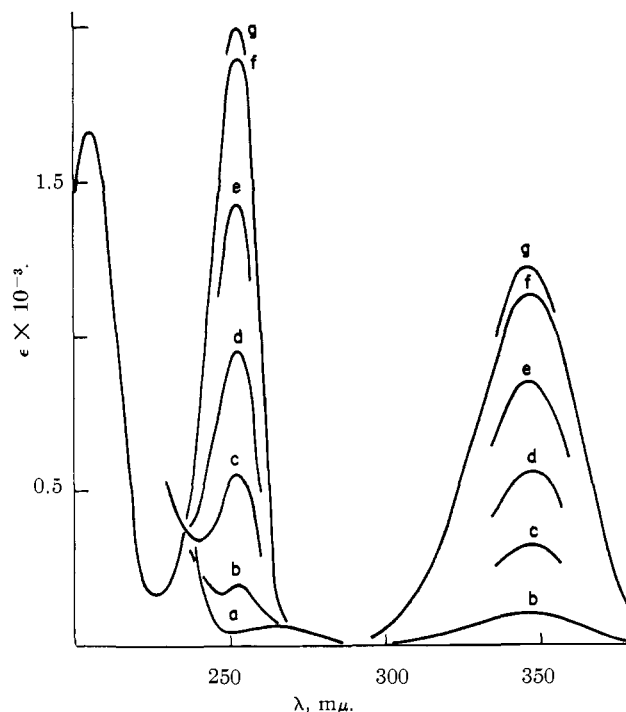


Fig. 1.—Plot of ϵ vs. λ for 1,3,5-trimethoxybenzene in aqueous perchloric acid: curve a, 95% ethanol; curves b-g, 44.7, 48.0, 50.0, 52.4, 55.7 and 63.5% HClO₄, respectively.

five times as fast as that of the monoether in the same medium, was too fast for reliable ϵ_{BH^+} values to be obtained by rapid spectral measurements in a per-

TABLE III

VALUES OF $\epsilon \times 10^{-3}$ FOR 1-METHOXY-3,5-DIHYDROXYBENZENE^a

HClO ₄ , %	λ , $m\mu$				
	244	335	340	345	350
0 ^b	0.38	0	0	0	0
43.8	2.34	1.18	1.25	1.23	1.09
44.8	2.95	1.54	1.64	1.61	1.43
47.8	5.69	3.09	3.31	3.27	2.91
48.1	6.04	3.35	3.59	3.53	3.16
50.2	8.65	4.85	5.22	5.17	4.64
52.2	11.56	6.52	7.01	6.95	6.27
54.2	13.31	7.56	8.20	8.17	7.43
55.7	14.39	8.08	8.86	8.85	8.08
60.0	16.03 ^c	9.24 ^c	10.11 ^c	10.16 ^c	9.33 ^c
^d	16.09	9.04	9.94	9.96	9.13

^a Measured at $22 \pm 2^\circ$, quickly after solution prepared.

^b Spectrum in 20% ethanol, taken as ϵ_B . ^c Measured within 45 sec. and taken as ϵ_{BH^+} . ^d Values of ϵ_{BH^+} calculated, using eq. 5 ($h = h_0$) for acids through 55.7%.

TABLE IV

VALUES OF $\epsilon \times 10^{-3}$ FOR 1,3-DIMETHOXY-5-HYDROXYBENZENE^a

HClO ₄ , %	λ , $m\mu$				
	246	335	340	345	350
0 ^b	0.36	0	0	0	0
43.8	1.83	1.13	1.21	1.17	1.04
47.8	5.95	3.56	3.82	3.78	3.37
50.0	9.27	5.61	6.06	6.03	5.44
52.2	12.79	7.71	8.41	8.42	7.61
54.0	14.52	8.78	9.58	9.65	8.81
55.7	16.39	9.89	11.00	11.25	10.26
^c	19.05	11.22	12.60	13.10	11.75

^a Measured rapidly at $22 \pm 2^\circ$. Protonation in 55.7% HClO₄ was still incomplete, but spectrum changed too rapidly in stronger acids. ^b Spectrum in 20% ethanol, taken as ϵ_B . ^c Values of ϵ_{BH^+} calculated, using eq. 5 ($h = h_0$).

(13) The half-life for the hydrolysis of 1-methoxy-3,5-dihydroxybenzene in 60% perchloric acid, in which the ether is greater than 98% protonated, is estimated to be about 160 minutes at 22° .⁹

TABLE V
 VALUES OF $[BH^+]/[B]$ AND pK FOR PHLOROGLUCINOL

HClO ₄ , %	$-H_0^a$	$-H^b_{R^c}$	$[BH^+]/[B]^{d,e,i}$	Direct method		Least squares	
				$-pK_{BH^+}$	$-pK'_{BH^+}$	$-pK_{BH^+}^f$	$-pK'_{BH^+}^g$
44.8	2.86	6.23	0.135 ± 0.008	3.73	7.10	3.64	6.95
47.8	3.29	6.83	.371 ± .013	3.72	7.26	3.64	7.11
50.0	3.64	7.36	.673 ± .005	3.81	7.53	3.72	7.35
52.2	3.95	7.93	1.30 ± .03	3.84	7.83	3.71	7.54
54.0	4.23	8.39	2.09 ± .04	3.91	8.07	3.72	7.63
55.7	4.50 ^b	8.83	3.48 ± .21	3.96	8.29	3.65	(7.09) ^h

