The Triplet State of Chloranil

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Summary The 500 nm transient observed at very short times after laser flash photolysis (347 nm) of chloranil in outgassed ethanol is assigned to the triplet state of chloranil.

NEITHER the emission spectra nor the absorption spectra of the triplet states of benzoquinone and its derivatives have yet been clearly established. Bridge and Porter[1] observed a transient with maximum absorption at 490 nm after flash photolysis of duroquinone in viscous paraffin which they assigned to absorption by the lowest triplet state of duroquinone. Subsequent[2,3] workers have given good evidence that a tautomer of duroquinone, possibly an orthoquinone methide, is formed on photolysis and accounts for the absorption at 490 nm. However, Land[4] has recently provided evidence that, on pulse radiolysis of duroquinone in benzene, the 490 nm transient is indeed the triplet.

We report some observations on chloranil using both laser and conventional flash photolysis which throw light on this problem. At very short times after laser flash photolysis at a wavelength of 347 nm of a solution of chloranil in outgassed ethanol, a spectrum is observed having maxima at 500 and at 440 nm [Figure (a)]. The 500 nm band decays rapidly and only bands at 450 and 420 nm remain after a few msec. [Figure (b)]. The band at 420 nm was beyond the limits of the laser apparatus. Kinetic studies by photoelectric methods showed that the 420 nm transient grows in as the 490 nm transient decays, both processes being first order with rate constants as follows:

Rate constant for 500 nm decay $= 8{\cdot}4 \pm 0{\cdot}1 \times 10^5$ sec.$^{-1}$.

Rate constant for 420 nm growth $= 9{\cdot}5 \pm 2{\cdot}5 \times 10^5$ sec.$^{-1}$.

The 420 nm band decayed over a period of milliseconds with second-order kinetics and a rate constant of $4{\cdot}5 \times 10^2$ ϵ M^{-1} sec.$^{-1}$, where ϵ is the extinction coefficient at 420 nm. This band can be confidently assigned to the semiquinone radical on the same arguments as have been given for the similar transient from duroquinone.[1] In order to establish that the growth of absorption at 420 nm was not due to a change of protonation of the radical, acid solutions of ethanol (pH 2·3) were investigated and found to show the same increase of 420 nm absorption with time.

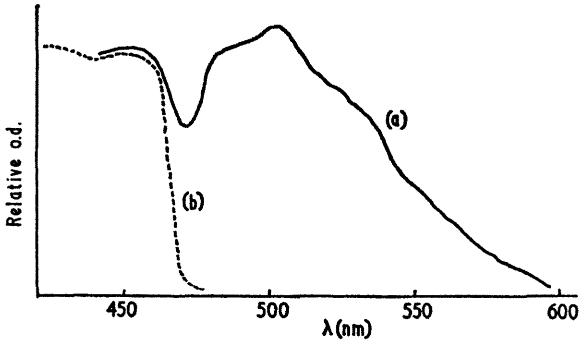

FIGURE. *Absorption spectra of chloranil in ethanol.* (a) 6 *nsec. delay spectra*; (b) 35 *μsec. delay spectra.*

On addition of air to the solution, the rate constants of decay of the 500 nm species was increased to $1{\cdot}83 \times 10^6$ sec.$^{-1}$ and the build-up in absorption at 420 nm was removed, although the same initial absorption was observed, which did not decay with the 490 nm band.

On addition of anthracene to chloranil in ethanol, the rate of decay of the 500 nm absorption was increased and the second order quenching constant was 10^{10} M^{-1} sec.$^{-1}$.

The transient absorption at 500 nm was also observed in cyclohexane solutions of chloranil. The decay at 500 nm was again predominantly first order with a rate constant of $5{\cdot}0 \pm 0{\cdot}8 \times 10^5$ sec.$^{-1}$.

These observations are consistent with the assignment of the 500 nm transient to the triplet state of chloranil, which is quenched both by anthracene and oxygen and which reacts with solvent to yield the semiquinone radical. Chloranil has the structure of duroquinone in which the four methyl groups have been replaced by chlorine so that the alternative assignment of the 500 nm band to a tautomer is clearly excluded.

Similar work on duroquinone and other derivatives of benzoquinone, which will be fully reported elsewhere, indicates that here the situation is more complex, that the triplet absorption is again near 490 nm but in some solvents other transients appear in the same region.

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[1] N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 276.

[2] F. Wilkinson, G. M. Seddon, and K. Tickle, *Ber. Bunsenges. Phys. Chem.*, 1968, **72**, 315.

[3] H. Hermann and G. O. Schenck, *Photochem. and Photobiol.*, 1968, **8**, 255.

[4] E. J. Land, personal communication.