Primary Photochemical Processes of two Phototendering Vat Dyes

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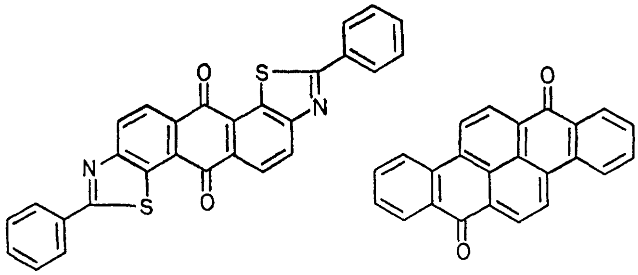
Summary A comparison of the spectroscopic and photochemical behaviour of two phototendering vat dyes shows that they undergo different primary photochemical processes, an observation which indicates that the mechanism of phototendering, even by this one class of dye, involves more than one type of photo-excited dye-substrate interaction.

MUCH effort has been directed to establishing the primary processes responsible for the important technological problem of phototendering of cellulosic textiles by the vat dyes.[1] In the 'model system' approach to the problem a comparison is made between tendering activity and the ability of the dye, in a photo-excited state, to abstract a hydrogen atom from an alcohol[2] or a hydrocarbon.[3] Such a correlation does exist for many dyes, but there are several important 'anomalies'.[4] An interesting example is provided by the two well-known tendering vat dyes (I) and (II).



(I)
(C.I. 67300)

(II)
(C.I. 59100)

Although both tender cellulose with comparable activity, (I) sensitises the photo-oxidation of tetralin, *via* a primary process of hydrogen atom abstraction, 30 times faster than (II).[3]

We now report the following significant differences in the spectroscopic properties and photochemical behaviour of (I) and (II): (1) Although the first excited singlet state of both dyes is π,π^*, (II) shows considerable intramolecular charge-transfer (c.t.) character. (2) While (I) exhibits strong phosphorescence with a first triplet energy of 218 kJ mol^{-1}, no phosphorescence was observed for (II). Energy-transfer experiments with (II) indicate a first triplet energy of <176 kJ mol^{-1}. (3) Whereas (I) is readily photoreduced to the hydroquinone (AH_2) in neutral air-free alcoholic solution, and to the radical anion ($A\cdot^-$) in alkaline air-free alcoholic solution, (II) can only be readily photoreduced to $A\cdot^-$ under the same conditions (Table). (4) Triethylamine quenches the fluorescence of (II) much more strongly than that of (I) (Table).

TABLE. *Quantum yields of anthrahydroquinone* (AH_2) *and radical anion* ($A\cdot^-$) *formation under neutral and alkaline air-free conditions respectively. Stern–Volmer quenching constants* (k_q) *for triethylamine in benzene solution*

Dye	ϕAH_2	$\phi A\cdot^-$	$\phi A\cdot^-/\phi AH_2$	k_q
(I)	*ca.* 1·0	1·5	*ca.* 1·5	5
(II)	0·013	*ca.* 1·0	*ca.* 80	70

The quantum yield data for dye (I) suggest that the major primary photochemical process is hydrogen atom abstraction from the alcohol (RCH_2OH):

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

followed by:

$$2\,AH\cdot \rightarrow AH_2 + A \qquad (2)$$

under neutral conditions, and by:

$$AH\cdot + OH^- \rightarrow A\cdot^- + H_2O \qquad (3)$$

under alkaline conditions. These reactions are well established from early 'model system' work.[2,5] With dye

(II), however, the situation is quite different. The low value of ϕAH_2 indicates that reaction (1) must be very inefficient, whereas the high ratio $\phi A^{\cdot -}/\phi AH_2$ indicates that the major primary process is one of electron abstraction.[6]

$$A^* + \left\{\begin{matrix} RCH_2O^- \\ OH^- \end{matrix}\right. \rightarrow A^{\cdot -} + \left.\begin{matrix} RCH_2O\cdot \\ OH\cdot \end{matrix}\right\} \tag{4}$$

The primary process is consistent with the considerable c.t. character of the excited state,[6] and the efficient fluorescence quenching observed with triethylamine. The identity of A* in reaction (4) will be considered later in a publication dealing with quenching of the excited states of anthraquinone derivatives. It is clear from these observations that on a cellulose substrate, particularly when moisture is also present, dyes (I) and (II) are capable of undergoing quite different primary photochemical processes. Not only does this account for the anomalous behaviour of (II) from the aspect of the hydrogen-atom abstraction theory of phototendering, but it emphasises our view that the mechanism of phototendering should not be considered in terms of only one primary process of photo-excited dye-substrate interaction.[1b,6]

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