The Oxidation of Methoxybenzenes[1]

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The half-wave polarographic oxidation potentials of the methoxybenzenes have been determined in acetonitrile at a rotating platinum electrode. The e.s.r. spectra of the methoxybenzene cation radicals and other radical oxidation products have been observed by means of controlled potential electrolysis in the microwave cavity of the e.s.r. spectrometer and also by oxidation of the methoxybenzenes in concentrated sulfuric acid. The measured properties are compared with previously obtained charge-transfer absorption data and calculations based on molecular orbital methods.

Introduction

In recent years magnetic resonance techniques have been successfully applied on a semiquantitative basis to the charting of π-electron distribution in conjugated molecules while charge-transfer absorption maxima, polarography in aprotic solvents, and ultraviolet spectroscopy have aided in determining the relative and absolute energies of molecular orbital levels.[2] Some of these physical methods have also aided in uncovering new and previously unsuspected organic reactions and compounds.[3]

Polarographic oxidation and characterization of the resulting cation radicals by e.s.r. techniques has been limited to aromatic hydrocarbons,[4-6] and to a few nitrogen and sulfur substituted aromatics.[7-9] One-electron oxidation of electron-rich aromatic substances is known to take place in concentrated sulfuric acid.[10] In this medium, however, side reactions often result in the misleading occurrence of other paramagnetic species.[11,12]

Methoxy-substituted aromatics comprise a type of compound with electron-rich molecular π-orbitals whose one-electron oxidations have not been previously investigated. The methoxybenzenes are a particularly attractive group of compounds for such study since all of the members of the set are known,[13] the substituent interacts strongly with the ring, and the high symmetry of benzene derivatives simplifies theoretical treatment of their properties.[14]

We report here a study of the polarographic oxidation of the methoxybenzenes in acetonitrile at a platinum electrode. Also reported are e.s.r. spectra which are obtained when controlled potential oxidation of the methoxybenzenes are performed in the microwave

cavity of the e.s.r. spectrometer and when these compounds are dissolved in concentrated (96%) sulfuric acid.

Experimental

Measurements.—The polarographic data were obtained at room temperature on a Leeds and Northrup Electrochemograph, Type E. Oxidations were carried out in dry (<0.01% H₂O) acetonitrile at a rotating platinum electrode with 0.1 M tetra-n-propylammonium perchlorate as supporting electrolyte. An aqueous saturated calomel reference electrode (s.c.e.) was used throughout. The electrochemical cell used to carry out controlled potential electrolyses in the e.s.r. cavity was essentially the same as that described in the literature.[15]

The e.s.r. spectrometer was a Varian Model V4502 with 100 Kc./sec. modulation and a Varian 6-in. magnet. Sulfuric acid solutions were prepared by dissolving a few milligrams of material in 96% sulfuric acid and then transferring to the Varian V4548 flat quartz cell. The spectra were calibrated against the hyperfine splitting of 13.0 gauss of an aqueous solution of peroxylamine disulfonate which was contained in a melting point capillary placed in the cavity along with the solutions of the radicals under investigation.

Molecular orbital calculations were made by a Burroughs Model 205 computer using programs especially written for this machine.

Materials.—Compounds were prepared as previously described.[13]

Results

Polarographic Oxidation Potentials.—The half-wave oxidation potentials of the methoxybenzenes vs. s.c.e. are reported in Table I. Also reported in Table I are the diffusion currents observed for oxidation wave, the

TABLE I

SOME HIGHEST FILLED MOLECULAR ORBITAL PROPERTIES OF METHOXYBENZENES

Compound	$E_{1/2(\text{oxid})}$, v. vs. s.c.e. in CH₃CN	Diffusion current[d]	$\bar{\nu}$c.t.,[a] cm.$^{-1}$ × 10³	x_i[b]
Methoxybenzene (anisole)	+1.76	19.4	19.7	−0.827
1,2-Dimethoxybenzene	1.45	29.7	16.9	− .726
1,3-Dimethoxybenzene	[c]	6.7[c]	18.2	− .773
1,4-Dimethoxybenzene	1.34	17.4	16.1	− .692
1,2,3-Trimethoxybenzene	1.42	20.1	19.4	− .705
1,2,4-Trimethoxybenzene	1.12	31.4	14.6	− .637
1,3,5-Trimethoxybenzene	1.49[c]	[c]	18.2	− .773
1,2,3,4-Tetramethoxybenzene	1.25	13.2	17.9	− .627
1,2,3,5-Tetramethoxybenzene	1.09	15.1	16.5	− .611
1,2,4,5-Tetramethoxybenzene	0.81	17.4	12.5	− .557
Pentamethoxybenzene	1.07	15.5	16.4	− .557
Hexamethoxybenzene	1.24	15.7	19.5	− .557

[a] Reference 13; with tetracyanoethylene in CH₂Cl₂. [b] Hückel highest filled molecular orbital energy parameter, in units of $|\beta|$. [c] A white solid rapidly deposited on the platinum electrode during oxidation of these two methoxybenzenes. [d] In μa. per mmole.

