Aromatic Protonation. VII. The Structure of the Conjugate Acids of Hydroxy- and Alkoxybenzenes[1]

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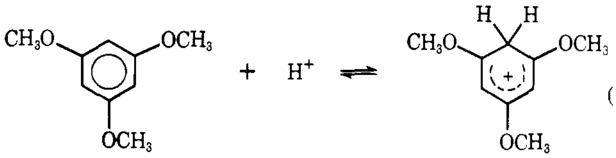
Abstract: The nmr and uv spectra of 1,3,5-trihydroxybenzene and its methyl and ethyl ethers, 1,3-dihydroxybenzene and 1,3-dihydroxy-2-methylbenzene and their methyl ethers, and some methyl derivatives of phenol and anisole dissolved in concentrated aqueous perchloric and sulfuric acids indicate that the conjugate acids of these aromatics are benzenonium ions (σ complexes). The partial methyl and ethyl ethers of 1,3,5-trihydroxybenzene show a marked preference for protonation para to hydroxyl rather than para to alkoxyl, and the uv spectra of all 17 benzenonium ions examined are correlated well by a relationship which assigns spectral shift parameters to the various substituent groups (OH, OR, and CH_3). This correlation predicts that λ_{max} for anisole protonated on carbon will be 285 nm, a result which is consistent with literature data on the uv spectra of oxygen-protonated cyclohexadienones and which indicates that carbon-protonated anisole is formed in perchloric acid more concentrated than 70%.

It is now well established that benzene and its derivatives form proton-addition compounds, commonly called σ complexes or benzenonium ions, in strongly acidic media.[2] Although no known aqueous system is sufficiently acidic to give this reaction with benzene itself, structural modifications can be made which increase the basicity of aromatic molecules enormously. For example, azulene is half-converted to its protonated form in 2 *M* aqueous perchloric acid, and alkyl-substituted azulenes are still more basic than that.[3]

Similar increases in basic strength can be effected in the benzene series itself by adding electron-supplying substituents to the ring, and, in fact, we[4] and others[5] have already reported that 1,3,5-trimethoxybenzene is converted to the 2,4,6-trimethoxybenzenonium ion (eq 1) by only moderately concentrated perchloric acid.



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Systems such as this are of considerable interest in themselves, but they also present an unusual opportunity for investigating the nature of concentrated aqueous acids: the position of equilibrium of the protonation reaction and its dependence upon acidity can be measured by standard indicator methods,[4,5] and the rate of protonation and its acidity dependence can be determined by using isotopic tracers to evaluate rates of aromatic hydrogen exchange;[1b,6] thus, both kinetics and equilibria of the same reaction with a single substrate may be studied, and the effects of changing acidity on the two can be intercompared. This system, moreover, permits ready structural variation in the substrate. For example, alkoxyl groups can be converted into hydroxyl groups or they may be removed completely; the former change would evaluate the effect of solvation through hydrogen bonding on kinetic and equilibrium acidity dependences, whereas the latter would reveal differences brought about by changes in reactivity.

In this series of papers we shall describe the results of such an investigation. First we present a full account of the structural evidence upon which we based our preliminary reports[4] of the formation of benzenonium ions from 1,3,5-trihydroxybenzene and its ethers, together with a description of similar experiments in related systems. We shall then take up the equilibrium[7] and kinetic[8] acidity dependences of these reactions, and then we will show how comparison of the two can lead to rather detailed information about transition state structure, and what implications this has on the use of kinetic acidity dependence as a criterion of reaction mechanism.

Results and Discussion

Nmr Spectra. 1,3,5-Trihydroxybenzene. The nmr spectrum of 1,3,5-trihydroxybenzene in 70% perchloric acid consists of two slightly broadened lines of equal area at τ 3.7 and 5.9 ppm (Table I). These signals narrow with increasing acid concentration and broaden further with decreasing acidity; at 65% perchloric acid they are no longer visible over noise level. In deuterated acid they disappear completely.

These observations are consistent with the fact that at these acidities 1,3,5-trihydroxybenzene is completely converted into a substance with a characteristic benzenonium ion ultraviolet spectrum (*vide infra*). The expected ion, **1**, contains two sets of equal numbers of carbon-bound protons as well as three hydroxyl hydro-

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(2) For recent reviews of the evidence see (a) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1970, Chapter 20; and (b) H. H. Perkampus, *Advan. Phys. Org. Chem.* 4, 196 (1966).

(3) F. A. Long and J. Schulze, *J. Amer. Chem. Soc.*, **86**, 322, 327 (1964).

(4) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961); A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Amer. Chem. Soc.*, **84**, 4343 (1962).

(5) W. M. Schubert and R. M. Quacchia, *ibid.*, **84**, 3778 (1962); **85**, 1278 (1963).

(6) A. J. Kresge and Y. Chiang, *ibid.*, **83**, 2877 (1961).

(7) A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *ibid.*, **93**, 6174 (1971).

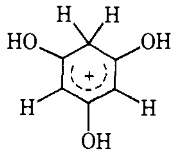
(8) A. J. Kresge, S. Mylonakis, Y. Sato, and V. P. Vitullo, *ibid.*, **93**, 6181 (1971).

