Participation of an Upper Excited n–π* Triplet State in the Photoreduction of 1-Dimethylaminoanthraquinone

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Energy-transfer experiments indicate that 1-dimethylaminoanthraquinone is photoreduced in alcoholic solution *via* an upper excited n–π* triplet state.

ANTHRAQUINONE derivatives have proved to be useful models for investigating the mechanism of phototendering of fabrics initiated by the anthraquinone vat dyes.[1] Previously we distinguished between the photoreduction in alcoholic solutions of 'strong' sensitisers, as for example, the anthraquinone sulphonates, and 'weak' sensitisers, such as the aminoanthraquinones.[2] For the former the photoreduction proceeds by the well known abstraction process[3] (1). It is generally assumed that

$$A^{*} + RCH_2OH \longrightarrow AH\cdot + R\dot{C}HOH \quad (1)$$

the excited state involved is the lowest n–π* triplet.[1] The lowest triplet level for the 'weak' sensitisers examined, 1- and 2-piperidinoanthraquinones, however, is intramolecular charge transfer (c.t.) in type and does not significantly initiate photoreduction by reaction (1). On protonation the charge-transfer band disappears and is replaced by a weak shoulder having characteristics of an n–π* band. Under these conditions photoreduction of the sensitiser in air-free alcoholic media occurs efficiently.[2]

Involvement of upper excited states in the photochemistry of anthraquinones is, therefore, important to our understanding of the mechanisms of fabric phototendering by anthraquinone dyes.[1] Indeed, there is evidence that flavanthrone, a non-tendering dye, is photoactive only when irradiated in the second absorption band.[4]

The 'wavelength effects' which initially indicated photoreaction of the piperidinoanthraquinones *via* an upper excited state[2,5] have been similarly observed by Dörr[6,7] with 1,4-bismethylaminoanthraquinone. Eremenko and Dain,[8] on the other hand, concluded that the 1- and 2-aminoanthraquinones are photoreduced in alcoholic solution *via* the lowest triplet state. In the interpretation of their results they assumed that 'in accordance with Karyakin's data,[9] the position of the lowest triplet in all the anthraquinone derivatives does not greatly differ from its position in anthraquinone.' However, we now have overwhelming evidence that for the aminoanthraquinones generally the lowest triplet is not n–π* but charge-transfer in nature.[5,10,11] Pulse-radiolysis experiments indicate that the energy of this charge-transfer triplet is significantly lower than that of the n–π* triplet of unsubstituted anthraquinone.[11]

In an attempt to establish unequivocally the identity of the photoactive state involved in photoreduction, we here use an alternative experimental approach based on energy transfer, first utilised for these compounds by

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[1] For recent reviews see: (*a*) G. O. Phillips and J. C. Arthur, *Textile Res. J.*, 1964, **34**, 497, 572; (*b*) J. F. McKellar, *Radiation Res. Rev.*, 1971, **3**, 141; (*c*) G. S. Egerton and A. G. Morgan, *J. Soc. Dyers and Colourists*, 1971, **87**, 268.

[2] A. K. Davies, J. F. McKellar, and G. O. Phillips, *Proc. Roy. Soc.*, 1971, *A*, **323**, 69.

[3] G. O. Phillips, N. W. Worthington, J. F. McKellar, and R. R. Sharp, *J. Chem. Soc.* (*A*), 1969, 767.

[4] M. Shorer and F. Dörr, *Ber. Bunsengesellschaft Phys. Chem.*, 1964, **68**, 478.

[5] A. K. Davies, Ph.D. Thesis, Salford, 1970, p. 85.

[6] F. Dörr, cited in ref. 7.

[7] W. Luck and H. Sand, *Angew. Chem. Internat. Edn.*, 1964, **3**, 570.

[8] S. M. Eremenko and B. Ya Dain, *Theoretical and Experimental Chem.*, 1966, **2**, 772.

[9] A. V. Karyakin, *Zhur. fiz. Khim.*, 1949, **23**, 1345.

[10] R. Ford, Ph.D. Thesis, Salford, 1972.

[11] B. E. Hulme, Ph.D. Thesis, Salford, 1971;

Wilkinson[12] and applied also by Eremenko and Dain.[8] We have used 1-dimethylaminoanthraquinone as donor, since the rate of photoreduction of this derivative in air-free alcoholic medium can be measured with a high degree of precision, and the product of the reaction readily characterised.

We find clear evidence for participation of an upper excited triplet state in the photochemistry of the amino-anthraquinones. Apart from the relevance of this observation to phototendering it is also of more general interest, since it is contrary to the usual rule that the excited state of a given multiplicity responsible for photoreaction is that of lowest energy.[13]

EXPERIMENTAL

Illumination for the energy-transfer experiments was provided by a medium-pressure mercury lamp (Hanovia UVS 220) and filtered by transmission first through a Pyrex filter and subsequently through 43 mm of an almost saturated solution of the appropriate triplet energy acceptor (anthracene, naphthalene, or biphenyl) in benzene. Air-free solutions of 1-dimethylaminoanthraquinone were thus irradiated in a circular quartz cell (20 mm diam., 10 mm long), and the resultant change in the absorbance of the solution measured with a Pye Unicam SP 1800 spectrophotometer. The flash-photolysis equipment is similar to the unit previously described.[14] Photoflash energies of 450 J were used. The transient spectra were recorded on Ilford HP 3 photographic plates and measured with a Joyce–Loebl double-beam microdensitometer.