(1) Cumulative Influence of Conjugated Substituents on the π-System Properties of Aromatic Hydrocarbons. VII. Part VI: A. Zweig, *Tetrahedron Letters*, No. 2, 89 (1964).

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(9) A. Zweig, W. G. Hodgson W. H. Jura, and D. L. Maricle, *Tetrahedron Letters*, No. 26, 1821 (1963).

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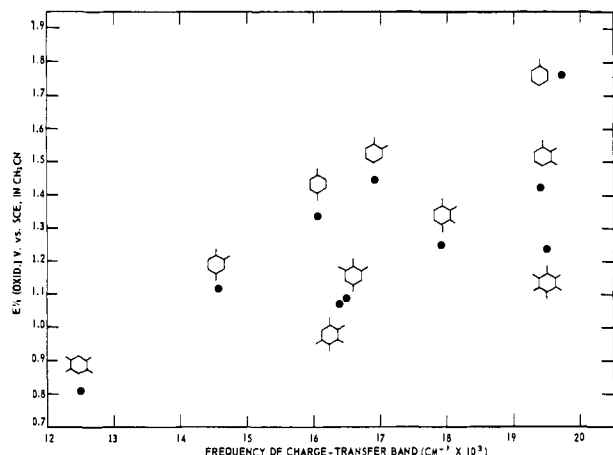
(15) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960); also see ref. 7.

Fig. 1.—Plot of half-wave oxidation potentials *vs.* frequency of first c.t. maxima with TCNE for the methoxybenzenes.

Fig. 2.—Plot of Hückel highest filled molecular orbital parameter *vs.* half-wave oxidation potentials of methoxybenzenes.

positions of the first charge-transfer absorption maxima of the methoxybenzenes with tetracyanoethylene,[13] and the Hückel molecular orbital parameters for the highest filled molecular orbital (h.f.m.o.) of each methoxybenzene[16,17] assuming that all β_{CO} integrals = $0.8\beta_{CC}$.

The measured half-wave potentials are plotted against the charge-transfer maxima with tetracyanoethylene in Fig. 1. In Fig. 2 the calculated h.f.m.o. parameters are plotted against the half-wave oxidation potentials. The oxidations of 1,3-dimethoxybenzene and *s*-trimethoxybenzene were irregular under the conditions employed. A colorless precipitate was formed on the platinum electrode during the oxidation of *s*-trimethoxybenzene, and in both cases the diffusion current dropped rapidly soon after oxidation began. The points for these compounds were therefore not included in the figures.

Electron Spin Resonance Spectra.—If the first step in the oxidation of methoxybenzenes occurs with one-electron transfer, then the e.s.r. spectrum of the resulting cation radical may be detectable. Even if the oxidation at the electrode surface involves two-electron transfer, the resulting dication may accept an electron from a neutral molecule to form two cation radicals as indicated in eq. 1.

$$R \xrightarrow{-2e} R^{++} \xrightarrow{R} 2R^{+} \qquad (1)$$
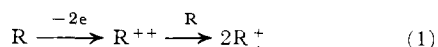
All of the methoxybenzenes on controlled potential oxidation in the e.s.r. microwave cavity displayed e.s.r. spectra when the potential was adjusted to the peak of their first oxidation wave. Sulfuric acid solutions of a number of the methoxybenzenes also gave e.s.r. spectra. The mode of reaction by which concentrated sulfuric acid causes one-electron oxidation has not been conclusively demonstrated. Protonation of the neutral material usually seems to be a preliminary step.[10] Many compounds then are oxidized to their cation radical, although in some instances the protonated species is stable and no further reaction occurs, and in other cases neither protonated species nor cation radical is stable and rapid further reactions occur. Protonation of some of the lower methoxybenzenes in sulfuric acid
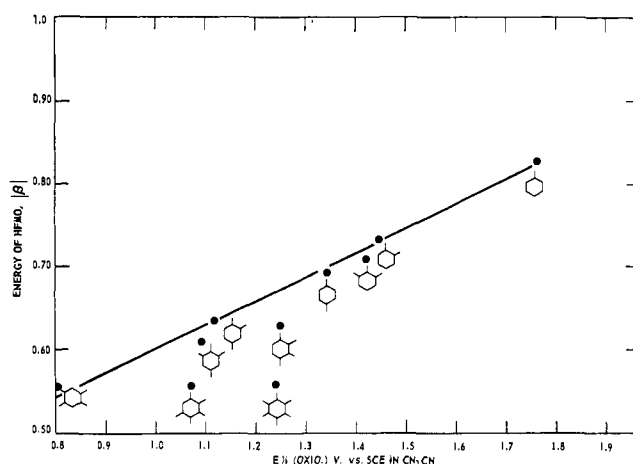
less concentrated than 96% has been fairly extensively studied,[18-22] and no radical formation has been noted. In 98% sulfuric acid containing an added oxidizing agent, anisole is reported[23] to give a solution with an e.s.r. spectrum identical with that of the hydroquinone cation radical. The e.s.r. spectra that have now been obtained by oxidation of the methoxybenzenes are discussed in the following section.