Table I. Nmr Spectra of Benzenonium Ions Derived from 1,3,5-Trihydroxybenzene and Its Completely O-Alkylated Derivatives[a]

		τ, ppm			
				Alkoxy protons	
Substrate	Solvent	Vinyl protons	Methylene protons	Ortho[b]	Para[b]
1,3,5-Trihydroxybenzene	70% $HClO_4$	3.68	5.85		
1,3,5-Trihydroxybenzene	H_2SO_4–TFA[c]	3.74	6.11		
1,3,5-Trimethoxybenzene	70% $HClO_4$	3.68	5.98	5.77	5.60
1,3,5-Trimethoxybenzene	H_2SO_4–TFA[c]	3.81	6.08	5.88	5.65
1,3,5-Triethoxybenzene	70% $HClO_4$	3.76	6.00	5.63,[d] 8.42[e]	5.40,[d] 8.40[e]
1,3,5-Triethoxybenzene	H_2SO_4–TFA[c]	3.87	6.12	5.64,[d] 8.48[e]	5.38,[d] 8.41[e]

[a] Measured as *ca.* 10% solutions at ambient temperature (38 ± 1°) and 60 MHz relative to $(CH_3)_4NCl$ (τ 6.68 ppm) as internal reference. [b] Relative to site of protonation. [c] 3 vol of H_2SO_4 + 25 vol of CF_3CO_2H. [d] Quartet, $J = 7$ Hz. [e] Triplet, $J = 7$ Hz.

gens. The latter will exchange rapidly with the solvent and will not be observable as separate nmr signals. The carbon-bound protons, on the other hand, as judged by rates of aromatic hydrogen exchange measured at low acidities[8] and equilibrium measurements made at intermediate acid concentrations,[7] will have lifetimes of the order of seconds in 70% perchloric acid; they should therefore give broadened nmr lines. Deprotonation of **1**, moreover, and thus exchange of its ring protons, will be a base-catalyzed process with rate inversely proportional to acid concentration.[9] The signals produced by the carbon-bound protons will therefore broaden (exchange more slowly) as acidity is decreased, just as is observed.



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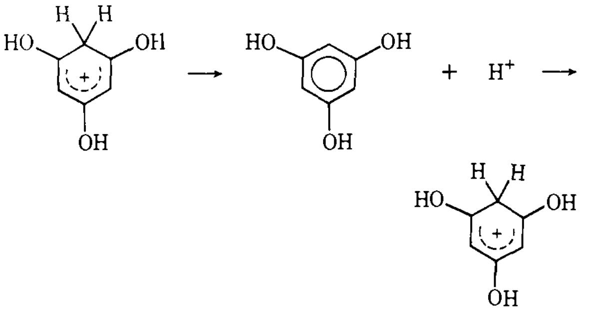
A further assignment of the high-field signal to the hydrogens of the methylene group and the low-field line to the vinyl hydrogens at positions 3 and 5 can be made on the basis of the fact that the high-field signal is consistently broader than the low-field resonance. Consider the two possible routes for proton loss from **1** and its subsequent re-formation: I, reprotonation at the same site (eq 2); and II, reprotonation at a different site (eq 3). If reprotonation at all three positions of 1,3,5-trihydroxybenzene is equally probable, reaction II will occur with twice the velocity of reaction I: $R_{\mathrm{I}} = v$ and $R_{\mathrm{II}} = 2v$. Since reaction I exchanges half of the methylene group hydrogens and none of the vinyl hydrogens, the rate of exchange of the former, R_a, by this mechanism will be $R_{\mathrm{I}}/2 = v/2$, and that of the latter, R_b, will be zero. Reaction II, on the other hand, exchanges all of the methylene group hydrogens and half of the vinyl hydrogens; this mechanism will therefore contribute $R_a = R_{\mathrm{II}} = 2v$ and $R_b = R_{\mathrm{II}}/2 = 2v/2 = v$. The sum of both mechanisms gives $R_a = v/2 + 2v = 5v/2$ and $R_b = 0 + v = v$, which shows that methylene group hydrogens will exchange at a rate (R_a) 2.5 times that of vinyl hydrogens (R_b); this in turn implies that the methylene group nmr signal will be *ca.* 2.5 times as broad as the vinyl hydrogen resonance. It is conceivable, of course, that reprotonation, instead of being the random process which gives reaction II twice the weight of reaction I, is concerted with proton loss and thus always occurs at a different site, *i.e.*, *via* the mechanism of eq 3 without the intermediate formation of unprotonated trimethoxybenzene. This reaction scheme gives the same rates of exchange as reaction II acting alone, $R_a = 2v$ and $R_b = v$, which does not alter the qualitative conclusion reached before: methylene group hydrogen exchange will be more rapid than vinyl hydrogen exchange.