^a Values of Paul and Long.⁶ ^b Value of Bonner and Lockhardt.²⁷ ^c $H^b_{R^c} = H_R - \log a_{H_2O}$; H_R values of Deno,² a_{H_2O} values of Robinson and Baker.²⁸ ^d Average for the five wave lengths in Table II. ^e The listed deviations are average deviations. ^f Equation 5, with $h = h_0$, applied at all wave lengths. ^g Equation 5, with $h = h'_R$, applied only at 345 m μ . ^h Considered unreliable because of large calculated $[BH^+]/[B]$. ⁱ In 63.5% HClO₄; the calculated values of $[BH^+]/[B]$ ranged from 14.9 to 31.1, illustrating the inaccuracy of determining very large indicator ratios.

 TABLE VI
 VALUES OF $[BH^+]/[B]$ AND pK FOR 1-METHOXY-3,5-DIHYDROXYBENZENE

HClO ₄ , %	$-H_0^a$	$-H^b_{R^c}$	$[BH^+]/[B]^{d,e}$	Direct method		Least squares	
				$-pK_{BH^+}$	$-pK'_{BH^+}$	$-pK_{BH^+}^f$	$-pK'_{BH^+}^g$
43.8	2.74	6.02	0.136 ± 0.005	3.60	6.89	3.58	6.82
44.8	2.86	6.23	.192 ± .006	3.58	6.94	3.57	6.89
47.8	3.29	6.83	.486 ± .018	3.60	7.14	3.59	7.07
48.1	3.35	6.91	.546 ± .019	3.61	7.17	3.60	7.10
50.2	3.65	7.41	1.05 ± .04	3.62	7.40	3.60	7.28
52.2	3.95	7.92	2.26 ± .04	3.59	7.56	3.57	7.38
54.2	4.26	8.44	4.29 ± .25	3.62	7.80	3.57	7.42
55.7	4.50 ^b	8.83	7.13 ± .33	3.64	7.99	3.59	(6.89) ^h

^{a-c,e-h} See corresponding footnotes in Table V. ^d Average for the five wave lengths in Table III.

chloric acid solution strong enough to assure its practically complete protonation.

Three methods of treating the spectral data were applied. The first method involved direct solution of eq. 4 at the various suitable wave lengths in each of a number of perchloric acid solutions. In eq. 4, ϵ is the extinction coefficient (per stoichiometric mole of substrate) at a particular wave length of a solution containing appreciable amounts of both B and BH⁺, and ϵ_B and ϵ_{BH^+} are those of the free base and conjugate acid in the same solution. In practice, of course, ϵ , ϵ_B and ϵ_{BH^+} must be measured in different media. When these media differ considerably, as they do for a weak base, and there are attendant appreciable medium effects on ϵ_B and ϵ_{BH^+} (usually largely as the result of lateral shifts of spectral bands with changing mineral acid percentage), the use of eq. 4 can lead to appreciable errors. A "correction" for medium effects is frequently made by the application of the Hammett "isosbestic" method.¹⁴ This consists of shifting entire spectra obtained in the various acidic media until they intersect at a common point, and then using the "corrected" ϵ -values in eq. 4. This procedure, which has its shortcomings,¹⁵ fortunately did not need to be applied here. Thus, the free base does not absorb at all in the region of the long wave length band of the conjugate acid, and this band of the conjugate acid is very little shifted with changing perchloric acid percentage, although its shape is changed slightly. The shorter wave length band of the conjugate acid also changes only slightly with medium, and the extinction coefficient of the free base is relatively small in this region of the spectrum.

(14) L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

(15) The isosbestic method makes false corrections when the spectra of free base and conjugate acid shift to a different extent with change in medium. As an example, the "principal" band of acetophenone shifts strongly to the red with increasing mineral acid strength, whereas that of its conjugate acid shifts very slightly.^{16a,b} Errors also are introduced if shapes of spectral bands change with medium, as, e.g., the flattening and broadening of the "principal" band of acetophenone in stronger mineral acids.^{16b}

(16) (a) W. M. Schubert, H. Steady and J. M. Craven, *J. Am. Chem. Soc.*, **82**, 1353 (1960); (b) W. M. Schubert, J. Robins and J. M. Craven, *J. Org. Chem.*, **24**, 943 (1959).

$$[BH^+]/[B] = (\epsilon - \epsilon_B)/(\epsilon_{BH^+} - \epsilon) \quad (4)$$

$$K + \epsilon_{BH^+} \left(\frac{h}{\epsilon_B - \epsilon} \right) - \frac{h\epsilon}{\epsilon_B - \epsilon} = 0 \quad (5)$$

$$[BH^+]/[B] = (A - A_B)/(A_{BH^+} + A) \quad (6)$$

The least squares method of Hammett¹⁴ also was used to determine pK values. This consists of a least squares solution of eq. 5, where K and h are either K_{BH^+} and h_0 or K'_{BH^+} and h'_R .¹⁷ In practice, eq. 5 is solved for the slope, ϵ_{BH^+} , at each of a number of wave lengths with h and ϵ as variables, and this value of ϵ_{BH^+} is used in eq. 4. The method is especially useful when ϵ_{BH^+} cannot be directly measured. It is most accurate in a region of the spectrum in which the conjugate acid absorbs strongly and the free base has a weak and flat absorption. When this condition is fulfilled the least squares method often is preferred over the isosbestic method, even when ϵ_{BH^+} is known, because it may "correct" better for medium effects.^{6,14,15} A serious shortcoming in the use of the least squares method is the assumption inherent in the use of eq. 5. This assumption is that the protonation equilibrium follows a specific acidity function, *i.e.*, that eq. 1 or 2 is obeyed (see Discussion).