Hexamethoxybenzene.—Electrolytic oxidation in acetonitrile resulted in an e.s.r. spectrum showing 15 equally spaced lines with a separation of 1.30 gauss. The line intensities were in good agreement with those expected for the central 15 lines of a nineteen line spectrum predicted for the cation radical of hexamethoxybenzene. It is reasonable that the two outer pairs of lines were not observed, since they are theoretically predicted to be very weak. The principal species present in 96% sulfuric acid gave a spectrum with 15 equally spaced lines with a separation of 1.40 gauss. The spectrum was somewhat distorted by the presence of additional lines and a slight asymmetry. Such asymmetry about the center line has been reported previously for sulfuric acid solutions of cation radicals.[24] This spectrum is most reasonably assigned to the cation radical of hexamethoxybenzene. The 0.1-gauss difference in coupling constants is due to the change of solvent.[25] Cyclic voltammetry indicated that the lifetime of the electrolytically produced hexamethoxybenzene cation radical is of the order of 1 sec.[26] In sulfuric acid the growth of additional lines distorted the e.s.r. spectrum after a few minutes. The products of decomposition are unknown.

Pentamethoxybenzene.—Electrolytic oxidation gave an e.s.r. derivative spectrum with nine groups of lines with alternating even and odd numbers of lines in each group (cf. Fig. 3a). This alternation is well represented

(16) The assumption is made in these molecular orbital calculations that all oxygens in the methoxybenzenes interact equally with the benzene ring and that the exchange integral for this interaction, β_{CO}, is equal to $0.8\beta_{CC}$. The coulomb integral of oxygen, α_0, is taken as $\alpha_c + 2\beta_{cc}$.

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(19) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).

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(22) E. M. Arnett, C. Y. Wu, J. N. Anderson, and R. D. Bushwick, *ibid.*, **84**, 1674 (1964).

(23) See ref. 11.

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(25) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

(26) We wish to thank Dr. D. L. Maricle of these laboratories for the cyclic voltammetry experiments. Details of this procedure are given in ref. 3.
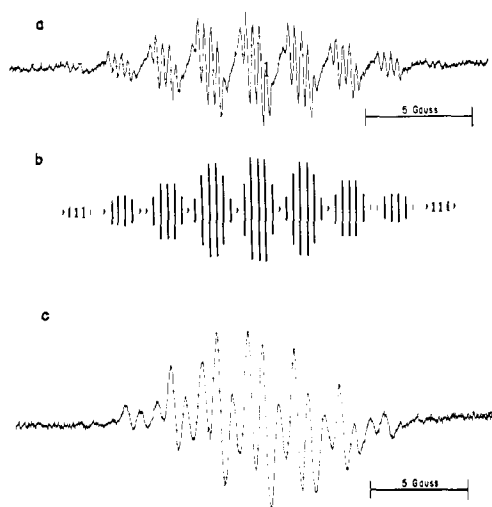
Fig. 3.—(a) First derivative of the e.s.r. absorption *vs.* magnetic field of the pentamethoxybenzene cation radical generated by electrolytic oxidation of pentamethoxybenzene in acetonitrile; (b) theoretical reconstruction of a spectrum with hyperfine coupling constants of 2.28 gauss (six equivalent protons), 1.98 gauss (six equivalent protons), and 0.60 gauss (one proton); (c) first derivative of the e.s.r. absorption *vs.* magnetic field of the radical generated by the dissolution of pentamethoxybenzene in 96% sulfuric acid.