Reaction I



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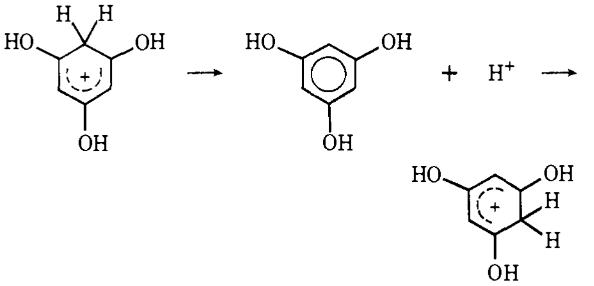
Reaction II



(3)

This assignment is in accord with published interpretations of the nmr spectra of methylbenzenonium ions,[2a,11] and it could in fact have been made by analogy with the observation that vinyl hydrogen lines in these spectra invariably appear at lower field than methylene group signals. The individual resonance positions found here for the methylene and vinyl hydrogens of the conjugate acid of 1,3,5-trihydroxybenzene are each somewhat upfield from those of the corresponding signals in the spectra of methylbenzenonium ions. The latter, however, show a general pattern of increasingly upfield resonance position with increasing number of methyl groups situated in positions ortho and para to the site of proton addition, which results from the fact

(9) In addition to base-catalyzed intermolecular hydrogen exchange, a base-independent intramolecular proton jump process has been identified.[10] The latter, however, occurs only in substrates which have adjacent sites of similar basic strength;[2a] it will, therefore, not take place in the case of 1,3,5-trihydroxybenzene.

(10) (a) C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, 165 (1962); (b) D. M. Brouwer, C. MacLean, and E. L. Mackor, *ibid.*, **39**, 121 (1965).

(11) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, **84**, 1564 (1956).

that such substitution reduces the positive charge density in the protonated ring and thus effects shielding of the attached hydrogens. Since hydroxyl groups are more effective than methyl groups at reducing positive charge on adjacent atoms, a further upfield shift in the case of protonated trihydroxybenzene is to be expected.

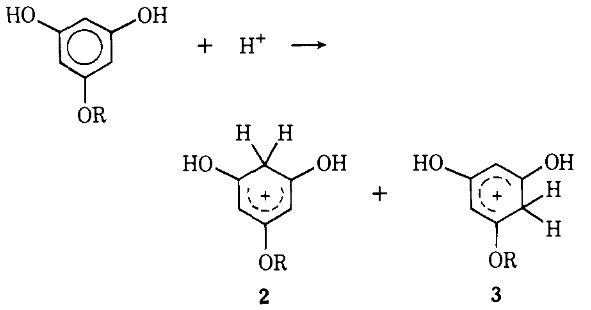
1,3,5-Trimethoxybenzene and 1,3,5-Triethoxybenzene. The nmr spectra of 1,3,5-trimethoxybenzene and 1,3,5-triethoxybenzene in 70% perchloric acid also contain signals near τ 3.7 and 5.9 ppm (Table I) which broaden with decreasing acid concentration and disappear in deuterated sulfuric acid. They can therefore be assigned to vinyl and methylene group hydrogens of the 2,4,6-trialkoxybenzenonium ions which are formed in these media.

The spectrum of the 1,3,5-trimethoxybenzenonium ion contains two additional lines at τ 5.6 and 5.8 ppm (Table I). These signals have areas corresponding to three and six hydrogens, respectively; the resonance at low field can therefore be ascribed to the single methoxyl group para to the site of protonation, and the high-field line, to the two equivalent methoxyl groups ortho to the site of the added proton. The slightly downfield chemical shift of the signal due to the para substituent relative to that of the ortho groups indicates that there is somewhat more positive charge at the para position of this benzenonium ion than at either ortho position; this is consistent with results obtained for methylbenzenenonium ions,[11,12] which are supported by theoretical calculations.[12b,13]

Additional lines also occur in the nmr spectrum of 1,3,5-triethoxybenzenonium ion: there are two overlapping quartets, both with $J = 7$ Hz, centered at τ 5.4 and 5.6 ppm and two overlapping triplets, also with $J = 7$ Hz, situated more closely together at τ 8.4 ppm (Table I). These characteristic ethyl group patterns may be assigned to ortho and para ethoxyl groups in the 2,4,6-triethoxybenzenonium ion. Again, the larger signals attributable to ortho substituents appear at higher fields, and the difference in chemical shifts between ortho and para substituents correctly falls off from methylene to methyl groups as the distance from the positive charge increases.

Unlike the situation with 1,3,5-trihydroxybenzene whose nmr spectrum in 70% $HClO_4$ does not change over a period of several hours, the spectra of 1,3,5-trialkoxybenzenes are not stable in this medium. In the case of 1,3,5-trimethoxybenzene, a new line appears within several minutes at τ 6.1 ppm and gradually grows in intensity; addition of methanol to the sample identifies this signal as originating from alcohol produced by hydrolysis of the ether. An analogous phenomenon occurs with 1,3,5-triethoxybenzene. This behavior is consistent with the known[14] rapid rate of hydrolysis of methyl ethers of 1,3,5-trihydroxybenzene in concentrated aqueous perchloric acid.