Another method used, which to the knowledge of the authors is applied for the first time here, involves measurement of the areas of spectral bands. Values of $[BH^+]/[B]$ in various perchloric acid solutions were obtained by solution of eq. 6, in which A is the molar integrated intensity (per stoichiometric mole of substrate) of the spectrum of a solution containing appreciable amounts of both B and BH⁺, A_B is that of the free base and A_{BH^+} is that of the conjugate acid.

Application of the direct method to the spectral data for phloroglucinol, 1-methoxy-3,5-dihydroxybenzene and 1,3,5-trimethoxybenzene gave the values of $[BH^+]/[B]$ listed in Tables V, VI and VII. The values of $[BH^+]/[B]$ in each perchloric acid solution are averages over all of the five or six wave lengths of spectral data in Tables II, III and I, respectively. Use of these values in eq. 1 gave the pK_{BH^+} values listed in the fifth column, and solution of eq. 2 gave

(17) Equation 5 is obtained by combining eq. 4 with the antilogarithmic form of eq. 1 or 2.¹⁴

TABLE VII
 VALUES OF $[BH^+]/[B]$ AND pK FOR 1,3,5-TRIMETHOXYBENZENE

HClO ₄ , %	-H ₀ ^a	-H' _R ^c	$[BH^+]/[B]$ ^{d,e}	Direct method		Least squares	
				-pK _{BH⁺}	-pK' _{BH⁺}	-pK _{BH⁺} ^f	-pK' _{BH⁺} ^g
44.7	2.84	6.19	0.085 ± 0.001	3.91	7.26	3.97	7.32
47.8	3.29	6.83	.289 ± .002	3.83	7.34	3.90	7.45
48.0	3.32	6.88	.349 ± .002	3.78	7.44	3.86	7.43
50.0	3.64	7.36	.833 ± .006	3.72	7.44	3.82	7.56
50.2	3.66	7.41	.847 ± .008	3.73	7.48	3.84	7.61
52.4	3.99	7.98	2.18 ± .02	3.65	7.64	3.82	7.83
54.2	4.26	8.44	4.41 ± .07	3.62	7.80	3.87	8.10
55.7	4.50 ^b	8.83	11.81 ± 1.23	3.43	7.75	3.89	8.29

^{a-c,g} See corresponding footnotes in Table V. ^d Average for the six wave lengths in Table I.

 TABLE VIII
 LEAST SQUARES pK VALUES FOR 1,3-DIMETHOXY-5-HYDROXYBENZENE

HClO ₄ , %	-H ₀ ^a	-H' _R ^c	$[BH^+]/[B]$ ^d	-pK _{BH⁺}	$[BH^+]/[B]$ ^e	-pK' _{BH⁺}
43.8	2.74	6.02	0.106 ± 0.005	3.72	0.117 ± 0.005	6.95
47.8	3.29	6.83	.441 ± .027	3.65	0.325 ± .019	7.12
50.0	3.64	7.36	.940 ± .070	3.66	1.18 ± .05	7.29
52.2	3.95	7.93	2.07 ± .20	3.67	3.04 ± .19	7.44
54.0	4.23	8.39	3.26 ± .33	3.63	6.12 ± .53	7.61
55.7	4.50 ^b	8.83	6.96 ± .38	3.72	(63.1 ± 1.0) ^f	(7.03) ^f

^{a-c} See corresponding footnotes in Table V. ^d Calculated from eq. 4 using ϵ_{BH^+} values obtained by solutions of eq. 5, with $h = h_0$, at the five wave lengths of Table IV. ^e Calculated from eq. 4 using ϵ_{BH^+} values obtained by solutions of eq. 5, with $h = h'_R$, using the wave lengths 335, 340 and 345 μ . ^f Considered unreliable because of the large calculated indicator ratio.

 TABLE IX
 THE AREA METHOD FOR pK_{BH^+} VALUES

HClO ₄ , %	Phloroglucinol		1,3,5-Trimethoxybenzene	
	A ^a	$\frac{[BH^+]}{[B]}$ ^b	A ^a	$\frac{[BH^+]}{[B]}$ ^b
44.7	671	0.072
44.8	142	0.133
47.8	332	.378	1880	.232
48.0	2160	.277
50.0	514	.740	3820	.621
50.2	3806	.617
52.2	718	1.46
52.4	5750	1.36
54.0	841	2.29
54.2	6903	2.25
55.7	963	3.94	7780	3.54

^a Relative area between 290 and 390 μ . ^b Values of $[BH^+]/[B]$ obtained from eq. 7, using a measured value of $A_{BH^+} = 1220$ in 63.5% HClO₄. The value of A in 71% HClO₄ was 1208. ^c The least squares value of pK_{BH^+} is 3.69 ± 0.03 . ^d The least squares procedure, eq. 7, was used to obtain A_{BH^+} (relative area, 9967) and hence pK_{BH^+} .

the pK'_{BH^+} values in the sixth column of these tables. Also listed are pK_{BH^+} and pK'_{BH^+} values obtained by the least squares method; *i.e.*, *via* eq. 5. For 1,3-dimethoxy-5-hydroxybenzene values of $[BH^+]/[B]$, pK_{BH^+} and pK'_{BH^+} , obtained only by the least squares method, are given in Table VIII.

