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Radical Cations of Halogenated Tetrahydroxybenzene Diethylene Ethers

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It was observed that two newly-prepared substances, 3,6-dichloro- and 3,6-dibromo-1,2,4,5-tetrahydroxybenzene diethylene ether, underwent one-electron oxidation to afford the corresponding radical cations in concentrated sulfuric acid. Their electronic spectra and ESR spectra were recorded in a sulfuric acid and nitromethane - $AlCl_3$ medium. The chloro - compound gives an ESR spectrum with a hyperfine structure, while the bromo-compound shows a spectrum without hyperfine splitting. Some different behavior was observed in several model compounds with similar structures.

Some aspect of the behavior of methoxybenzenes in concentrated sulfuric acid have been investigated, and the formation of the corresponding radical cations has been confirmed by means of a study of the ESR[1] and electronic absorption spectra.[2] We reported in a preceding paper[3] the syntheses of 3,6-dichloro- and 3,6-dibromo-1,2,4,5-tetrahydroxybenzene diethylene ether

1) A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 4124 (1964).

2) K. Kimura and H. Yamada, This Bulletin, **42**, 3032 (1969).

3) T. Asahara, M. Senō, S. Shiraishi, and T. Teshirogi, *Kogyo Kagaku Zasshi*, **74**, 231 (1971).

(I and II) through the reaction of 2,5-dichloro- and 2,5-dibromo-3,6-dihydroxy-*p*-benzoquinone respectively with ethylene glycol. During the course of investigation of these properties, we observed the red coloration and ESR spectra of the compounds I and II in a sulfuric acid medium.

For comparison, some model compounds–2,5-dichloro- and 2,5-dibromohydroquinone dimethyl ether (III and IV), tetrachloro- and tetrabromohydroquinone dimethyl ether (V and VI), and 3,6-dichloro- and 3,6-dibromo-1,2,4,5-tetramethoxybenzene (VII and VIII)– were synthesized, and their ESR and electronic spectra were examined in sulfuric acid. The results will be presented in this paper.

Experimental

Syntheses. Compounds I and II synthesized according to the description in a previous paper.[3] Compound III was prepared from hydroquinone dimethyl ether and chlorine gas according to the method of Habermann,[4] mp 125°C (lit, 126°C), while V was prepared by treating III with chlorine gas, mp 165°C (lit, 164°C). Compound IV was prepared from the reaction of hydroquinone dimethyl ether with bromine, mp 141°C (lit, 142°C), and VI was prepared by the reaction of tetrabromohydroquinone with a potassium hydroxide solution of dimethyl sulfate, mp 193°C (lit, 194°C). Although the syntheses of compounds VII and VIII were described by Marini-Bettolo's report,[5] where chloranil or bromanil was methoxylated reductively in a zinc-methanol system, another procedure was adopted here; that is, 2,5-dichloro- or 2,5-dibromo-3,6-dimethoxy-*p*-benzoquinone was reduced with sodium dithionite and then reacted with dimethyl sulfate in an aqueous potassium solution. The products were recrystallized from ethanol-water; mp 114°C (VII) and 107°C (VIII). The electronic spectra were recorded on a Hitachi EPS-3T spectrophotometer, while the ESR spectra were measured by means of a JEX-3X ESR spectrometer. The sulfuric acid used for the solvent was of a special grade (98%) and nitromethane - aulminium chloride was prepared according to the description in the literature.[6]

Results and Discussion

The electronic spectra of I and II in concentrated sulfuric acid are shown in Fig. 1. The absorptions in the visible region (500 and 540 mμ) may be supposed to result from the radical cations which are formed through the one-electron oxidation of the original compounds. These absorptions correspond to the peaks at 440 and 460 mμ respectively of hydroquinone dimethyl ether, which was analysed by Kimura.[2]

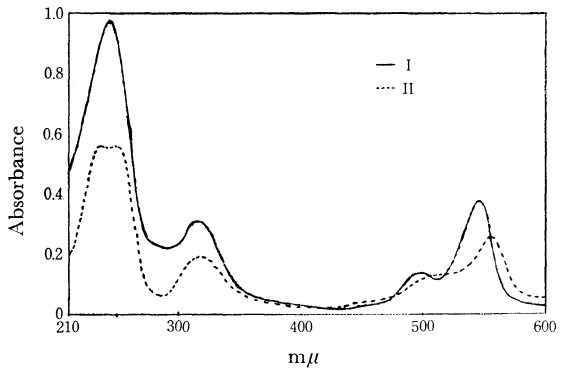


Fig. 1. Electronic spectra of I and II in sulfuric acid. (concn. 4×10^{-5} mol/*l*)

The ESR spectra of I and II in sulfuric acid are shown in Figs. 2 and 3. The spectrum of I has an hfs with nine

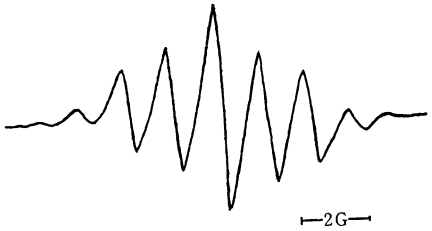


Fig. 2. ESR spectrum of I in concentrated sulfuric acid. (concn. 2×10^{-4} mol/*l*).