Partial Ethers of 1,3,5-Trihydroxybenzene. The partial methyl and ethyl ethers of 1,3,5-trihydroxybenzene also give characteristic benzenonium ion spectra in 70% perchloric acid. These spectra, however, differ in detail from those of 1,3,5-trihydroxybenzene and its triethers in that the vinyl hydrogen and methylene group signals no longer consist of single-line resonances. Each of the partial ethers, of course, contains two different proton addition sites, and each may therefore form two isomeric benzenonium ions (eq 4 and 5): the symmetrical species **2** or **5** and the unsymmetrical species **3** or **4**. The pair of ions formed in each reaction could produce as many as three different vinyl hydrogen signals (one from symmetrical and two from unsymmetrical ions) and two different methylene group resonances; the fact that these maximum numbers are observed in each case indicates that both symmetrical and unsymmetrical ions are in fact formed in each reaction.



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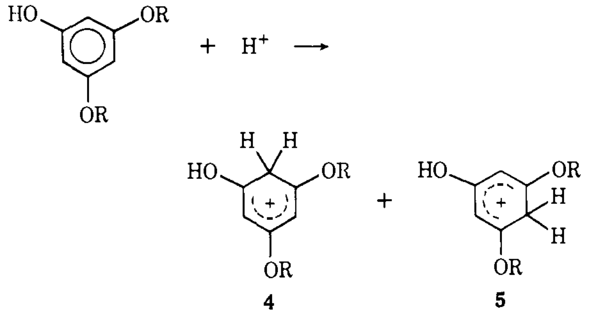

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These nmr spectra of partial ethers dissolved in 70% perchloric acid are difficult to analyze in detail because the hydrolysis and exchange reactions which occur in this medium impair their quality. These difficulties, however, can be largely removed by operating in a nonaqueous solvent, such as a mixture of trifluoroacetic and sulfuric acids. A medium consisting of *ca.* 10 vol % sulfuric acid (3 vol of H_2SO_4 + 25 vol of CF_3CO_2H) was found to be suitable; this solvent gives chemical shifts quite similar to those observed in 70% perchloric acid (see Table I) and is only slightly more acidic (H_0 values are -8.2[15] and -7.8[16]).

Spectral assignments were made on the basis of the fact that both protonation reactions (eq 4 and 5) produce unequal amounts of symmetrical and unsymmetrical benzenonium ions. For example, 1,3-dihydroxy-5-methoxybenzene dissolved in the sulfuric–trifluoroacetic acid medium gives three signals in the vinyl proton region, at τ 3.68, 3.73, and 3.88 ppm, whose intensities can stand in the ratio 5:1:5; the two outer lines of equal intensity must be due to the two different vinyl hydrogens of the unsymmetrical ion **3**, which leaves the center line for the symmetrical species **2**. It follows from this that the symmetrical and unsymmetrical ions are formed in this case in the ratio 1:10. This result is supported

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[12] (a) C. MacLean, J. H. van der Waals, and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958); (b) C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2208 (1961).

[13] C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961); J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron*, **19**, 65 (1963).

[14] W. M. Schubert and R. H. Quacchia, *J. Amer. Chem. Soc.*, **85**, 1284 (1963).

[15] H. H. Hyman and R. A. Garber, *ibid.*, **81**, 1847 (1959).

[16] K. Yates and H. Wai, *ibid.*, **86**, 5408 (1964).

Table II. Nmr Spectra of Benzenonium Ions Derived from Partial Ethers of 1,3,5-Trihydroxybenzene[a]

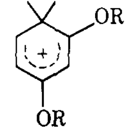
			τ, ppm			
					Alkoxy protons	
Substrate	Ion[b]	Rel abundance	Vinyl protons	Methylene group protons	Ortho[c]	Para[c]
1,3-Dihydroxy-5-methoxybenzene	s	1	3.73	6.04		5.74
	u	10	3.68, 3.88	6.12	5.93	
1-Hydroxy-3,5-dimethoxybenzene	u	1	3.64, 3.90	6.06	5.90	5.69
	s	2	3.81	6.13	5.90	
1,3-Dihydroxy-5-ethoxybenzene	s	1	3.74	6.05		5.45,[d] 8.47[e]
	u	10	3.70, 3.90	6.13	5.75,[d] 8.53[e]	
1-Hydroxy-3,5-diethoxybenzene	u	1	3.70, 3.95	6.09	5.67,[d] 8.48[e]	5.42,[d] 8.43[e]
	s	2	3.87	6.16	5.67,[d] 8.48[e]	

[a] Measured as *ca.* 10% solutions in 3 vol of H_2SO_4 + 25 vol of CF_3CO_2H at ambient temperature (38 ± 1°) and 60 MHz relative to $(CH_3)_4NCl$ (τ 6.68 ppm) as internal reference. [b] s and u refer to the symmetrical (**2** and **5**) and unsymmetrical (**3** and **4**) species of eq 4 and 5. [c] Relative to the site of protonation. [d] Quartet, J = 7 Hz. [e] Triplet, J = 7 Hz.

by the fact that pairs of signals in the intensity ratio 1:10 appear in the methylene hydrogen and in the alkoxyl group regions; the less intense signal in the latter region, moreover, is in the downfield position expected for the para methoxyl group of the symmetrical ion. The assignments made using this and analogous reasoning are listed in Table II.