by a splitting scheme in which there are two sets of six equivalent protons with hyperfine coupling constants of 2.28 and 1.98 gauss. There are further splittings of these lines, but the resolution was not sufficient to make a firm decision as to the origin of the extra splittings. From theoretical reconstructions of the spectra the best fit was obtained with the further interaction with a single proton and a hyperfine coupling constant for this interaction of 0.60 gauss. The reconstruction of this spectrum is shown in Fig. 3b. Interaction of the unpaired electron with four equivalent protons with a hyperfine coupling constant of 0.3 gauss could not be excluded. In sulfuric acid a markedly different spectrum was obtained as shown in Fig. 3c. We were unable to reproduce this spectrum by any combination of splittings which would be reasonable for the cation radical of pentamethoxybenzene and thus consider probable that this radical species is not the latter. Cyclic voltammetry[26] on pentamethoxybenzene in acetonitrile indicated a reversible lifetime of at least 10 sec. for the first oxidation product, confirming the identification of the cation radical in this solvent.

1,2,4,5-Tetramethoxybenzene.—The spectrum obtained by electrolytic oxidation and by dissolution in sulfuric acid are well represented by coupling to sets of 12 and 2 equivalent protons. The coupling constant to the 12 protons was 2.21 gauss, and to the 2 protons 0.89 gauss. The coupling constants were the same in both solvents. The coupling scheme was most clearly seen in sulfuric acid but there was asymmetry of the spectrum, whereas in acetonitrile the resolution was poorer but the spectrum was symmetrical.

1,2,3,5-Tetramethoxybenzene.—The electrolytic oxidation gave an e.s.r. derivative spectrum which had 13 well-resolved lines. Some asymmetry was observed, presumably caused by a second radical species since extra lines were eventually seen as the voltage was increased above the first oxidation wave. The intensities were a fairly good fit for unpaired electron inter-

action with three equivalent protons having a coupling constant of 4.40 gauss and six equivalent protons with a coupling constant of 2.20 gauss. Other splitting schemes could not be excluded. In 96% sulfuric acid, a poorly resolved spectrum was obtained which had an *even* number of lines (eight or more). The lines were equally spaced 2.3 gauss apart.

1,2,3,4-Tetramethoxybenzene.—The electrolytic e.s.r. derivative spectrum showed nine broad lines (line width 1.5 gauss). Interaction with eight magnetically equivalent or near equivalent protons with a coupling constant of approximately 2.7 gauss is indicated. In sulfuric acid, only a weak spectrum with at least seven broad overlapping lines was observed.

1,3,5-Trimethoxybenzene.—On first passing current, a very weak broad e.s.r. derivative line was observed. This disappeared on prolonged electrolysis. No e.s.r. signal was observed in concentrated sulfuric acid.

1,2,4-Trimethoxybenzene, when purified by preparative vapor phase chromatography (v.p.c.) and then oxidized, gave a complex e.s.r. derivative spectrum which rapidly changed to a poorly resolved spectrum of broad lines. Coupling constants could not be assigned. It was found by v.p.c. that commercial 1,2,4-trimethoxybenzene contains ~0.1% 1,2,4,5-tetramethoxybenzene which is not removed by distillation. The latter as its stable cation radical is seen in the e.s.r. spectrum when unpurified 1,2,4-trimethoxybenzene is subjected to oxidizing conditions.

1,2,3-Trimethoxybenzene.—Electrolytic oxidation gave an extremely weak spectrum with some signs of hyperfine structure. No interpretation was possible. No e.s.r. signal was observed in 96% sulfuric acid.

1,4-Dimethoxybenzene.—In sulfuric acid, this compound gave a well resolved e.s.r. spectrum with many lines (Fig. 4a). The spectrum shows dissimilarities between the high field and low field sides, suggesting that there are two radical species present. The occurrence of *cis–trans* isomerism seemed a possibility, but
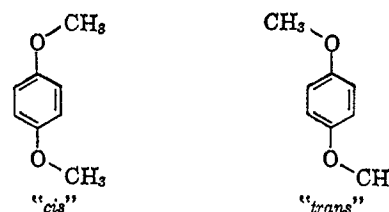
attempts to alter the balance between the contributing species by heating the sulfuric acid solution reduced all parts of the spectrum proportionately until it entirely disappeared. Electrolytic oxidation at 1.0 v. *vs.* s.c.e. gave a spectrum (Fig. 4b) which was similar to that seen in concentrated sulfuric acid. Differences in the spectra were explicable by the poorer resolution in acetonitrile. However, as the voltage was increased, there was a considerable change in the balance between the different sections of the spectrum as seen in Fig. 4c in which the spectrum measured at 1.5 v. is shown. The simplest assumption which would explain the changes is that there is a spectrum with an odd number of lines (spectrum A) and a spectrum with an even number of lines (spectrum B). In the electrolytically produced spectra the relative intensities of the A components are a reasonable fit to that expected for interaction with

six equivalent protons having a hyperfine coupling constant of 3.45 gauss, and a further splitting with an even number of protons (*i.e.*, odd number of lines). The B spectrum had a spacing of 3.37 gauss, but could not be fitted to any splitting scheme presumably because of overlap with some components from the A spectrum.