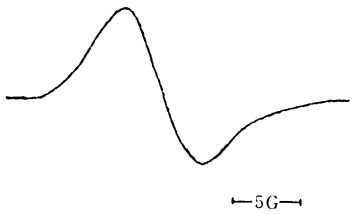


Fig. 3. ESR spectrum of II in concentrated sulfuric acid. (concn. 2×10^{-4} mol/*l*)

peaks. This is ascribed to the splitting by eight equivalent hydrogen atoms of I and has the expected intensity ratio of 1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1. The coupling constant, a^H is 1.33 gauss; this may be compared with the value, 2.21 gauss, for 1,2,4,5-tetramethoxybenzene.[1] The spectrum of II shows no hfs. Shine *et al.*[7] observed that 2,7-dichlothianthrene shows a three-line spectrum, but 2,7-dibromothianthrene shows a single broad-line spectrum.

Similar ESR spectra were observed in the nitromethane-aluminium chloride medium.[6] The hfs splitting of the spectrum of I is poorer under similar conditions in this medium than in sulfuric acid. The spectrum of II is a single broad line in this medium. The lack of any splitting into hfs in the spectra of II is probably the result of the spin-orbit coupling, as has been suggested by Shine *et al.*[7] An anisotropy is observed in these spectra; it is probably the result of the high viscosity of the medium and the spin-orbit interaction. The electronic spectra of I and II in this medium are nearly the same as those in sulfuric acid, (I, λ_{max} 498, 538 mμ; II λ_{max} 508, 546 mμ).

As has been stated above, the spectra of the radical cations of the chloro derivative are different from those of the bromo derivative. In order to obtain further information on this question, the spectra of several model compounds were examined. The model compounds synthesized for this purpose were as follows:

4) J. Habermann, *Chem. Ber.*, **11**, 1034 (1878).
5) C. B. Marini-Bettolo and F. S. Trucco, *Gazz. Chim. Ital.*, **73**, 300 (1943).
6) W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, **88**, 2862 (1966).
7) H. J. Shine, C. F. Dais, and R. J. Small, *J. Chem. Phys.*, **38**, 569 (1963).

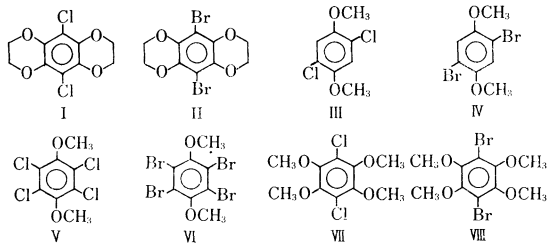
Table 1. Electronic spectra in sulfuric acid

Compound	I		II		III		IV		VII		VIII	
λ_{max} (mμ)	502	542	512	552	457	490	485	518	454	481	438	464
log ε	3.62	3.99	3.57	3.83	3.48	3.68	3.45	3.63	2.04	2.18	1.90	2.32

Table 2. ESR spectra

Compound	No. of lines (in concentrated sulfuric acid)	Hyperfine splitting	Over-all splitting	g-Values	No. of lines (in nitromethane - aluminium chloride)	Hyperfine splitting	Over-all splitting
I	9	1.33	12.0	2.0025	5[a)]	—	18.5
II	1	—	16.5	2.0036	1	—	20.0
VII	5	1.74	12.0	2.0023	9	1.97	19.0
VIII	11[a)]	—	20.5	2.0034	11	2.25	19.5

a) Poorly resolved.



The tetrahalogeno compounds (V and VI) are insoluble in sulfuric acid, probably because of the electron-withdrawing property of halogens. The other compounds are soluble in sulfuric acid to form red solutions. The absorption peaks in the visible region, which are supposed to be due to radical cations, are characterized as is shown in Table 1. While the red solutions of VII and VIII show ESR spectra, no signals of ESR were observed for the red solutions of III and IV. The chloro compound VII has an ESR spectrum with only five peaks. The bromo compound VIII also shows an hfs; this hfs is very complicated, probably because of the restricted rotation of the four methoxy groups. When nitromethane - aluminium chloride was used instead of sulfuric acid as an oxidation medium, the hfs was also observed for the compounds VII and VIII. The results of the ESR spectra are summarized in Table 2. It should be noted that nitromethane - aluminium chloride is a stronger oxidation medium than sulfuric acid and that the radical cations of the bromo compounds have a more labile unpaired electron than the radical cations of chloro compounds. Moreover, a comparison of the signal intensities revealed that the chloro compounds have a higher radical concentration than the corresponding bromo compounds. The g-values are smaller for the chloro compounds than for the bromo compounds, as is to be expected from the values of the spin-orbit coupling constant.

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