The relative abundances of symmetrical and unsymmetrical species formed in these reactions (Table II) indicate that protonation para to a hydroxyl group is invariably preferred over protonation para to an alkoxyl group. The magnitude of this selectivity, moreover, is much the same for the monoethers as for the diethers, for the former have two hydroxyl groups, and their 10:1 preference should therefore be reduced by half to 5:1, whereas the latter have two alkoxyl groups, and their preference of 2:1 should be raised to 4:1. This selectivity, coupled with the fact that the positive charge density in the para position of a benzenonium ion exceeds that in an ortho position, implies that hydroxyl groups are better at stabilizing positive charge on adjacent atoms than are alkoxyl groups. This, of course, goes against the order of inductive electron release, R > H, but it is consistent with the fact that electrophilic aromatic substitution, *e.g.*, acid-catalyzed hydrogen exchange,[8] occurs more rapidly in phenols than in the corresponding ethers and that σ^+ for –OH is more negative than σ^+ for $-OCH_3$.[17] The reason for this effect is not clear; O–H hyperconjugation has been advanced as a possible cause,[18] but this cannot be the complete explanation for the effect appears to be medium dependent, *i.e.*, the relative basicities of 1,3,5-trihydroxybenzene and its ethers invert in going from dilute to concentrated aqueous acids.[7]

1,3-Dihydroxybenzene and 1,3-Dimethoxybenzene. The nmr spectrum of 1,3-dihydroxybenzene in 70% perchloric acid contains only broad signals at τ 2.4 and 3.3 ppm, and that of its dimethyl ether in the same medium has an additional, somewhat narrower, but still broadened line at τ 5.8 ppm. These observations are in accord with the fact that these substances are largely though not completely protonated in this medium,[7] and that hydrogen exchange at some but not all of the ring positions of the dihydroxy- and dimethoxybenzenonium ions, **6**, can therefore be expected to occur rapidly on the nmr time scale.



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In the much more acidic medium 95% sulfuric acid, on the other hand, deprotonation of **6** is slowed considerably, and 1,3-dimethoxybenzene gives a spectrum with appreciable fine structure. There are three signals in the vinyl proton region, each of intensity corresponding to one hydrogen, at τ 2.14, 2.86, and 3.35 ppm and three signals in the methoxyl and methylene group region at τ 5.52, 5.62, and 5.90 ppm, with intensities of three, three, and two hydrogens, respectively. In deuteriosulfuric acid only the lines at τ 2.14, 5.52, and 5.62 ppm remain; the former may therefore be assigned to the vinyl proton at position 6 in the 2,4-dimethoxybenzenonium ion, which is the only ring hydrogen in 1,3-dimethoxybenzene not activated toward acid-catalyzed exchange, and the two signals of three-hydrogen intensity at τ 5.52 and 5.62 ppm are of course from the para and ortho (with respect to the position of protonation) methoxy groups, respectively.

As solvent acidity is decreased by adding 70% perchloric acid to 95% sulfuric acid, these spectral lines broaden and some eventually disappear. These changes approach the spectrum described above for 70% perchloric acid itself as a limit; no new lines are introduced, which implies that no new solute species, *e.g.*, oxygen-protonated conjugate acids, are formed. The two vinyl proton signals at τ 2.86 and 3.35 ppm, moreover, do not broaden at the same rate with decreasing solvent acidity, which is consistent with the fact that the two kinds of exchangeable hydrogen in 1,3-dimethoxybenzene, that at position 2 and those at (the equivalent) positions 4 and 6, exchange at different rates.[8] In fact, on this basis, the line at τ 3.35 ppm can be assigned to the more slowly exchanging vinyl proton between the two methoxyl groups in the 2,4-dimethoxybenzenonium ion.

The nmr spectrum of the 2,4-dimethoxybenzenonium ion has also been observed in hydrogen fluoride solution.[10b] The fact that it is similar in all respects to the spectrum found here for 1,3-dimethoxybenzene in 95% sulfuric acid indicates that sulfonation of this highly reactive benzene derivative does not take place in this medium, which is to be expected if it exists virtually completely as the conjugate acid. Hydrolysis to give methanol, however, does occur gradually, just as is the case with 1,3,5-trimethoxybenzene in 70% per-

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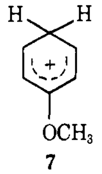
(17) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(18) P. B. D. de la Mare, *Tetrahedron*, **5**, 107 (1959).

chloric acid. 1,3-Dihydroxybenzene, on the other hand, gives a rapidly changing spectrum in 95% sulfuric acid, and the solution in fact develops a precipitate in *ca.* 20 min. This could be a sulfonation product, for, since the ratio of unprotonated to protonated aromatic in 95% sulfuric acid will be greater for 1,3-dihydroxybenzene than for its dimethyl ether,[7] sulfonation of the former could occur where that of the latter does not.