Discussion

Position of Protonation.—From the fact that the spectral changes that occur on protonation of phloroglucinol and each of its methyl ethers are very similar (see Fig. 1), it is safe to conclude that the protonation equilibrium reaction is the same for each of the four compounds, *i.e.*, that all protonate on oxygen or all protonate on carbon (eq. 3). Kresge and Chiang considered the protonation of 1,3,5-trimethoxybenzene to be on carbon, and with good evidence.⁵ The ready exchange of the aromatic protons even in weakly acidic media¹⁸ indicates that the carbon-conjugate acid exists in acidic media, but does not necessarily mean that this is the conjugate acid present in the greatest concentration. However, the spectral changes

(18) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **81**, 5509 (1959); **83**, 2877 (1961).

that occur on protonation of phloroglucinol and its methyl ethers (Fig. 1) are very similar to those that occur on formation of the conjugate acids of a number of polyalkylated benzenes¹⁹ and of 1,3,5-triaminobenzene,²⁰ which have been assigned a carbon-protonated, σ -complex, structure. For example, 1,3,5-triaminobenzene has a strong band at 240 μ (ϵ 8000) and a weak one at 280 μ (ϵ 700) and its monoprotonated form has a new band at 275 μ (ϵ 8000) and another at 360 μ (ϵ 3000). The spectrum of the conjugate acid resembles that of cyanine dyes such as $C_2H_5NHCH=CHCH=CHCH=NHC_2H_5$.²⁰ As another example, the conjugate acid of mesitylene has strong bands at 255 μ and 335 μ .¹⁹ Similar spectral changes also have been observed in the ring protonation of aromatic hydrocarbons with HF-BF₃ solutions.^{21,22}

The spectral changes that occur on the protonation of the hetero atom of benzenes having a single amino, hydroxyl or alkoxyl substituent are entirely different. An example is aniline, which has an intense band at 230 μ (ϵ 9000) and a weak one at 280 μ (ϵ 1400). The new bands that appear upon protonation are to the blue of those of the free base, an intense one at 230 μ (ϵ 7500) and a weak one at 254 μ (ϵ 160).²³ In fact, anilinium ion has a spectrum similar to that of benzene. The spectral changes that occur on protonation of phenol and its alkyl ethers are similar to those that occur on protonation of aniline.²⁴

The n.m.r. spectrum of 1,3,5-trimethoxybenzene in 63.5% perchloric acid at 0° constitutes direct evidence for the carbon-protonated structure II. Four sharp unsplit proton signals at 1.93, 3.78, 4.03 and 4.16 p.p.m. upfield from the signal of the solvent protons were observed. These signals had a relative intensity of 2, 3, 6 and 2, and hence correspond, respectively, to the *meta* ring protons, the *p*-methoxyl protons, the *o*-methoxyl protons and the methylenic protons.^{25,26}

(19) M. Kilpatrick and W. H. Hyman, *ibid.*, **80**, 77 (1958).

(20) H. Köhler and G. Scheibe, *Z. anorg. u. allgem. Chem.*, **285**, 221 (1956).

(21) C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954).

(22) G. Dalinga, E. L. Mackor and A. A. Stuart, *Mol. Phys.*, **1**, 123 (1958).

(23) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(24) E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 5663 (1960).

(25) Kresge and Chiang report n.m.r. evidence that the conjugate acid of phloroglucinol has the structure II, R = H.⁸

The results indicate that the *p*-methoxy protons are less shielded than the *o*-methoxyl protons. This may constitute direct evidence that the *p*-quinoid resonance structure makes a greater contribution than the *o*-quinoid ones. Work along these lines is continuing. An entirely different appearing n.m.r. spectrum would be expected for the oxygen conjugate acid, whether or not the proton exchange would be slow enough to give separate signals for the various methoxyl protons and for the various ring protons.

Finally, the fact that the basicities of phloroglucinol and its methyl ethers are much greater than those of phenol and its alkyl ethers rules strongly against the oxygen-protonated structure for the principal conjugate acid. For example, phenol has a pK_{BH^+} value of -6.7 ,²⁴ and phloroglucinol a pK_{BH^+} value of -3.8 . It is difficult to conceive that two *m*-hydroxyl substituents would have this thousand-fold base strengthening effect were protonation primarily on oxygen.

Acidity Dependence of the Protonation.—Consider first the protonation of phloroglucinol, 1-methoxy-3,5-dihydroxybenzene and 1,3,5-trimethoxybenzene, for which values of $[BH^+]/[B]$ were obtained by the direct method, *i.e.*, by solution of eq. 4 using measured values of ϵ_{BH^+} . For all three compounds, eq. 1 is followed better than eq. 2; *i.e.*, their equilibrium protonation is more nearly dependent on H_0 than on H'_R . However, the observed degree of dependence on H_0 varies with the compound.