1,3-Dimethoxybenzene.—A poorly resolved spectrum containing an odd number of lines was obtained by electrolytic oxidation. Nine lines were seen separated by about 1.4 gauss. As the polarographic data indicated that this is an irreversible oxidation, it is unlikely that this spectrum is due to the cation radical. No signal was observed in 96% sulfuric acid.

1,2-Dimethoxybenzene.—A single line was observed in the e.s.r. spectrum on electrolytic oxidation of this methoxybenzene. There was no sign of hyperfine structure. The line width was 1.8 gauss. No signal was seen in 96% sulfuric acid.

Anisole.—On electrolytic oxidation a weak single line with a width of approximately 4 gauss was observed. No signal was obtained in 96% sulfuric acid.

Discussion

Polarographic Oxidation Potentials.—In order to compare the polarographic half-wave oxidation potentials of a series of compounds with other measurements of their π-electron basicity, the electrode processes must be reversible. When such electrochemical equilibrium is achieved, the half-wave oxidation potential $(E_{1/2(\text{oxid})})$ is related to the ionization potential by eq. 2, where ΔE-

$$E_{1/2(\text{oxid})} = \text{IP} + \Delta E(\text{solv.}) - \frac{T\Delta S^\circ}{F} - \frac{RT}{F}\ln\frac{f^+D}{fD^+} + \text{constant} \quad (2)$$

(solv.) is the difference in solvation energy between the compound and its positive ion, f^+ and f are the activity coefficients of the ion and the neutral molecule, and D^+ and D are the respective diffusion constants. A reasonable assumption in eq. 2 for a series of similar molecules is that the logarithmic term is small. Pysh and Yang[5] found that the linear relationship of eq. 3 correlates

$$\text{IP} = (1.473 \pm 0.027)E_{1/2(\text{oxid})} + (5.821 \pm 0.0009) \quad (3)$$

photoionization potentials and polarographic oxidation potentials for aromatic hydrocarbons. They concluded that either the solvation energy variations are small as compared with ionization potential variations or the solvation energy varies in an approximately regular manner with the IP's.

Ionization potential data for the methoxybenzenes is very limited. Direct measurement of the ionization potential of anisole has been made both by electron impact[27] and by photoionization.[28] The impact value (8.83 e.v.) is more than 0.6 e.v. higher than the reported photoionization value (8.20 e.v.). This difference is thought to occur because the electron impact method measures a vertical (Franck–Condon) transition, while the photoionization value is an adiabatic ionization

(27) K. Biemann, "Mass Spectroscopy, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 202.

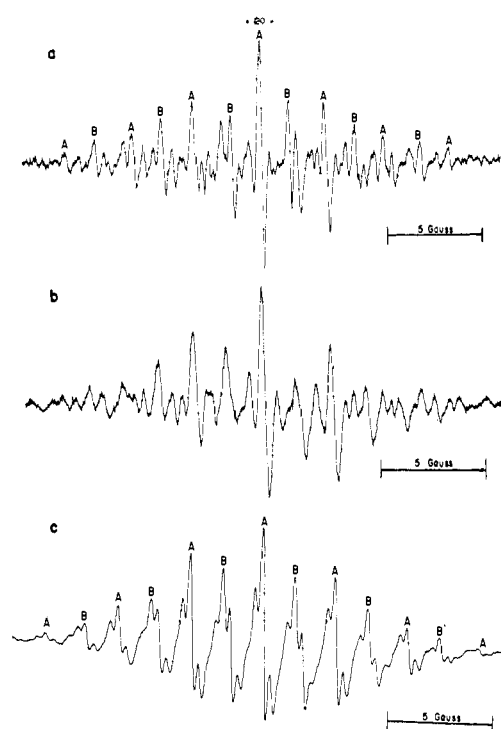(28) K. Wanatabe, *J. Chem. Phys.*, **26**, 542 (1957).