Phenol and Anisole. The nmr spectrum of anisole in 70% perchloric acid consists of a complex five-hydrogen pattern centered at τ 2.6 ppm and a three-hydrogen singlet at τ 5.9 ppm. The low-field portion of this spectrum is quite unlike the four-hydrogen AB pattern observed for the 4-methoxybenzenonium ion (**7**) formed from anisole in very acidic media such as hydrogen fluoride containing boron trifluoride[10a,19] or fluorosulfonic acid,[20] but it does bear a strong resemblance to the spectrum of anisole dissolved in nonacidic solvents such as carbon tetrachloride. This observation is in accord with the fact that anisole is not sufficiently basic to be protonated on carbon to an appreciable extent by 70% perchloric acid.[7]



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This spectrum in 70% perchloric acid does differ in detail from that of anisole in neutral solvents, the principal difference being a downfield shift of all signals by some 0.4 ppm. This change can be traced through solvents of intermediate acidity: in acetic acid the lines appear in essentially their carbon tetrachloride positions, but in trifluoroacetic acid they have moved downfield approximately halfway to their 70% perchloric acid values. This suggests that there is an interaction, *e.g.*, hydrogen bonding to the oxygen atom, between anisole and acidic solvents which becomes stronger with increasing strength of the acid but does not alter the structure of the molecule in any fundamental way. An analogous gradual change in the uv spectrum of anisole in aqueous perchloric acid solutions has been observed and has been interpreted in a similar way.[21]

In 95% sulfuric acid, which is acidic enought to effect its protonation on carbon,[7] anisole does show a four-hydrogen AB pattern at τ 2.4 ppm in addition to the three-hydrogen singlet at τ 5.9 ppm. No methylene group signal is visible, but none would be expected, for exchange of these hydrogens with the solvent should be quite rapid. This spectrum, however, may not be that of the 4-methoxybenzenonium ion, **7**, for, although it appears immediately in 95% sulfuric acid, in 85% acid it grows in only slowly (1–2 hr) from an initial trace characteristic of unprotonated anisole; in 85% sulfuric acid, protonation of anisole, as judged from rates of aromatic hydrogen exchange measured at lower acidities,[8] should occur in much less than 1 sec.

Anisole is converted immediately to a water-soluble substance by 95% sulfuric acid, and it has been suggested that the reaction which occurs is sulfonation.[22] Hydrolysis would produce the same result, for the products of hydrolysis, phenol and methanol, are also water soluble, but this can be eliminated by virtue of the fact that a methanol signal appears only slowly in the spectrum of anisole dissolved in 95% sulfuric acid. It seems likely, therefore, that the spectrum which develops from anisole in 85% sulfuric acid, and thus the closely similar one in 95% sulfuric acid as well, is due to 4-methoxybenzenesulfonic acid.

Phenol shows similar behavior in 95% sulfuric acid, insofar as it immediately gives the spectrum expected for 4-hydroxybenzenesulfonic acid. Within minutes, however, further signals appear. Similar changes occur in the case of anisole, but these take place more slowly. No attempt was made to identify the reactions taking place; they could be further sulfonation.

Ultraviolet Spectra. In neutral and weakly acidic solvents 1,3,5-trihydroxybenzene and its methyl and ethyl ethers show the weak uv absorption at *ca.* 265 nm, $\epsilon \simeq 500\ M^{-1}\ \mathrm{cm}^{-1}$, which is characteristic of hydroxy- and alkoxybenzenes, but in more acidic media this band is replaced by two much stronger absorptions at 240–245 and 340–345 nm, $\epsilon \simeq 20{,}000$ and $10{,}000\ M^{-1}\ \mathrm{cm}^{-1}$, respectively. In perchloric acid solution the transition from one kind of spectrum to the other occurs between 35 and 65% acid; spectra in this intermediate region show good isosbestic points, and plots of absorbance *vs.* any of the usual measures of acid strength (weight %, M, H_0, etc.) are sigmoid in shape. The spectral changes, moreover, can be reversed, and original substrates may be recovered unchanged from neutralized solutions.

This behavior suggests that a simple protonation reaction is occurring. There is, of course, independent nmr evidence (*vide supra*) that this is indeed the case and that the species formed are hydroxy- or alkoxybenzenonium ions. Quantitative analysis of these and the related spectral changes which occur in the mono- and dihydroxybenzene series, moreover, provides a set of basicity constants for a series of aromatic molecules which is in complete accord with the expected relationship between structure and basic strength.[7] Similar uv spectral changes have also been observed for alkylbenzenes and other benzenoid aromatics, and these have also been attributed to benzenonium ion formation for similar reasons.[2,23]

The uv spectra of mono- and dihydroxybenzenonium ions differ from those of benzenonium ions derived from trihydroxybenzene in that the absorption maxima are shifted to shorter wavelengths. In fact, the position of the long-wavelength uv band of benzenonium ions depends markedly on the number of oxy groups ortho or para to the site of protonation and only slightly on whether the group is hydroxyl, methoxyl, or ethoxyl. For example, the data collected in Table III show that all of the bases in the 1,3,5-trihydroxybenzene series, with the sole exception of 1,3,5-triethoxybenzene, give benzenonium ion bands with $\lambda_{\max}$ in the relatively narrow region 340–344 nm, and that 1,3-dihydroxybenzene