In Table V, it is seen that the pK_{BH^+} values for phloroglucinol are fairly constant, whereas pK'_{BH^+} decreases sharply, by 1.14 units between 44.8 and 55.7% perchloric acid. Clearly, the equilibrium carbon protonation of phloroglucinol is described much better by the H_0 than the H'_R function. However, the pK_{BH^+} values show a trend that is outside of the experimental error, decreasing by 0.23 unit between 44.8 and 55.7% perchloric acid; *i.e.*, $[BH^+]/[B]$ increases somewhat less rapidly than h_0 . More exactly expressed, the slope $-d \log ([BH^+]/[B])/dH_0$ has the least squares value of 0.85 ± 0.03 .

The protonation of 1-methoxy-3,5-dihydroxybenzene follows H_0 more closely than one has a right to expect, with pK_{BH^+} fluctuating by only 0.06 unit over the entire range of acids, whereas the pK'_{BH^+} values show a marked trend (Table VI). The quantity $-d \log ([BH^+]/[B])/dH_0$ has the value 0.98 ± 0.01 in this instance. Clearly, the H'_R function is not the one to use for the protonation of this particular base.

The protonation of 1,3,5-trimethoxybenzene follows neither the H_0 nor the H'_R function very well, as can be seen in the trends for both pK_{BH^+} and pK'_{BH^+} in Table VII. The increase in $[BH^+]/[B]$ is greater than the increase in h_0 and less than the increase in h'_R with $-d \log ([BH^+]/[B])/dH_0$ being 1.26 ± 0.04 and $-d \log ([BH^+]/[B])/dH'_R$ being 0.78 ± 0.05 . In other words, according to the data obtained in this work, one function is about as good, or as bad, as the other in describing the protonation of 1,3,5-trimethoxybenzene. Kresge and Chiang also have recently reported results on 1,3,5-trimethoxybenzene in agreement with ours,^{7,8} although they had earlier concluded that its protonation follows H'_R .⁵

In compiling the values of Tables V–IX we have judiciously avoided using very large or very small values of $[BH^+]/[B]$ because of the large inherent experimental error in determining such extreme values (*cf.* footnote *i*, Table V). The H_0 values used here are

(26) The assignment of the relative positions of the methylenic and *meta* ring protons is based on the work of Mackor and co-workers: C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

those of Paul and Long,⁶ except for the value in 55.7% perchloric acid, which is that of Bonner and Lockhardt.²⁷ Kresge and Chiang used the values of H_0 listed by Deno.² However, the values of Deno are larger than those of Paul and Long by a constant factor (0.52 unit) and larger than the value of Bonner and Lockhardt for 55.7% perchloric acid by a factor of 0.47 unit. In other words, had we used the values of H_0 listed by Deno instead, the picture would have remained essentially unchanged, except that our pK_{BH^+} values would have been larger by about 0.5 unit.

In calculating pK'_{BH^+} values using $H'_R = H_R - \log a_{H_2O}$, we used the values of a_{H_2O} reported by Robinson and Baker,²⁸ rather than those of Pierce and Nelson.²⁹ However, in logarithmic form, the slight differences between the two sets of a_{H_2O} values are practically lost.

The least squares method also was used to evaluate pK_{BH^+} and pK'_{BH^+} values for phloroglucinol, 1-methoxy-3,5-dihydroxybenzene and 1,3,5-trimethoxybenzene (Tables V, VI and VII). However, these values are not to be considered as having the validity of those obtained by the direct method, and are reported for comparison purposes only. That is, the least squares pK values are derived from values of $[BH^+]/[B]$ that in turn are based on values of ϵ_{BH^+} calculated by means of eq. 5; and in eq. 5, a specific acidity function, h_0 or h'_r , has been used. This procedure is strictly valid only when the protonation actually follows the acidity function used. Thus, the direct and least squares methods check closely only in the pK_{BH^+} values of 1-methoxy-3,5-dihydroxybenzene (Table VI), the protonation of which closely follows h_0 . The least squares pK'_{BH^+} values for 1-methoxy-3,5-dihydroxybenzene, although they have the same trend as the direct method pK'_{BH^+} values, do not change as greatly with acid percentage. This is because in deriving the least squares pK'_{BH^+} values the acidity function h_r has been used in eq. 5, whereas the protonation actually follows h_0 .³⁰ For phloroglucinol and 1,3,5-trimethoxybenzene, the least squares values of pK_{BH^+} and pK'_{BH^+} change in the same direction as do the corresponding direct method values (Tables V and VII). Here again the trends in the least squares values are more subdued since in these instances eq. 5 is not linear for $h = h_0$ or $h = h_r$, but only for h equal to h_0 raised to the appropriate power.^{30,31}

Only the least squares method was used to obtain pK values for 1,3-dimethoxy-5-hydroxybenzene (Table VIII), since ϵ_{BH^+} could not be directly measured in this instance. From the relative constancy of the pK_{BH^+} values and the bad drift in pK'_{BH^+} values, it is evident that the protonation of this compound is more closely dependent on H_0 than on H'_R . The value of 1.02 ± 0.04 for $-d \log ([BH^+]/[B])/dH_0$ probably represents a lower limit, however.³⁰

The Area Method.—Since the area of the spectrum of a species (one or more spectral bands may be used) is proportional to the concentration of the species, provided that the Beer–Lambert law is followed, eq. 6 can be used to determine the quantity $[BH^+]/[B]$. Two conditions must be met for eq. 6 to be applicable. First, there must be little medium effect on the area

(27) T. G. Bonner and J. C. Lockhardt, *J. Chem. Soc.*, 2840 (1957).

