The Electronic Spectrum of *p*-Benzosemiquinone Anion in Aqueous Solution

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The electronic spectrum of *p*-benzosemiquinone anion in aqueous solution formed through the oxidation of hydroquinone with manganese dioxide was measured at room temperature. The absorption maxima were found at 430, 404, and 316 mμ with shoulders at 371 and 310 mμ. It was confirmed that these absorption maxima are due to the same species *p*-benzosemiquinone anion, on the ground that their kinetic behaviors are the same. The molar extinction coefficients of the absorption maxima and the oscillator strengths of the absorption bands were estimated.

Semiquinones are known to be intermediates in the quinone–hydroquinone redox systems. ESR studies gave unambiguous evidence for the presence of these important radicals.[1] While the electronic spectra of the substituted *p*-benzosemiquinones such as durosemiquinone or 2,5-di-*t*-butyl-*p*-benzosemiquinone have been established,[2–5] the spectrum of non-substituted *p*-benzosemiquinone has hardly been studied at all.

Two methods of producing *p*-benzosemiquinone anions have been employed so far; the chemical oxidation of hydroquinone in alkaline solutions[4,6] and the photolysis of hydroquinone in rigid media at 77 K.[7–9]

Using a rapid flow method for the air oxidation of hydroquinone in an alkaline solution, Diebler *et al.*[6] found the absorption maxima at 430 and 404 mμ. Harada and Matsunaga[4] succeeded in the observation of fairly good electronic spectra of several substituted *p*-benzosemiquinone anions, stabilized sterically by bulky substituents, in highly viscous solutions at room temperature, but could not record a good spectrum of the simplest *p*-benzosemiquinone anion though they found the absorption maxima at 432 and 408 mμ in the visible region. A drawback in this method of preparation is that *p*-benzosemiquinone anions are too unstable in an alkaline solution.

By the ultraviolet irradiation of hydroquinone in an alkaline ethanol solution at 77 K, Kimura *et al.*[9] obtained a spectrum with three bands, each with several absorption maxima and ascribed the spectrum to *p*-benzosemiquinone anion [$\cdot OC_6H_4O^-$], on the ground that it was similar to that of 2,5-di-*t*-butyl-*p*-benzosemiquinone anion mentioned above. However, interference by the presence of other species cannot be completely eliminated with this method. It seemed of prime importance therefore to prepare semiquinone anions in a stable condition. We have found that *p*-benzosemiquinone anion is easily formed when a neutral aqueous solution of hydroquinone is passed through a column of manganese dioxide, and that the anion thus formed is quite stable at room temperature even in the atmosphere. The rate of radical decay follows the first order kinetics with the rate constant 5.7×10^{-3} (min^{-1}).

By applying this technique to the preparation of the radical we could distinctly observe the electronic spectra of *p*-benzosemiquinone anion and the molar extinction coefficients were determined.

Experimental

p-Benzosemiquinone anion was prepared by passing an aqueous solution of hydroquinone through tubing (I.D. 6 mm) packed with 0.7 g of manganese dioxide (20—30 mesh). The initial concentrations of hydroquinone were 10—30 mM. The outlet of the MnO_2 column was directly connected to the optical cell. A flat type ESR cell for aqueous solutions, supplied by Japan Electron Optics Laboratory (JEOL), was also used for the measurements of electronic spectra, enabling us to measure both electronic and ESR spectra under the same conditions. The path length of the cell is 0.38 mm.

The electronic spectra were registered with a Shimadzu spectrophotometer, Model MPS-5000. The ESR measurements were carried out with a JEOL-X band spectrometer (JES-3BS-X). The concentration of *p*-benzosemiquinone anion was determined by comparison of the area under the absorption curve of the anion and that of 1,1-diphenyl-2-picrylhydrazyl (DPPH) in benzene.

Results and Discussion

The electronic spectra were measured with various feed rates of the hydroquinone solution. Besides the bands due to hydroquinone and *p*-benzoquinone, bands appeared in the near ultraviolet and visible regions, as shown in Figs. 1 and 2, respectively. Figure 1 was obtained by subtracting the absorption of hydroquinone of the initial concentration from the observed spectra. In the visible region, there is no appreciable overlapping of the bands due to hydroquinone or *p*-benzoquinone.