1-Dimethylaminoanthraquinone was purified by chromatography on a column of alkaline alumina from carbon tetrachloride solution, the main red band being eluted with acetone. Four recrystallisations of the solid from alcohol gave red crystals, m.p. 139·5 °C. The purified material, in rigid glass at 77 K, showed no phosphoresence due to 1-chloroanthraquinone. The absence of this compound was further confirmed by mass spectrometry.

Propan-2-ol was purified by refluxing for several hours with 2,4-dinitrophenylhydrazine and then fractionating. Anthracene, naphthalene, and biphenyl were purified by repeated recrystallisation from alcohol. Deoxygenation of solutions before irradiation was achieved by bubbling with B.O.C. White-spot nitrogen for 40 min.

RESULTS AND DISCUSSION

Irradiation of 1-dimethylaminoanthraquinone in air-free propan-2-ol with light of wavelength >300 nm produces the corresponding dihydroxyanthracene. The spectra showed good isosbestic points at 356 and 463 nm (Figure 1). The inset of Figure 1 shows a typical plot of absorbance against irradiation-time at 400 nm. From the slope of these plots, the initial rate of hydroquinone formation was calculated.

Flash photolysis of 1-dimethylaminoanthraquinone in air-free alcoholic solution produces a transient species with $\lambda_{max.}$ 380 nm; the transient species decays to produce the hydroquinone. By analogy with the corresponding observations on the piperidinoanthraquinones,[2] we can assign this transient species to the semiquinone radical AH•. Photoreduction thus takes place by way of the intermolecular hydrogen abstraction process (1) followed by (2), where AH_2 represents the 9,10-dihydroxyanthracene.

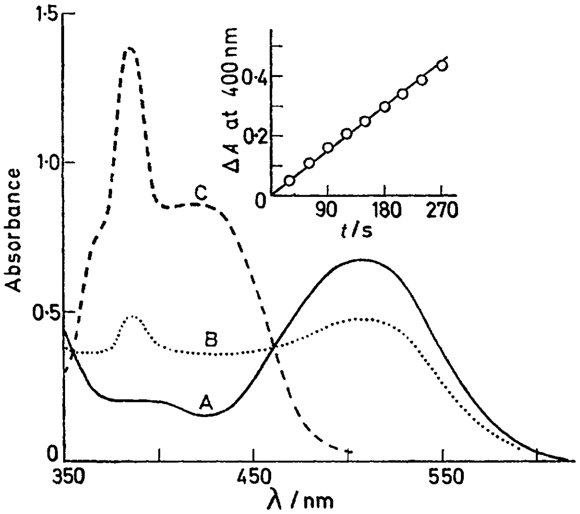

FIGURE 1 Spectral changes accompanying the photoreduction of 1-dimethylaminoanthraquinone in air-free propan-2-ol solution, with light of wavelength >300 nm; A, original absorption spectrum; B, spectrum during irradiation; C, spectrum of the 9,10-dihydroxyanthracene. Inset: Typical plot of absorbance against irradiation-time for the formation of the 1-dimethylamino-9,10-dihydroxyanthracene

$$2AH\cdot \longrightarrow AH_2 + A \qquad (2)$$

In the energy-transfer experiments photoreduction was strongly inhibited by the presence of anthracene.

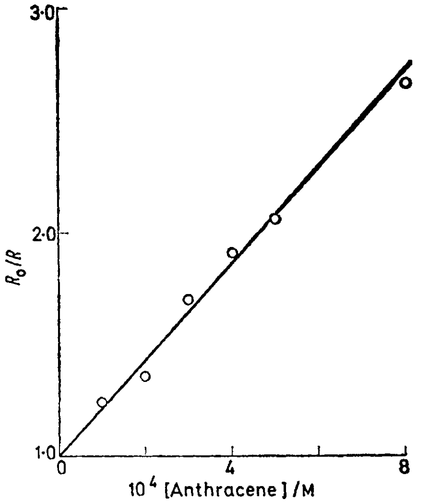

FIGURE 2 Stern–Volmer plot for the quenching of the photoreduction of 1-dimethylaminoanthraquinone by anthracene, R_0 = rate in absence of anthracene; R = rate in presence of anthracene

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[12] F. Wilkinson, *J. Phys. Chem.*, 1962, **66**, 2569.

[13] N. J. Turro, 'Molecular Photochemistry,' W. A. Benjamin, Inc., New York, 1967, p. 138.

[14] J. H. Allen and J. F. McKellar, *Lab. Practice*, 1967, **16**, 991.

