SHORT COMMUNICATIONS

On the Optical Absorption Spectra of Semiquinone Ions

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Although extensive experimental studies have been made of the electron spin resonance absorption spectra of semiquinone ions, the optical absorption spectra, especially of the semiquinone ions with simple molecular structure, have scarcely been investigated. As semiquinone ions are unstable intermediates in oxidation-reduction systems, the details of the optical spectra are usually obscured by overlapping with the spectra due to the other species. For instance, *p*-benzosemiquinone formed by photoöxidation of hydroquinone or by photoreduction of quinone in rigid solvents has been examined by Lewis and Bigeleisen(1) and by Linschitz et al.(2) The appearance of a single absorption peak at about 410 mμ has been reported. Therefore, it seemed valuable to seek for the experimental condition in which the desired semiquinone ion is well stabilized and exists practically as the sole species in the reaction system.

The semiquinone ions were prepared either by reduction of the quinones dissolved in a mixture of ethylene glycol and 2 M potassium hydroxide aqueous solution with a suitable reagent or by oxidation of the hydroquinones in ethylene glycol with atmospheric oxygen. By the latter method the formation of semiquinone ion occurs after the addition of a small amount of potassium hydroxide solution. Our viscous medium was found to be not only inert to most of the semiquinone ions but to be of great advantage to protect the free radicals from the rapid undesired reactions, namely over-oxidation or reduction and some side reactions. With our solvent system we could

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1) G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 2424 (1943).

2) H. Linschitz, J. Rennert and T. M. Korn, ibid., **76**, 5839 (1954).

control the reaction to some extent and succeeded in observing the fine structure in the optical absorption spectra of several semiquinone ions. The measurements were carried out using a Cary model 14 spectrophotometer at room temperature.

The unsubstituted *p*-benzosemiquinone ion was found to be too unstable to be examined even in our solvent system. However, we could successfully prepare a yellow solution of stable 2, 5-di-*tert*-butyl-*p*-benzosemiquinone ion. This radical seems to be sterically stabilized by the bulky substitutents. It has been shown by the hyperfine structure in the electron spin resonance that unpaired electrons can migrate to the hydrogen atoms in tertialy butyl groups with a probability of 10^{-4} for a 1s orbit[3], but we may hope that the main feature of π-electronic structure of *p*-benzosemiquinone ion is not modified very much by this substituent. The spectral reponse curves obtained on oxidation of di-*tert*-butyl-*p*-hydroquinone dissolved in ethylene glycol are given in Fig. 1. Curve 1 shows the absorption spectrum of the original hydroquinone. When a small amount of potassium hydroxide solution was added to the sample solution, the hydroquinone was oxidized gently with atmospheric oxygen. Weak absorption peaks appeared at 436, 411 and 374 mμ, and a strong peak at 323 mμ, while the intensity of the 293 mμ peak was decreased considerably as shown by curve 2. The molar extinction coefficient for the peak of 323 mμ was estimated to be in the order of 10^4. By further oxidation the spectrum of the quinone like curve 3 could be obtained. The original reduced form could be reproduced by the addition of a reducing reagent through the intermediate stage. Therefore, it is evident that the spectrum given by curve 2 is mostly ascribed to the semiquinone ion.

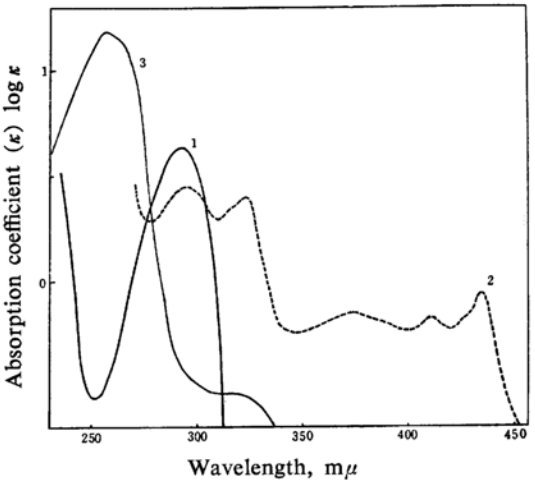

Fig. 1. Absorption spectra of 2,5-di-*tert*-butyl-*p*-benzohydroquinone: curve 1; semiquinone ion with some amount of hydroquinone, curve 2; and quinone; curve 3. The total concentration is 0.99×10^{-3} mol. per l.

The absorption spectra of anthra- and phenanthra-semiquinone ions were also examined with success. The stabilities of these two semiquinone ions must be largely due to resonance. The reduction of the quinones was performed in the above-mentioned solvent with sodium dithionite or zinc dust. We should avoid the excessive use of dithionite because this reagent gives an absorption peak in the ultraviolet region studied for the semiquinone ions. In the anthrasemiquinone ion three peaks were observed at a wavelength of 480 mμ, at 400 mμ and at 297 mμ, and in the phenanthrasemiquinone ion two weak peaks at 507 and 475 mμ, two with medium intensity at 404 and 326 mμ and a strong peak at 270 mμ.

In order to analyse these optical absorption spectra we are attempting to study the π-electronic structure of these semiquinone ions by the aid of the semiempirical MO method developed by Pariser and Parr. The details of experiments and theoretical discussion will be submitted elsewhere.

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[3] G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, **67**, 546 (1957).