(28) R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. New Zealand*, **76**, 250 (1946).

(29) J. N. Pierce and A. F. Nelson, *J. Am. Chem. Soc.*, **55**, 3075 (1933).

(30) The use of h_0 or h'_r in eq. 5 (or in eq. 7) in effect tends to force the data to conform to the specific acidity function and thus suppresses the change with acid percentage of the least squares pK_{BH^+} or pK'_{BH^+} values.

(31) The "least squares" treatment could be set up so as to make h_0 , in addition to ϵ_{BH^+} and K , a disposable parameter.

of the spectral band (or bands) used for the free base, or on the area of the band (or bands) used for the conjugate acid.³² This is independent of whether the bands that are used suffer lateral shifts or changes in shape with changing medium. A second condition is that the region of the spectrum used be relatively isolated, *i.e.*, that there be no strong overlapping tail absorption by bands outside of the region of the spectrum used, especially if these bands are subject to such medium effects as lateral shifts. Of course the Area Method is not applicable in the event the spectrum of the free base and conjugate acid have the same area.

Provided the above conditions are met, the Area Method may offer distinct advantages over the usual ϵ -method, especially if the spectral bands of base and conjugate acid strongly overlap or the values of ϵ at particular wave lengths are subject to strong medium effects due either to lateral shifts or changes in the shapes of bands.

The Area Method, which is ideally suited for phloroglucinol and its methyl ethers since an isolated region of the spectrum is available (see Fig. 1), was applied to phloroglucinol and 1,3,5-trimethoxybenzene. Only the region of the spectrum that embraces the long wave length band of the conjugate acid was used. In the case of phloroglucinol, A_{BH^+} was directly measured. The relative integrated intensity of the band was 1220 in 66.5% perchloric acid and 1208 in 70.7% perchloric acid, indicating protonation was essentially complete in the former acid. It is interesting to note that ϵ_{max} increases by about 1% between 66.5 and 70.7% perchloric acid, whereas ϵ readings beginning about 10 μ on either side of the maximum become slightly less; *i.e.*, the band becomes slightly sharper but does not increase in area. This suggests that the Area Method is actually better than the ϵ -method in this instance. In Table IX it is seen that the pK_{BH^+} values obtained by this method agree very well with those obtained by the ϵ -method (Table V). The quantity $-d \log ([BH^+]/[B])/dH_0$ has the value 0.89.

Only a least squares method, involving application of eq. 7, the analog of eq. 5, was applied to 1,3,5-trimethoxybenzene, since A_{BH^+} was not directly determined. The pK_{BH^+} values obtained, Table IX, are remarkably constant. This constancy may be fortuitous, however (see footnote 30 and the above discussion of the least squares treatment).

$$K_{BH^+} + A_{BH^+} \left(\frac{h_0}{A_B - A} \right) - \frac{h_0 A}{A_B - A} = 0 \quad (7)$$

Conclusions.—The results obtained constitute an exception to any belief that carbon protonation should, in general, be dependent on the H'_R function. The difference in behavior between these equilibria and the carbon protonation of diaryl olefins may lie in the fact that, in the former instance, both the free bases and the conjugate acids of the phenolic compounds of the series have structures not unlike the free bases and conjugate acids of the indicator bases used to determine H_0 in the media used; *i.e.*, solvation of free base and conjugate acid is such that f_B/f_{BH^+} changes with medium more nearly like the corresponding ratio for the Hammett indicator bases than like f_{ROH}/f_R in the arylmethanol-arylmethyl cation equilibria.

The greatest departure from H_0 behavior (toward H'_R behavior) found in this work is for 1,3,5-trimethoxybenzene. The conjugate acid has no positive hydrogens bonded to a hetero-atom, and of the conjugate acids studied herein is structurally most akin to the

arylmethyl cations. It is to be noted further that the quantity $-d \log ([BH^+]/[B])/dH_0$ declines as the methoxyl substituents of the triether are successively replaced by hydroxyl. An explanation in terms of hydrogen-bonding solvation of the positive hydroxyl hydrogens of the conjugate acids of the phenolic members of the series has been advanced.^{7,8} Such solvent stabilization of BH^+ relative to B would be expected to decrease as the mineral acid percentage is increased, *i.e.*, a_{H_2O} decreased. Thus a smaller increase in $[BH^+]/[B]$ with increased mineral acid strength would be expected, *i.e.*, $-d \log ([BH^+]/[B])/dH_0$ would be lowered.³³ Or, in terms of activity coefficients, $-d \log ([BH^+]/[B])/dH_0$ would be lowered as methoxyl groups are replaced by hydroxyl because of the effect the hydrogen-bonding solvation has in lowering $-d \log (f_B/f_{BH^+})/dH_0$.

