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Electronic Absorption Spectra of Cation Radicals of *p*-Dialkoxybenzenes in Concentrated Sulfuric Acid

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The cation radicals of *p*-dialkoxybenzenes produced by different methods of oxidation have been studied mainly with ESR technique:[1-4] Oxidations have been performed with concentrated sulfuric acid,[1] lead tetra-acetate-boron trifluoride in dichloromethane,[2] aluminum chloride in nitromethane[3] and polarographically.[4]

This note is concerned with the electronic absorption spectra of cation radicals formed from several *p*-dialkoxybenzenes (hydroquinone, *p*-methoxyphenol, *p*-dimethoxybenzene, *p*-ethoxyphenol, *p*-

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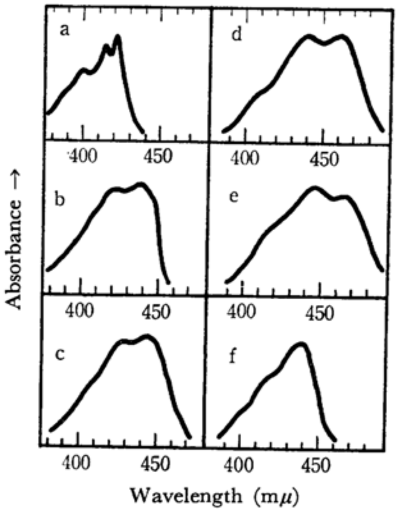

Fig. 1. Electronic absorption bands of the cation radicals of various *p*-dialkoxybenzenes in concentrated sulfuric acid at room temperature.
a) [hydroquinone]$^+$, b) [*p*-methoxyphenol]$^+$, c) [*p*-ethoxyphenol]$^+$, d) [*p*-dimethoxybenzene]$^+$, e) [*p*-diethoxybenzene]$^+$ and f) [2,3,5-trimethylhydroquinone]$^+$.

diethoxybenzene and 2,3,5-trimethylhydroquinone) in concentrated sulfuric acid. The electronic absorption bands of the cation redicals of these compounds in concentrated sulfuric acid were first measured (Fig. 1). These spectra may be ascribed to the cation radicals of the *p*-dialkyoxybenzenes, since the solution of hydroquinone gives an ESR spectrum identical to that already assigned to the cation.[1]

In order to confirm the existence of the cation radicals, the absorption band obtained by the oxidation with concentrated sulfuric acid (Method 1) from *p*-dimethoxybenzene was compared with the absorption spectra which were obtained by other methods of oxidation: oxidation with $SbCl_5$ in acetonitrile at room temperature (Method 2), and photo-oxidation in a deaerated transparent rigid matrix of the mixture of concentrated sulfuric acid and glacial acetic acid at 77°K (Method 3). It was found that the electronic absorption bands around 450 mμ obtained by these three kinds of oxidation are very similar to one another. The absorption band obtained through photo-oxidation (Method 3) has been reported.[5] However, in the present work, the photo-oxidation study has been carried out by means of optical absorption as well as ESR technique. The photolyzed solution was confirmed to have the ESR spectrum with the same hyperfine structure as that reported,[1] when the photolyzed rigid solution is warmed up to room temperature.

It is interesting to note that when a concentrated sulfuric-acid solution of *p*-dimethoxybenzene was bubbled with nitrogen gas in order to remove oxygen, neither electronic absorption in the visible region nor the ESR spectrum of the cation was detected. This indicates that the oxygen molecule participates in the oxidation of the compound in concentrated sulfuric acid.

The cations of the compounds studied here are iso-electronic to one another, as well as to Würster's cations. Thus it seems that the absorption bands obtained herewith are similar to the long wavelength bands of Würster's cations. Electronic spectra of the cations of several aminophenols have been studied by Kimura *et al.*,[6] and shifts in wavelength of the absorption spectrum from the absorption spectrum of the *p*-phenylenediamine cation were interpreted in terms of ionization-potential differences of the substituents by using a first-order perturbation theory. The same situation may occur in the case of the cations of *p*-dialkoxybenzenes. Let us consider how the ionization potential of a substituent affects the transition energy of the hydroquinone cation. Expressing its MO's with linear combinations of $2p\pi$ AO's ($\varphi_i=\sum_\mu c_{i\mu}\phi_i$), energies of the MO's may be given by $\varepsilon_i=\sum_{\mu\nu}c_{i\mu}c_{i\nu}F_{\mu\nu}$, where $F_{\mu\nu}$'s are Fock-Hamiltonian elements. Assuming the same molecular orbitals for all these cations to

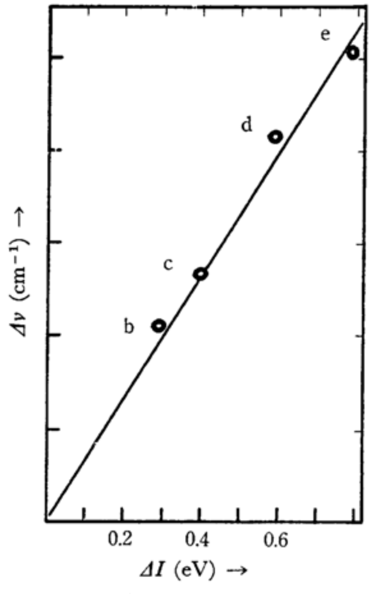

Fig. 2. The shifts of the longest absorption bands of the several cations from that of the hydroquinone cation are plotted against the ionization-potential differences of substituents.
b) [*p*-methoxyphenol]$^+$, c) [*p*-ethoxyphenol]$^+$, d) [*p*-dimethoxybenzene]$^+$ and e) [*p*-diethoxybenzene]$^+$.

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the first approximation and taking only the differences ΔI_1 and ΔI_2 in the valence-state ionization potentials of two substituents at the *para* position into account, we find that the resulting differences in transition energy may be proportional to $\Delta I_1 + \Delta I_2$. This means that the effect of two substituents at the *para* position can be expressed as the sum of the ionization potentials of the substituents. In Fig. 2, the shifts ($\Delta \nu$ in cm^{-1} units) of the longest absorption bands of the several cations from that of the hydroquinone cation are plotted against the ionization-potential differences of the substituents (ΔI in eV units). In this calculation, values for ionization potentials of the hydroxy, methoxy and ethoxy groups were taken from those used in the previous calculations of phenol, anisole and phenetole.[7] It is seen from Fig. 2 that a good linearity is obtained between the band shift and the ionization potential difference.

Experimental

Commercial materials of the compounds studied; *e. g.*, hydroquinone, *p*-methoxyphenol, *p*-dimethoxybenzene, *p*-ethoxyphenol, *p*-diethoxybenzene and 2,3,5-trimethylhydroquinone were purified by vacuum sublimation. Commercial $SbCl_5$, sulfuric acid (95%), and glacial acetic acid of G. R. grade were used without further purification. Acetonitrile was distilled after reflux and dehydration on P_2O_5.

Measurement of electronic absorption spectra was carried out with a Cary spectrophotometer Model 15. ESR spectra were measured by a JES-3BX ESR spectrometer at 100 kc/s modulation.

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