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OPTICAL ABSORPTION SPECTRUM OF HALF-REDUCED UBIQUINONE

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SUMMARY

Absorption spectra in the 230–500 nm range are recorded for anionic and neutral ubisemiquinone free radicals produced by pulse radiolysis.

Short-lived changes in absorbance occur when ubiquinone is reduced by solvated electrons and free radicals. The changes can readily be observed by pulse radiolysis[1], and can be used to construct the optical absorption spectrum of the semiquinone formed. We have now extended previous observations[1] into the wavelength region where ubiquinone itself absorbs, and are able to report the full optical absorption spectrum of ubisemiquinone in both its anionic and neutral forms in the 230–500 nm region.

The equipment and methods used were the same as previously described[2,3], except that in order to obtain an adequate amount of transmitted light in the region of the ubiquinone absorption it was necessary to employ an optical cell with a light path of only 4 mm. Solutions of ubiquinone ($1 \cdot 10^{-4}$ M) in methanol which had been made $1 \cdot 10^{-2}$ M in NaOH were used to obtain the spectrum of the anionic semiquinone, and ubiquinone solutions ($1 \cdot 10^{-4}$ M) in methanol which had been made $1 \cdot 10^{-2}$ M in H_2SO_4 were used for the neutral semiquinone. The radiation dose was about 1500 rads, and for each wavelength the difference between the absorption of the original solution and that of the solution containing semiquinone was recorded at 50 μsec after the end of the pulse. The absorption spectra of the semiquinones were obtained by subtracting from the observed differences the loss in ubiquinone absorption resulting from semiquinone formation. These losses were calculated assuming the extinction coefficient of ubiquinone[4] at 274 nm to be 15150 $M^{-1} \cdot cm^{-1}$, the extinction coefficient of the anionic semiquinone[1] at 445 nm to be 6400 $M^{-1} \cdot cm^{-1}$ and that of the neutral semiquinone[1] at 420 nm to be 3000 $M^{-1} \cdot cm^{-1}$. Use of the alternative extinction coefficient[1] for the anionic form of 8000 $M^{-1} \cdot cm^{-1}$ led to apparent negative absorptions around 270 nm so that the low value must be the more correct.

The absorption spectra obtained are shown in Fig. 1. The greatest errors are in the 250–290 nm region where ubiquinone absorbs most strongly, and extinctions here are considered to be accurate to about $\pm$ 25 %. Outside this region the error is probably $\pm$ 10 %.

The spectra of the neutral ubisemiquinone and anion radicals, and the wave-

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length shift of the various maxima caused by protonation, are very reminiscent of those found with other benzosemiquinones[5]. It should be noted that the neutral ubisemiquinone absorbs quite strongly ($\varepsilon = 7400\ M^{-1}\cdot cm^{-1}$) in the region of the intense parent quinone absorption around 274 nm ($\varepsilon = 15150\ M^{-1}\cdot cm^{-1}$), whereas the radical anion has much weaker absorption in this region ($\varepsilon = 2500\ M^{-1}\cdot cm^{-1}$).

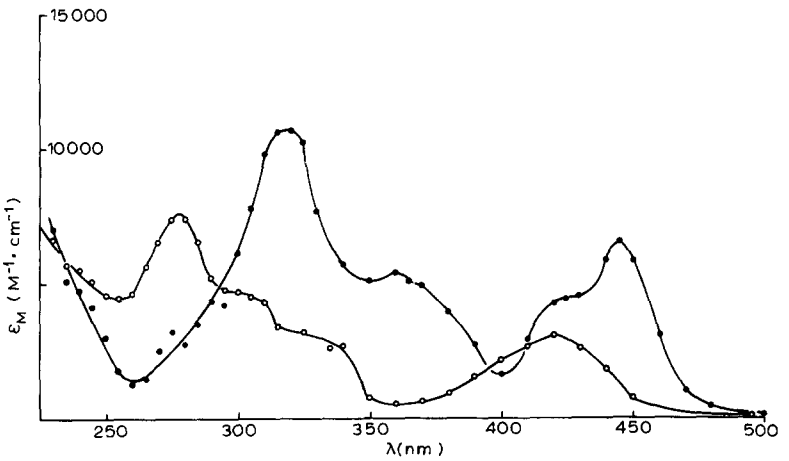

Fig. 1. Absorption spectrum of ubisemiquinone. ●—●, anionic form; ○—○, neutral form.

It seems likely that the half-reduced form of ubiquinone and other quinones, such as plastoquinone, may be important in numerous biological oxidation–reduction processes. In particular, it is noted that CHANCE AND HAGIHARA[6] have observed a "modified form of ubiquinone" absorbing at 315 nm in digitonin-treated preparations of rat liver and in intact pigeon heart mitochondria. This may well be the ubisemiquinone anion radical since the most intense semiquinone anion absorption in the wavelength region studied here occurs at 320 nm.

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