Fig. 4.—First derivative of the e.s.r. absorption *vs.* magnetic field of the radicals generated from 1,4-dimethoxybenzene by (a) dissolution in 96% sulfuric acid, (b) electrolytic oxidation in acetonitrile at 1.0 v., (c) oxidation at 1.5 v.

potential.[29] When the photoionization potential of anisole is used in eq. 3 a polarographic oxidation potential of 1.62 ± 0.03 v. *vs.* the standard calomel electrode is indicated. The value found experimentally (1.76 v.) for the polarographic oxidation potential of anisole is only 0.14 v. larger than that indicated by eq. 3. This difference may be due to the solvation term or may simply be an artifact. Further exploration of the relationship of IP and $E_{1/2(\text{oxid})}$ for these compounds cannot be directly made, since photoionization potentials for the higher methoxybenzenes are not available. According to Koopmans' theorem,[30] the ionization potential is equal to minus the energy of the highest filled molecular orbital. In a comparison of the charge-transfer absorption maxima (with a given acceptor molecule) of the sterically unhindered methoxybenzenes with Hückel molecular orbitals, an excellent linear relationship has been found.[13,17] Since an approximately linear relationship exists between IP and $\bar{v}_{\text{ct}}$,[31] the relationship between $E_{1/2 \text{ (oxid)}}$ and the Hückel highest filled molecular orbitals of this series of similar compounds is of particular interest.

The half-wave oxidation potentials of the sterically unhindered methoxybenzenes (those which do not contain methoxy groups on three contiguous ring positions) were found to correlate well with the first charge-transfer bands of these methoxybenzenes with tetracyanoethylene as shown in Fig. 1. The equation for the five points is

$$\Delta E_{\text{ct}} \text{ (e.v.)} = 0.935E_{1/2(\text{oxid})} \text{ v.} + 0.77 \quad (4)$$

The small difference from unit slope in this equation may partially be due to experimental error particularly

(29) Ref. 2, p. 189.

(30) T. Koopmans, *Physica*, **1**, 104 (1933).

(31) (a) M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961); (b) also see R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

in the assignment of charge-transfer absorption maxima, but also may be caused, in part, by differences in solvation energies in the different systems. Values for 1,3-dimethoxybenzene and s-trimethoxybenzene were not plotted as neither gave a reversible oxidation potential in acetonitrile. This irreversibility coupled with the good behavior of the charge-transfer maxima of these two compounds shows that charge-transfer absorption maxima can be used to obtain experimental evidence for molecular orbital energy levels in instances where polarographic methods fail.

Inspection of Fig. 1 indicates that with the exception of hexamethoxybenzene, the half-wave oxidation potentials of the hindered methoxybenzenes and their charge-transfer absorption maxima with tetracyanoethylene are also linearly related. These points appear to fall on a line parallel to that of the unhindered methoxybenzenes. Systematic differences in solvation energies between the hindered and unhindered methoxybenzenes may be responsible for this effect.

The correlation of polarographic oxidation potentials of the unhindered methoxybenzenes, excluding 1,3-dimethoxybenzene and s-trimethoxybenzene, with the calculated Hückel h.f.m.o.'s was also satisfactory, as seen in Fig. 2. The linear equation relating the experimental and theoretical values is expressed by (5), where χ_i is the coefficient in the Hückel molecular orbital formula I

$$\chi_i = -0.282 E_{1/2(\text{oxid})} - 0.324 \qquad (5)$$

$\alpha - \chi_i\beta$ for the minimum ionization energy I of the donor, and the half-wave oxidation potentials are measured against a s.c.e.

Electron Spin Resonance.—Information about the spin distribution in radicals can be obtained by using eq. 6, first suggested by McConnell,[32] relating isotropic hyperfine interactions with protons in the

$$a_\mathrm{H} = Q\rho_\mathrm{c} \qquad (6)$$

plane of an aromatic ring, a_H, with the unpaired π-electron density at the contiguous carbon atom, ρ_c.[33] In this equation, Q is a constant which may be evaluated either theoretically or experimentally. For unpaired electrons interacting with other magnetic nuclei, with different geometric considerations, theoretical examination leads to a more complex relationship.[34] In practice, however, the relationship of the coupling constants of methyl protons and the N^{14} nucleus and calculated spin densities very closely follow linear relationship as in eq. 5.[35,36] The e.s.r. spectra of cation radicals obtained by one-electron oxidation of substituted aromatics should give insight into the electron distribution of the highest filled molecular orbital of the corresponding neutral molecule.[37] This may be of interest in view of Fukui's[38] suggestion that the electron distribution of the h.f.m.o. determines the path of electrophilic substitution reactions.