A Stern–Volmer plot for quenching by anthracene is shown in Figure 2. Naphthalene also strongly inhibited the reaction, but biphenyl was without effect. The inhibition of the photoreaction was not due to quenching of the singlet state, since the fluorescence of 1-dimethylaminoanthraquinone is unaffected by high concentrations of the hydrocarbon additives. We conclude, therefore, that the excited state responsible for reaction (1) is a triplet whose potential energy is greater than those of the lowest triplets of anthracene and naphthalene, but less than that of biphenyl.

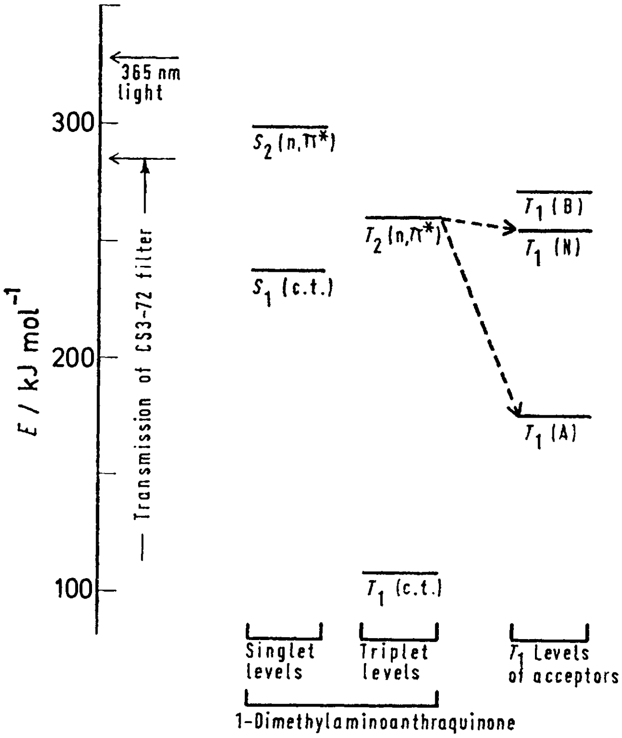

FIGURE 3 Energy levels of the excited states of 1-dimethylaminoanthraquinone, and the lowest triplet levels of anthracene (A), naphthalene (N), and biphenyl (B). The dashed lines show the energy-transfer processes leading to inhibition of photoreduction

The observed quenching effects can thus be considered in terms of the potential-energy levels shown in Figure 3. The levels for 1-dimethylaminoanthraquinone were estimated as follows. The first excited singlet is charge-transfer in nature and full details of the spectral characteristics of this compound will be given elsewhere. Meanwhile, to support our charge-transfer assignment we illustrate the effect of solvent polarity on the energy of the longest wavelength transition in the Table. We cannot detect phosphorescence from the compound in rigid glass at 77 K, so that we are unable to define the level of the charge-transfer triplet precisely. However, 1-piperidinoanthraquinone has a lowest triplet level[11] between 123 and 94·5 kJ mol^{-1}, and since 1-dimethylaminoanthraquinone is similar in structure and spectral and photochemical properties,[10] we consider a reasonable estimate of the lowest triplet energy for this derivative to be 109 ± 15 kJ mol^{-1}.

Effect of solvent dielectric constant (D) on the wavelength maximum, and corresponding transition energy $E_{\lambda_{\max}}$ of the longest-wavelength absorption band of 1-dimethylaminoanthraquinone

Solvent	D	$\lambda_{\max.}$/nm	$E_{\lambda_{\max.}}$/kJ mol^{-1}
Cyclohexane	2·023	483	248
Diethyl ether	4·335	492	243
Ethyl acetate	6·02	500	239
Ethanol	24·30	506	236

It is significant that the resultant T_1—T_2 separation is large and should inhibit the rate of internal conversion within the triplet manifold. An interesting comparison is the large S_1—S_2 separation in azulene, which is probably responsible for its fluorescence from the S_2 state.

When 1-dimethylaminoanthraquinone is protonated, the long-wavelength charge-transfer band disappears, revealing an n–π^* band with $\lambda_{\max.}$ near 400 nm. A singlet–triplet splitting being assumed for this band comparable with that in anthraquinone,[12] the n–π^* triplet has an energy *ca.* 260 kJ mol^{-1}. Although there are uncertainties arising from our assumptions, it is highly probable that the level of the n–π^* triplet is higher than the lowest triplet states of anthracene and naphthalene, but lower than that of biphenyl. Indeed, only by assuming the energy transfer processes shown by the dashed lines in Figure 3 can the observed quenching effects be satisfactorily accounted for. Additional confirmation that the active triplet in the photoreduction of 1-dimethylaminoanthraquinone is the upper n–π^* triplet was obtained as follows. An air-free propan-2-ol solution of 1-dimethylaminoanthraquinone was irradiated with use of a sharp cut-off filter (Corning CS 3–72), which transmits light of wavelength >420 nm. The cut-off of this filter, shown in Figure 3, is directly below the level of the n–π^* singlet. No photoreduction was observed, even after prolonged periods of irradiation.

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