REDUCTIVE PHOTO-BLEACHING OF EOSINE

Primary Processes indicated by the Flash Technique

It is well known that a de-aerated solution of eosine in ethanol when irradiated undergoes reductive bleaching. Imamura and Koizumi[1] concluded, from the kinetic studies of this reaction, that a semiquinone radical with a life-time not less than 10^{-3} sec. is formed from the triplet state of dye and ethanol.

The primary processes of this photo-bleaching have now been studied by the flash technique, and in addition to semiquinone, another intermediate with a life-time of the order of 10^{-3} sec. was found spectroscopically. A photolysis flash lamp and a spectro-flash of 'half-width' approximately 60 and less than 20 μsec. respectively were used. The results obtained may be summarized as follows.

At 0·6 msec. after the start of the photolysis flash, the main absorption of eosine decreased to 60 per cent of that of the initial solution and a transient increase of absorbance was observed in the region from 350 to 480 mμ. Subtracting from this the absorbance due to the remaining eosine, the quantity of which was evaluated from the depression of the absorbance in the region of wave-lengths longer than 480 mμ, the spectra of the transient species were obtained (see Fig. 1).

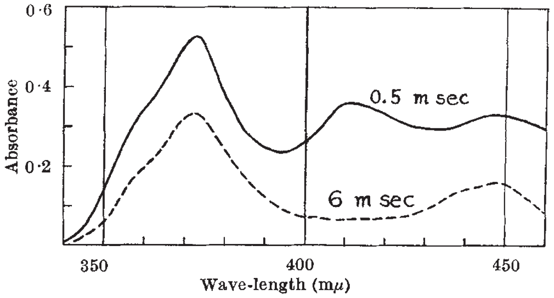

Fig. 1. Absorption spectra of transient species in eosine

Three peaks occur, at 373, 410 and about 450 mμ. After 5 msec., the peaks at 373 and 450 mμ (*A* band) still maintained considerable intensity, whereas 410 mμ (*B* band) declined appreciably. After several minutes, the former band also completely vanished and the eosine spectrum was recovered, corresponding to 88 per cent of that of the original solution. The 12 per cent loss is attributable, without doubt, to permanent bleaching.

In the presence of air, neither transient spectral change nor permanent bleaching was observed. The de-aerated aqueous solution of eosine also showed no such transient spectral change.

These results imply that two transient species are formed in the initial stage of the reductive photobleaching of eosine, and that at a certain early stage after flashing, most of the dye molecules are converted into such intermediate species with life-times not less than about 10^{-3} sec.

There is little doubt that the *A* band is due to the semiquinone radical of eosine. As regards the *B* band, it is certain that this is not due to a triplet state, because no similar band is observed in an aqueous solution in which the triplet state is not deactivated so efficiently as in ethanol solution. Hence the *B* band must be attributed to some unknown molecular species which perhaps precedes semiquinone; it would be reasonable to attribute this to a certain kind of molecular complex between excited dye and ethanol.

The primary processes of the photo-bleaching may be pictured as follows:

$$\begin{array}{llllllll}
D & + & h\nu & \rightarrow & D^{*} & & & (1)\\
D^{*} & & & \rightarrow & D & + & h\nu' & (2)\\
D^{*} & & & \rightarrow & D^{t} & & & (3)\\
D^{t} & + & R\mathrm{H} & \rightarrow & X & & & (4)\\
X & & & \rightarrow & D & + & R\mathrm{H} & (5)\\
X & & & \rightarrow & D\mathrm{H}^{\cdot} & + & R^{\cdot} & (6)
\end{array}$$

where *D* and *R*H represent dye and ethanol, and *X* is the molecular complex suggested above; the other symbols have the usual meaning. This scheme accounts for all the experimental results, including those formerly obtained from kinetic studies. Only two of them will be taken up here. (*a*) The observation that only 12 per cent is permanently bleached in spite of the fact that almost all the dye molecules are converted to intermediates with life-times not less than about 10^{-3} sec. is due to process (5), which plausibly proceeds faster than (6). (*b*) The fact already established that the reductive photo-bleaching is completely inhibited by the presence of a very small quantity of oxygen is interpreted as due to *X* being deactivated by oxygen by the process $X + O_2 \rightarrow D + R\mathrm{H} + O_2$. Imamura and Koizumi's scheme that semiquinone is destroyed by oxygen is not in agreement with the fact that the *B* band is not observed in the aerated ethanol solution.

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Effect of Added Substances on the Rate of Reductive Photo-bleaching

THE alcoholic solution of eosine, when de-aerated and irradiated by visible light, undergoes photobleaching which proceeds via the formation of a semiquinone of the dye[1]. The effect of the added substances on the rate of bleaching has now been examined, and it is found that some substances accelerate the rate appreciably and in a very specific manner.

A sample degassed carefully by repeated vacuum distillation was illuminated by light from a tungsten projection lamp, transmitted through a filter cutting off wave-lengths less than 450 mμ.

Since the absorption spectra of the irradiated solution, in all cases, gradually declined, keeping the same shape as that of the original solution, the rate of bleaching was traced simply by measuring the absorption spectra at suitable time intervals with a Hitachi spectrophotometer *EP U-2A*.

The rate of bleaching can always be expressed by the formula:

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{k}{d} I_0 \left\{1 - \exp(-\alpha c d)\right\} \times 10^3 \quad (1)$$

where *c* is the concentration of dye in mole/litre, I_0 is the intensity of illuminating light (mole cm.$^{-2}$ sec.$^{-1}$), α is the effective molar absorption coefficient and *d* the thickness of the solution in centimetres.

Integration of (1) gives:

$$\ln(\exp \alpha c_0 d - 1) - \ln(\exp \alpha c d - 1) = 10^3\, k I_0 \alpha t \quad (2)$$