(32) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).
(33) A. Carrington, *Quart. Rev.* (London), **17**, 67 (1963).
(34) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(35) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).
(36) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).
(37) This is true only in the one-electron m.o. approximation where removal of one electron from a molecule is assumed not to affect the distribution of the remaining electrons.
(38) K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954); also see discussion in ref. 2, p. 329.

In Table II we report the spin densities calculated for the ring and oxygen positions of the methoxybenzene cation radicals. The parameters used were the

ELECTRON DISTRIBUTION OF HIGHEST FILLED M.O.'S OF METHOXYBENZENES

$\alpha_\mathrm{O} = \alpha_\mathrm{C} + 2.0\,\beta_\mathrm{CC}; \quad \beta_\mathrm{CO} = 0.8\,\beta_\mathrm{CC}$

Compound	Position	Spin density on Carbon	Oxygen	a_H	a_H/ρ_n
Methoxybenzene (anisole)	1	0.258	0.120		
	2,6	.122	...		
	3,5	.048	...		
	4	.282	...		
1,2-Dimethoxybenzene	1,2	.233	0.092		
	3,6	.012	...		
	4,5	.162	...		
1,3-Dimethoxybenzene	1,3	.161	0.069		
	2	0	...		
	4,6	0.270	...		
	5	0	...		
1,4-Dimethoxybenzene	1,4	0.241	0.090	3.45	38.3
	2,3,5,6	.084	...		
1,2,3-Trimethoxybenzene	1,3	.113	0.043		
	2	.316	0.120		
	4,6	.025	...		
	5	.201	...		
1,2,4-Trimethoxybenzene	1	.262	0.090		
	2	.143	.049		
	4	.191	.066		
	3	.009	...		
	5	.154	...		
	6	.035	...		
1,3,5-Trimethoxybenzene	1,3,5	.107	0.046		
	2,4,6	.180	...		
1,2,3,4-Tetramethoxy-benzene	1,4	.247	0.084	2.7	32.1
	2,3	.056	0.019		
	5,6	.093	...	2.7	
1,2,3,5-Tetramethoxy-benzene	1,3	.087	0.029		
	2	.303	.100		
	5	.192	.064		
	4,6	.055	...		
1,2,4,5-Tetramethoxy-benzene	1,2,4,5	.191	0.059	2.21	37.5
	3,6	0	...	0.89	
Pentamethoxybenzene	1,5	0.191	0.059	2.28	38.6
	2,4	0.191	0.059	1.98	33.6
	3	0	0		
	6	0	...	0.60	
Hexamethoxybenzene	1–6	0.127	0.040	1.30	32.5

same as those used to calculate the energy levels.[16] Also reported are the tentative assignments of proton coupling constants and the resulting proportionality of coupling constants to spin density. Despite many complicating factors, these proportionality factors all have nearly the same value.

Hexamethoxybenzene.—The e.s.r. spectrum of the hexamethoxybenzene cation radical is of particular interest as the simple molecular orbital picture of this molecule suggests an orbitally degenerate ground state. It has been suggested[39] that radicals of this type have broadened hyperfine lines due to Jahn–Teller distortions which modulate the spin densities. Examination of the e.s.r. spectrum of the coronene cation radical[40] and the hexamethylbenzene cation radicals[41] have borne this out. In the present study, the narrowest line width between derivative extremes for the hexamethoxybenzene cation radical was 0.25 gauss. The iso-

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(40) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 271 (1961).
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tropic coupling constant of 1.4 gauss found for the hexamethoxybenzene cation radical in sulfuric acid should be compared to the 6.45-gauss coupling constant reported for hexamethylbenzene in the same solvent.[41] The molecular orbital calculations, using $\alpha_0 = \alpha_C + 2\beta_{CC}$ and $\beta_{CO} = 0.8\,\beta_{CC}$, suggest that 0.128 e is localized at each ring carbon and that 0.039 e is at each oxygen in the degenerate h.f.m.o. of hexamethoxybenzene. If β_{CO} is reduced to $0.4\beta_{CC}$ to adjust for the probable nonplanarity of the p-orbitals on carbon and oxygen, the unpaired spin on the ring carbons is calculated to increase to 0.149 with concomitant decrease of e on oxygen to 0.018. The highest filled m.o.'s are thus weakly perturbed benzene orbitals. The experimental data and the molecular orbital picture are in agreement in suggesting that most of the spin density is located on the benzene ring and little seeps out to the oxygens.