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Table III. Uv Spectra of Hydroxy- and Alkoxybenzenonium Ions[a]

Substrate	λ_{max}, nm of longest wavelength band: Obsd	Calcd	Calcd − obsd
1,3,5-Trihydroxybenzene	340	339	−1
1,3-Dihydroxy-5-methoxybenzene	343	341	−2
1-Hydroxy-3,5-dimethoxybenzene	343	343	0
1,3,5-Trimethoxybenzene	344	345	+1
1,3-Dihydroxy-5-ethoxybenzene	343	342	−1
1-Hydroxy-3,5-diethoxybenzene	344	345	+1
1,3,5-Triethoxybenzene	348	348	0
1,3-Dihydroxybenzene	311	311	0
1-Hydroxy-3-methoxybenzene	313	313	0
1,3-Dimethoxybenzene	314	315	+1
1,3-Dihydroxy-2-methylbenzene	327	322	−5
1,3-Dimethoxy-2-methylbenzene	341	326	−15
1,3-Dihydroxy-5-methylbenzene	326	326	0
1-Hydroxy-3,5-dimethylbenzene	313[b]	313	0
1-Methoxy-3,5-dimethylbenzene	315[b]	315	0
1-Hydroxy-3-methylbenzene	298[b]	298	0
1-Hydroxy-2,3,5,6-tetramethylbenzene	330	331	+1
Anisole[c]	285[b]	285	0

[a] Measured in 70% $HClO_4$ except as indicated otherwise. [b] Measured in $HClO_4$ more concentrated than 70%. [c] K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

and its methyl ethers all fall into the range $\lambda_{max} = 311$–314 nm. Methyl groups have a similar though weaker effect on λ_{max}, and, in fact, the data for all 17 compounds examined here can be correlated quite well by assigning characteristic spectral shift parameters to the individual substituent groups. The relationship obeyed is given by eq 6, where n_i is the number of groups of a

$$\lambda_{max} = 255 \text{ nm} + \sum_i n_i \Delta\lambda_i \qquad (6)$$

given kind and $\Delta\lambda_i$ are the spectral shift parameters listed in Table IV. The last column of Table III shows that the agreement between observed values and those calculated in this way is, on the whole, quite good.

Table IV. Spectral Shift Parameters for Benzenonium Ions

Substituent[a]	$\Delta\lambda$, nm
Ortho or para ethoxyl	31
Ortho or para methoxyl	30
Ortho or para hydroxyl	28
Ortho methyl	15
Meta methyl	11

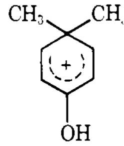
[a] Positions are relative to the site of protonation.

The spectral shift parameters for methyl groups deduced here seem to be applicable also to the uv spectra of purely methyl-substituted benzenonium ions. For example, the value of 15 nm for ortho methyl (Table IV) predicts a difference of 30 nm in λ_{max} for benzenonium ions derived from toluene and mesitylene, which compares well with the observed values 326[24] and 354[23c] or 355[23b] nm, respectively. Similarly, $\Delta\lambda_{max}$ along the series of benzenonium ions derived from mesitylene, isodurene, and pentamethylbenzene (354 or 355,[23b,c] 365,[23b] and 377[23b] nm), which differ successively by one meta methyl group, is 10–12 nm; the value of $\Delta\lambda$ for meta methyl in Table IV is 11 nm.

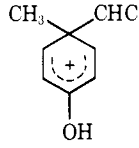
Although spectral shift parameters seem to be transferable between hydroxy- and purely methyl-substituted benzenonium ions in this way, the two series of spectra do not obey the same correlation, in that they require different constant terms: in the hydroxy series, this constant is 255 nm (eq 6), and in the purely methyl-substituted series, 310 nm. The fact that these constants are different, and that neither one, moreover, is equal to the value of λ_{max} reported for the benzenonium ion itself, 332 nm,[24] indicates that the basic chromophore being correlated here is not the completely unsubstituted ion. It would seem, rather, that the 4-oxybenzenonium ion is the fundamental species in one case, and that it is the 4-methyl-substituted ion in the other.

The relationship of eq 6 predicts λ_{max} 285 nm for anisole protonated in the para position. This coincides exactly with the position of a new absorption band which has been reported to appear as a shoulder on the normal 260-nm band of (unprotonated) anisole when the latter is dissolved in perchloric acid more concentrated than 70%;[21] the carbon basicity of anisole,[7] moreover, indicates that this molecule will begin to be protonated to a measurable extent in perchloric acid of this strength. Nevertheless, our assignment[25] of this absorption at 285 nm to the 4-methoxybenzenonium ion has been questioned.[22]