Of course, the exact value of the quantity $-d \log ([BH^+]/[B])/dH_0$ in each instance depends on the indicator bases used to determine the H_0 values. That is, $-d \log ([BH^+]/[B])/dH_0 = 1 - d \log (f_B f_{IH^-} / f_{BH^+} f_I) / dH_0$, where f_I and f_{IH^-} are activity coefficients of indicator base and conjugate acid, respectively. However, the $[BH^+]/[B]$ values for each of the four compounds were measured over practically the same range of perchloric acid strength. This was possible because of the similar base strength of the compounds. Consequently, the change in the quantity $-d \log ([BH^+]/[B])/dH_0$ in proceeding from phloroglucinol to 1,3,5-trimethoxybenzene depends only on the effect of the structure of B on the quantity $-d \log (f_B/f_{BH^+})/dH_0$ and is independent of the indicator bases used to determine H_0 .³⁴

It appears, from results such as herein reported, that neither the H_0 nor the H'_R function may be unique in describing protonation equilibria and that departure of protonation equilibria from either strict H_0 or H'_R behavior may not be so exceptional. This would not be surprising, since the variation in f_B/f_{BH^+} , while presumably primarily dependent on charge type (and possibly on whether BH^+ is a hetero-atom conjugate acid or a carbon conjugate acid),² should also depend somewhat on the specific structure and the charge distribution of both the base and the conjugate acid.^{2,33,35} A careful re-examination of the protonation equilibria of bases considered to follow H_0 appears to be in order (*cf.* ref. 33).

It follows from the results here obtained, and those obtained by Deno,² Kresge,^{5,8} Taft³³ and Long³⁶ that even a fairly large departure of the Hammett plot³⁷ from unit slope cannot be used as a sole basis for excluding the Hammett or A-1 mechanism. This is a matter to which a number of workers have directed their attention (see, *e.g.*, ref. 6, 33 and 38).

(33) Taft has used a similar argument to explain a difference between the protonation behavior of primary, secondary and tertiary amines and has suggested a re-examination of acidity function theory; R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2695 (1960).

(34) A widely recognized weakness of the entire H_0 scale (see, *e.g.*, ref. 6) is the assumption that f_B/f_{BH^+} varies in the same way for all the indicator bases throughout the entire range of acidities. This could be experimentally verified only for "adjoining" bases in a very narrow region of mineral acid in which $[BH^+]/[B]$ could be measured for both bases.^{1,6}

(35) This was recognized by Hammett: L. P. Hammett, *Chem. Rev.*, **16**, 67 (1935); see also the comments of Paul and Long, p. 10 of ref. 6.

(36) F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **83**, 3340 (1961).

(37) The Hammett plot in its most generalized form is a plot of $\log k_{obs} - \log ([S]/[S]_{stoich})$ against $-H_0$, where $[S]_{stoich}$ is the stoichiometric concentration of the substrate.⁴⁰ For most reactions that have been studied, including those originally treated by Hammett, it has either been known or tacitly assumed that $[S] \approx [S]_{stoich}$ and the more familiar plot of $\log k_{obs}$ against $-H_0$ has been used.⁶ In such instances, k_{obs} increases very rapidly with $-H_0$, placing a practical limitation of the range of mineral acid media in which k_{obs} can be measured (quite often, an acid range of less than 10% is used). In a few instances, the substrate has been substantially in the form of its conjugate acid, enabling k_{obs} to be determined over a much wider range of mineral acid strength (see, *e.g.*, ref. 40 and 41).

(32) Evidence that the area of a spectral band is much less subject to medium effects than its position is given in ref. 16.

On the other hand, a unit or near unit slope in the Hammett plot is not a *sufficient* basis on which to assign the A-1 mechanism. This was first shown a number of years ago.^{39,40} Since then, the entire Zucker-Hammett hypothesis has been undergoing considerable

(38) N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957).

(39) It was also suggested that a general catalysis mechanism of one or more bimolecular proton transfer steps might well give an approximately linear Hammett plot.⁴⁰

(40) W. M. Schubert and R. E. Zahler, *J. Am. Chem. Soc.*, **76**, 1 (1954); W. M. Schubert and H. Burkett, *ibid.*, **78**, 64 (1956); W. M. Schubert and P. C. Myhre, *ibid.*, **80**, 1755 (1958).

reappraisal.^{5,6,33,38,40-42} One definite conclusion emerges, and that is that generally much more than a study of the acidity dependence of a reaction catalyzed in strong acids is necessary to establish unambiguously its mechanism.

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(41) J. F. Bunnett, *ibid.*, **83**, 4956, 4968, 4973, 4978 (1961).

(42) L. Melander and P. C. Myhre, *Arkiv Kemi*, **13**, 507 (1959).

