

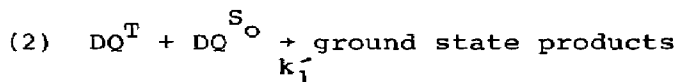
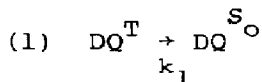
THE TRIPLET STATE OF DUROQUINONE STUDIED BY PULSE RADIOLYSIS

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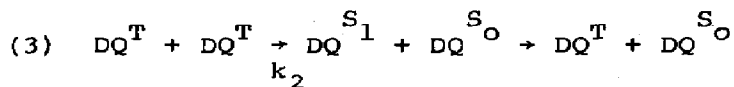
Molecules which are strong electron-acceptors or -donors in their lowest electronic excited states have been the subject of a number of studies because of their potential in photochemical storage of solar energy. Among these is duroquinone which is a strongly oxidizing species in its lowest triplet state (1). Here we report a reinvestigation of the electronic absorption spectrum of duroquinone in its lowest triplet state and determination of the rate constants involved in the decay of the triplet in liquid benzene solution.

The triplet state is formed in high yield upon pulse radiolysis of a Ar-saturated solution of duroquinone in benzene. A Febetron 705B electron accelerator was used as irradiation source and the absorption spectrum was recorded by using a pulsed Xe-lamp as light source and a streak camera coupled to a TV-camera as detector. This allowed recording of the spectrum by only one pulse from the electron accelerator. The measurements of triplet decay were then performed at the maximum of absorption after replacing the optical multichannel system by a photomultiplier coupled to a transient recorder. All data were digitized and handled by computer. Wavelengths were calibrated with a mercury spectral lamp. Concentrations were calculated using $\epsilon = 6.95 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (2).

The absorption spectrum of the triplet state of duroquinone is shown in the figure. The maximum determined by us at 495-505 nm is redshifted approximately 10 nm compared with previously published spectra (3-4). The transient absorption appeared immediately after the exciting 30 ns electron pulse. At low triplet concentration the decay measured at 500 nm is essentially first order, while at higher concentrations it becomes mixed first and second order. The decay curves were analyzed on the basis of the following scheme



*Fellows of the Danish Natural Science Research Council.



That is

$$-\frac{d \ln(\text{DQ}^{\text{T}})}{dt} = k_1 + k_1' (\text{DQ}^{\text{S}_0}) + k_2 (\text{DQ}^{\text{T}})$$

From the linear plots of $\frac{d \ln(\text{DQ}^{\text{T}})}{dt}$ versus $(\text{DQ}^{\text{T}})_{t=0}$ and

$[k_1 + k_1' (\text{DQ}^{\text{S}_0})]$ versus $(\text{DQ})_0$ we obtained the following values of the rate constants:

$$k_1 = (3.5 \pm 0.7) \cdot 10^4 \text{ s}^{-1}$$

$$k_1' = (1.2 \pm 0.1) \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2 = (5.7 \pm 1.6) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

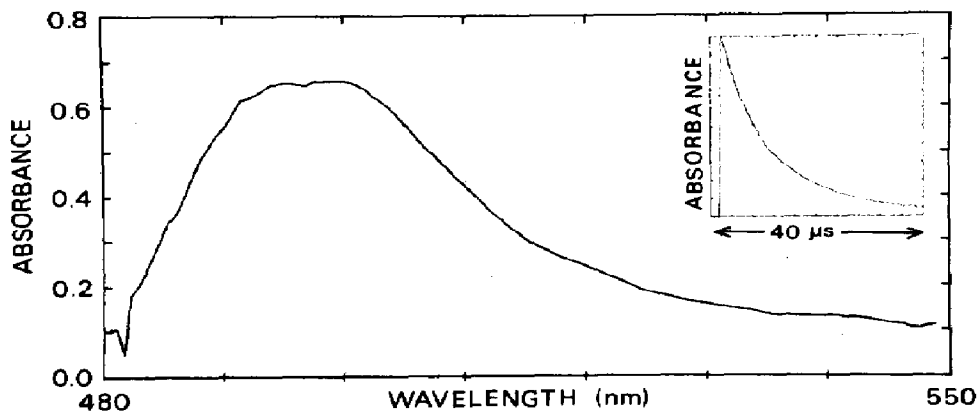


Figure: Transient spectrum obtained 2.2 μs after electron pulse. $3 \cdot 10^{-2}$ M duroquinone in benzene. Dose \approx 25 krad. Path length = 5 cm.
 Insert: Decay curve from 10^{-2} M duroquinone in benzene. Dose \approx 15 krad. Path length = 5 cm. Maximum absorbance = 0.53

Amouyal and Bensasson (5) reported a value of $4.2 \cdot 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ for k_2 in cyclohexane but they found that selfquenching is unimportant in this solvent. This observation can probably be explained by the low duroquinone concentrations used by these workers. On the other hand our value of the rate constant for self-quenching k_1 , compares well with the approximate value $1 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$ reported by Land (3).

One of our initial goals with this work was recording the resonance Raman spectrum of the duroquinone triplet. This has yet been unsuccessful, but further work is in progress.

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