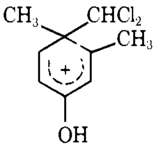
The criticism is based primarily on an estimate that λ_{max} for 4,4-dimethylcyclohexa-2,5-dien-1-one protonated on oxygen, *i.e.*, the 4-hydroxy-1,1-dimethylbenzenonium ion **8**, cannot exceed 270 nm; λ_{max} for the unmethylated ion would be expected to be even lower (*vide infra*). Oxygen-protonated 4,4-dimethylcyclohexa-2,5-dien-1-one has, however, recently been observed for the first time, and λ_{max} has been found to be 295 nm.[26] Furthermore, comparison of λ_{max} = 295 nm for **8** with λ_{max} = 294[27] or 297[28] nm for **9** shows that replacement of methyl with dichloromethyl has essentially no effect, and the difference in λ_{max} of −12 nm between **10** and **11** and that of −7 nm between **12** and **13** then gives −10 nm as the average effect of re-



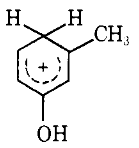
8, λ_{max} = 295 nm[26]



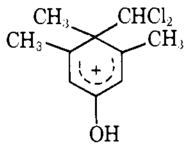
9, λ_{max} = 294,[27] 297[28] nm



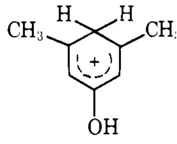
10, λ_{max} = 310 nm[28]



11, λ_{max} = 298 nm (Table IV)



12, λ_{max} = 320 nm[27]



13, λ_{max} = 313 nm (Table IV)

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moving the geminal methyl groups completely. Use of this spectral shift parameter with $\lambda_{max} = 295$ nm for the 4-hydroxy-1,1-dimethylbenzenonium ion, **8**, then gives 285 nm as λ_{max} for para-protonated phenol, and the difference of 2 nm between the spectral shift parameters of methoxyl and hydroxyl groups shown in Table IV leads to 287 nm as λ_{max} for para-protonated anisole. This, of course, agrees well with our earlier estimate of $\lambda_{max} = 285$ nm for 4-methoxybenzenonium ion and thus reinforces our assignment of the absorption observed at 285 nm in concentrated perchloric acid to this species.

Experimental Section

Materials. 1,3,5-Trimethoxybenzene was prepared from phloroglucinol by alkylation with dimethyl sulfate;[29] mp 51.5–52.0° (lit.[30] mp 52°). It is reported[29,31] that phloroglucinol can also be alkylated to either of its partial methyl ethers by carefully controlling the reaction conditions, but in our hands these methods resulted in mixtures of products from which single substances of sufficient purity could not be obtained. The monomethyl ether was therefore prepared from 1,3,5-trinitrobenzene using standard methods[32] to replace one nitro group by methoxyl,[33] selectively reduce the product of that reaction to 3-amino-5-nitroanisole,[34] diazotize and hydrolyze the diazonium salt to 3-hydroxy-5-nitroanisole,[35] reduce that to 3-hydroxy-5-aminoanisole, and finally hydrolyze the latter to 1,3-dihydroxy-5-methoxybenzene;[36] mp 77–78° (lit.[37] mp 78–79°). The remaining methyl ether was prepared by diazotization and hydrolysis of 3,5-dimethoxyaniline (Sapon Laboratories); the 1-hydroxy-3,5-dimethoxybenzene so obtained had mp 42–43° (lit.[38] mp 44.5°).

Partial alkylation was more successful in the synthesis of the ethyl ethers. 1-Hydroxy-3,5-diethoxybenzene, mp 77–79° (lit.[39] mp 75–76°), was made in this way[31] and was subsequently ethylated further to furnish 1,3,5-triethoxybenzene; mp 42.5–43.0° (lit.[40] 42–43°). The monoethyl ether was prepared from 1,3,5-trinitrobenzene by replacing one nitro group with ethoxyl,[41] double reduction to 3,5-diaminophenetole, and hydrolysis[36] of the latter to 1,3-diethoxy-5-ethoxybenzene; mp 87–88° (lit.[42] 84–86°).

The identity of these ethers was confirmed by their nmr spectra. All substances gave aromatic hydrogen and alkoxyl group signals in the expected area ratios; aromatic hydrogen lines appeared at τ 4.08–4.16 ppm, methoxyl groups at τ 6.34–6.40 ppm, and ethoxyl groups at τ 6.09–6.17 (quartets) and 8.65–8.81 ppm (triplets).

All other substrates were obtained from commercial sources and were purified as necessary by distillation, recrystallization, or sublimation. Trifluoroacetic acid (Matheson Coleman and Bell, reagent grade) was distilled before use; perchloric acid monohydrate (*ca.* 84% $HClO_4$) was purchased from the G. Frederick Smith Chemical Co. and was diluted with 70% $HClO_4$ as needed.

Spectral Measurements. Nmr spectra were measured using a Varian A-60 instrument with probe at ambient temperature (38 ± 1°); uv spectra were determined with either Beckmann DK-2 or Cary 11PM machines whose cell compartments were thermostated at 25 ± 0.1°. Substrate concentrations were of the order of 10^{-4} *M* for uv measurements and *ca.* 10% by weight for nmr work. With substrates showing time-dependent spectra, initial recordings were made as soon as possible after sample preparation (0.5–2.0 min).

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