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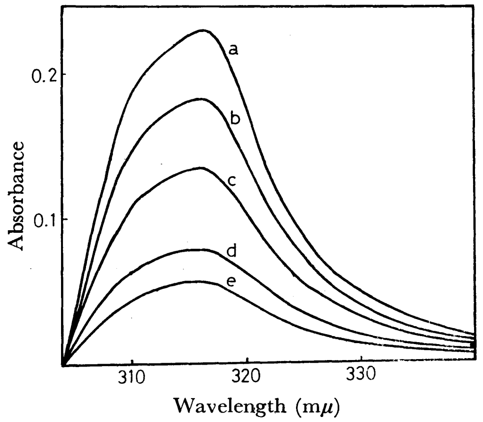


Fig. 1. Electronic spectra of *p*-benzosemiquinone anion in the ultraviolet region. The 20 mM hydroquinone solution was fed with the rates of (a) 0.15, (b) 0.38, (c) 0.81, (d) 3.9, and (e) 7.0 ml/min. (path length 0.38 mm)

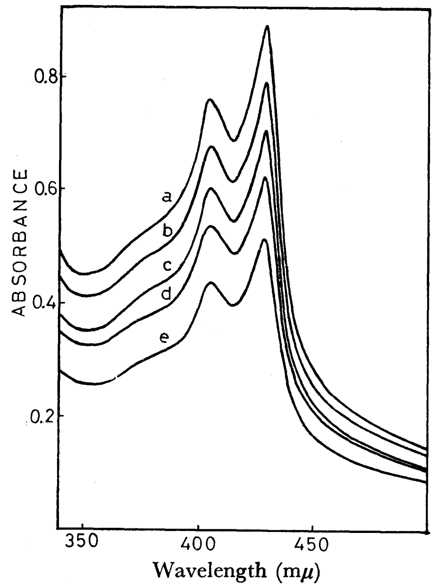


Fig. 2. Electronic spectra of *p*-benzosemiquinone anion in the visible region. The 30 mM hydroquinone solution was fed with the rates of (a): 0.68, (b): 1.0, (c): 1.3, (d): 2.2, and (e): 4.7 ml/min. (path length 1.0 cm)

The absorption maxima were observed at 430, 404, ~371, and ~310 mμ.

The kinetic behavior of the bands was studied in order to ascertain whether all the absorption maxima are due to *p*-benzosemiquinone anion. Previous ESR work showed that the concentration of the semiquinone anion was expressed as a function of the feed rate of the solution in the following way:

$$\ln\frac{[S]_\infty-[S]}{[S]_\infty} = -k\frac{V}{F} \tag{1}$$

where [S] is the concentration of semiquinone anion at the exit of the MnO_2 column of volume *V*, when the feed rate of the solution is *F*, $[S]_\infty$ is the concentration at the infinitesimal feed rate and *k* the rate constant. Thus, if the absorption at the wavelength λ is caused solely by the semiquinone anion, the following relationship should hold.

$$\ln\frac{[A]^\lambda_\infty-[A]^\lambda}{[A]^\lambda_\infty} = -k\frac{V}{F} \tag{2}$$

where $[A]^\lambda$ and $[A]^\lambda_\infty$ are the absorbance at wavelength λ when the feed rates are *F* and infinitesimal, respectively.

log([A^λ_∞—$[A]^\lambda$) is plotted against 1/*F* at the wave-

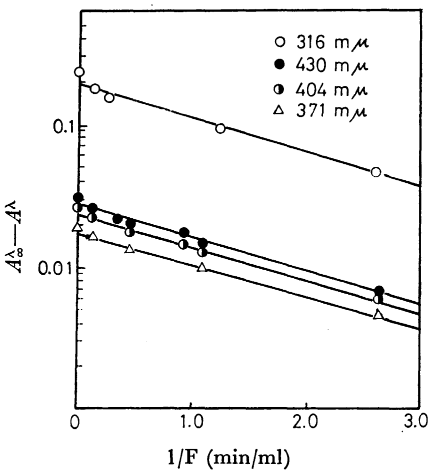
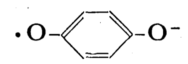
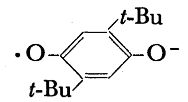


Fig. 3. Change in the absorbance with the feed rate of the 20 mM hydroquinone solution.