Pentamethoxybenzene.—The e.s.r. spectrum of the electrolytically oxidized pentamethoxybenzene is in very good agreement with what would be expected from the m.o. calculations. The latter predict that the orbital occupied by the unpaired electron is antisymmetric with regard to the symmetry plane perpendicular to the benzene ring. Thus the protons of the 1-,2-,4-, and 5-methoxy groups should contribute most significantly to the hyperfine structure of the e.s.r. spectrum. The splitting due to the methoxy protons on positions 1 and 5 should be somewhat larger than those of positions 2 and 4 owing to inability of the latter methoxy groups to be planar with the benzene ring. On this basis we assign the 2.28-gauss splitting to the 1- and 5-groups and the 1.98-gauss splitting to the 2- and 4-groups. Hückel theory predicts no spin density at the nodal 3- and 6-positions so that the small further splitting that is observed is probably caused by negative spin density at one or both of these positions.[42]

1,2,4,5-Tetramethoxybenzene.—This cation radical is also of particular interest because all of its magnetic nuclei are accounted for by the hyperfine structure and because the splitting caused by the protons at the nodal 3- and 6-positions are not predicted by the Hückel calculations (cf. Table II). In this case and in hydrocarbon anions and cations where such nodes occur,[42] it is necessary to improve the wave function that describes the π-electron distribution in order to account for the discrepancy. This can be accomplished either by including excited state configurations or by self-consistent field methods. The McLachlan method[43] derived from the latter theory, which may be formulated in terms of Hückel molecular orbital quantities, has been widely used in such cases.[43-49] In this theory the spin density at position r is given by ρ_r in eq. 7

$$\rho_r = C^2_{or} + \lambda \Sigma \pi_{r,s}\, C^2_{os} \qquad (7)$$

where C_{or}^2 and C_{os}^2 are the Hückel spin densities at

positions r and s, λ is an empirical constant, the value for which 1.2 has proved to be experimentally successful,[45-49] and π_{rs} is the atom–atom polarizability calculated from the Hückel theory.[50]

In Table III is reported the calculated spin densities for the cation radical of 1,2,4,5-tetramethoxybenzene

TABLE III

CALCULATED SPIN DENSITIES 1,2,4,5-TETRAMETHOXYBENZENE

Position	Hückel	McLachlan ($\lambda = 1.2$)
1,2,4,5	0.1912	0.2265
3,6	0	− .0675
Oxygens	0.0588	.0573

by the Hückel and the McLachlan methods. The McLachlan method results in a negative spin density at the nodal positions.

1,2,3,5-Tetramethoxybenzene.—The molecular orbital calculations indicate that the h.f.m.o. of this molecule has about twice as much spin localized on oxygen at position 5 as on the oxygens at positions 1 and 3. The protons of the methyl groups attached to these oxygens can therefore account for the major features of the e.s.r. spectrum. Although the' calculations indicate a still larger unpaired spin localization at the oxygen on the 2-position of the benzene nucleus, steric inhibition of coplanarity of the p_z-orbital on this oxygen with the benzene ring probably greatly diminished the spin density and also decreases the hyperfine coupling owing to the methyl protons. This interpretation must, however, be regarded as tentative.

1,2,3,4-Tetramethoxybenzene.—The hyperfine splitting in the e.s.r. spectrum of the cation radical obtained from electrolytic oxidation of this compound is in reasonable agreement with the simple m.o. picture, which predicts that the major couplings will be with the two ring protons and the methoxy protons at the 1- and 4-positions. The splitting due to the methoxy protons at the 2- and 3-positions is expected to be even smaller than suggested by Table II because of steric hindrance.

1,4-Dimethoxybenzene.—Oxidation of this compound either by sulfuric acid or electrolytically in acetonitrile apparently gives two radical species. The seven-line A species, which seems to appear first electrolytically, has a coupling constant of 3.45 gauss, apparently due to six equivalent protons. That these may be the six methoxy protons of the 1,4-dimethoxybenzene cation radical (the oxygen analog of Wurster's Blue) is strongly suggested, although not proved by the molecular orbital calculations. The calculated spin densities on oxygen in both 1,2,4,5-tetramethoxybenzene and 1,4-dimethoxybenzene are in the same proportions as the methyl proton coupling constants of the former cation radical and this coupling constant obtained by oxidation of the latter. The species responsible for the "B" spectrum is not known, although a report of dimerizations of dimethoxybenzenes by electrochemical oxidations in methanol may prove a clue to its identification.[51]

(42) For a discussion of negative spin density see ref. 33.
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