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Kinetics of the Acid-catalyzed Hydrolysis of 1-Methoxy-3,5-dihydroxybenzene and 1,3,5-Trimethoxybenzene

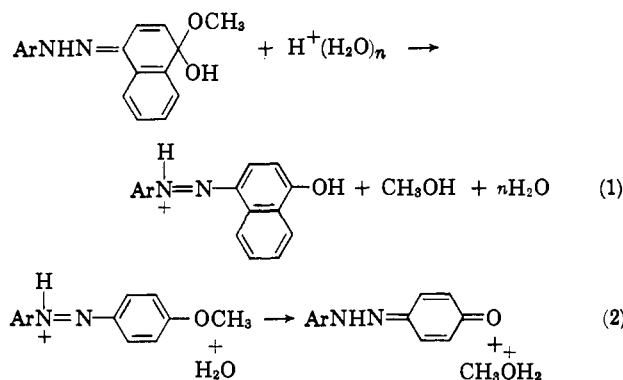
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First-order rate constants for the hydrolysis of 1-methoxy-3,5-dihydroxybenzene and 1,3,5-trimethoxybenzene in strong perchloric acid solutions have been determined. Methanol containing the natural abundance of O¹⁸ has been isolated from a hydrolysis in O¹⁸-enriched acid, showing that Ar-O rather than CH₃-O cleavage occurs. The large increase in *k*_{obs} with increased mineral acid percentage, continuing on after equilibrium protonation to the carbon conjugate acid is extensive, is difficult to reconcile with a one-proton process. Analysis of the results indicates that both a one-proton and two-proton process contribute to the total rate in the lowest acid percentages used and that the two-proton process becomes predominant in higher acid percentages. Clear-cut mechanistic assignments based on the data at hand are not possible, however.

In a spectrophotometric study of the acid-catalyzed decarbonylation of 2,4,6-trimethoxybenzaldehyde, it was observed that the ultraviolet spectrum of the product of this reaction, 1,3,5-trimethoxybenzene, suffered slow change in moderately strong mineral acids and became identical with the spectrum of phloroglucinol.¹ It appeared from this that ethers of phloroglucinol would be suitable substrates for a kinetic study of ether hydrolysis. No detailed studies of the acidity dependence of the rates of ether hydrolysis reactions had been published at the time work on the problem commenced (see, e.g., ref. 2 and 3), and as a first objective it appeared desirable to study the effect of mineral acid acidity on the rate of hydrolysis of 1-methoxy-3,5-dihydroxybenzene and 1,3,5-trimethoxybenzene. Since the extent of equilibrium carbon protonation of these ethers (eq. 3) is extensive in the perchloric acid solutions in which hydrolysis rates were measured, it also was necessary to study the acidity dependence of this equilibrium.⁴

After this work was begun, Bunnett and Bunzel published the results of an extensive kinetic study of the acid-catalyzed hydrolysis of 4-(*p*-sulfophenylazo)-1-methoxynaphthalene and 4-(*p*-sulfophenylazo)-1-anisole,⁵ reactions that are similar to the hydrolysis of phloroglucinol ethers. The hydrolysis of the naphthyl ether was assigned a mechanistic path proceeding *via* nucleophilic attack of water on the aromatic 1-position of the conjugate acid followed by the rate-controlling step represented by eq. 1. The assignment was based on the magnitude of the *w*-value⁶ and the recovery of O¹⁸-enriched naphthol from a hydrolysis carried out in O¹⁸-enriched acid.^{5a} The hydrolysis of the structurally very similar 4-(*p*-sulfophenylazo)-1-anisole was tentatively assigned a different path, involving rate-control-



ling attack of water on the methyl group of the conjugate acid, eq. 2.^{5a} More recently, however, as the result of further work including O¹⁸-exchange experiments, the hydrolysis of 4-(*p*-sulfophenylazo)-1-anisole has been assigned the same mechanistic path as the hydrolysis of the naphthyl analog.^{5b}

Rate constants for the hydrolysis of diethyl ether in 0.2–5.65 molar perchloric acid at 120° have been reported by Koskikallio and Whalley.⁷ They concluded that the reaction proceeded by an A-2 mechanism (rate-controlling attack of water on the conjugate acid). Log *k*_{obs} increased faster than log [H₃O⁺], in contradiction to the Zucker-Hammett hypothesis,⁸ and the plot of log *k*_{obs} against $-H_0$ (*H*₀ values at room temperature) was approximately linear, with slope ~0.5.

Experimental

Materials.—The preparation of materials used is described in the preceding paper.^{4b}

Kinetic Method.—The decline in the spectrum of perchloric acid solutions about 10⁻⁴ molar in ether was followed by the method previously described, using a Beckman DU instrument fitted with a constant temperature water-bath.⁹ Temperature was maintained to within ±0.03° by means of a Sargent Thermometer unit.

Hydrolysis in O¹⁸-Enriched Acid.—A solution of 1.4 g. of 1,3,5-trimethoxybenzene in 100 ml. of 38% hydrochloric acid contain-

(1) H. Burkett, W. M. Schubert, F. Schulz, R. B. Murphy and R. Talbot, *J. Am. Chem. Soc.*, **81**, 3923 (1959).

(2) R. L. Burwell, Jr., *Chem. Rev.*, **54**, 616 (1954).

(3) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

(4) (a) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **84**, 3778 (1962); (b) **85**, 1278 (1963).

(5) (a) J. F. Bunnett and E. Bunzel, *ibid.*, **83**, 1117 (1961); (b) J. F. Bunnett, E. Bunzel and K. V. Nahabedian, *ibid.*, **84**, 4136 (1962).

(6) (a) J. F. Bunnett, *ibid.*, **83**, 4956 (1961); (b) **83**, 4968 (1961).

(7) J. Koskikallio and E. Whalley, *Can. J. Chem.*, **37**, 788 (1959).

(8) L. Zucker and L. P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).

(9) W. M. Schubert and R. E. Zahler, *ibid.*, **76**, 1 (1954).