Table 1. Wavelengths of the absorption maxima and molar extinction coefficients of *p*-benzosemiquinone anion

Species	Method of preparation	Wavelengths (mμ) and molar extinction coefficients (×10^{-3})	Reference
	hydroquinone+MnO_2	λ 430, 404 371* 316 310* ε 5.4, 4.6 3.7 40 33	This work
	hydroquinone+alkaline solution	λ 430, 404 — — — ε 7.4 — — — —	6)
	hydroquinone+alkaline solution	λ 432, 408 — — — ε — — — — —	5)
	photolysis of hydroquinone at 77K	λ 432, 407 385 316, 308, 301, 295* ε — — — — — — —	9)
	2,5-di-*t*-butylhydroquinone+ alkaline solution	λ 436, 411 373 323.5 ε 5.3 4.0 4.2 14	5)

* designates a shoulder

lengths of the absorption maxima in Fig. 3. It is evident that the changes of absorbance with feed rates are well expressed by Eq. (2) and the slope of each line gives the same value of *k*. In the case of other initial concentrations of hydroquinone, 20 and 30 mM, the same results were obtained. Since all the absorption maxima show the same kinetic behavior, it is concluded that all absorption maxima in Figs. 1 and 2 are due to the same species, *viz.*, *p*-benzosemiquinone anion. The ESR work confirmed that *p*-benzosemiquinone anion was the only paramagnetic species in the solution, and the neutral semiquinone ($\cdot OC_6H_4$-OH) or hydroquinone cation did not exist.

The positions of absorption maxima observed in this work are compared with those observed by other workers in Table 1. The values of the two maxima at the longer wavelengths agree with those obtained by Diebler *et al.*6) The absorption maxima at the shorter wavelengths have not been reported for non-substituted *p*-benzosemiquinone anion at room temperature, but the corresponding maxima have been obtained for 2,5-di-*t*-butyl-*p*-benzosemiquinone anion.4) Comparing the maxima for 2,5-di-*t*-butyl-*p*-benzosemiquinone anion with those of the non-substituted, all the bands of the former slightly red-shift. This can be understood as the effect of the electron-donating substituents [$-C(CH_3)_3$] on the benzene ring.

The molar extinction coefficients (ε_{max}) of the absorption maxima were calculated. The absolute concentration of the *p*-benzosemiquinone anion was determined from ESR intensity. The results are given in Table 1. The magnitude of the extinction coefficients suggests that all the absorption bands are caused by π-π^* transitions. The absorption maxima of 430 and 404 mμ are considered to be caused by the same π-π^* transition and their splitting is due to the C–O stretching vibration in the exited state.4)

Table 2. Comparison between the observed and the calculated values of transition energy and the oscillator strength (f)

Observed		Calculated (11)		
Transition energy (eV)	f a)	Transition energy (eV)	f	Symmetry type
2.88	0.06	2.960	0.03	$^2B_{3g}$–$^2B_{1u}$
3.34	0.03	3.479	0.11	$^2B_{3g}$–^2A_u
3.93	0.35	4.458	0.69	$^2B_{3g}$–$^2B_{1u}$

a) The oscillator strength f is evaluated from the well-known formula, $f=4.23\times10^{-9}\int\varepsilon(\nu)d\nu$.

Harada11) carried out the molecular orbital calculation with the Pariser-Parr method on *p*-benzosemiquinone anion and estimated the transition energies and the oscillator strengths. The experimental values obtained in this study are compared with those calculated by Harada in Table 2. The agreement between the observed and the calculated values is fairly good for this type of calculation on molecules with hetero atoms.

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