Photochemical Debromination of Eosin in Basic Methanolic Solution

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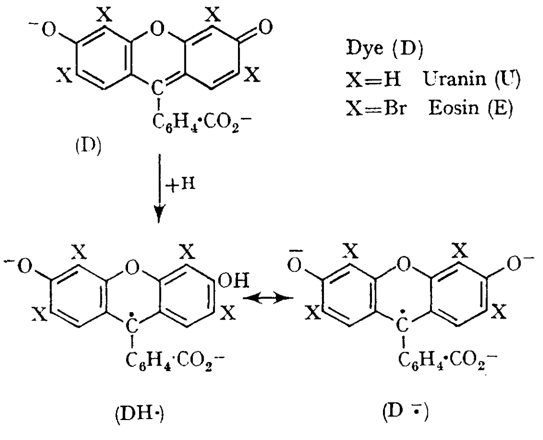
THE irradiation with visible light of xanthene dyes in basic solutions containing alcohols,[1] tertiary amines,[2] and phenol,[3] has been found to lead to debromination; this is indicated by a hypsochromic shift of their absorption spectra. We re-investigated this system using γ-rays and light.



Dye (D)
X=H Uranin (U)
X=Br Eosin (E)

Semireduced dye, DH· in neutral and $D^{\overset{\cdot}{-}}$ in basic solutions

Eosin ($\sim 10^{-5}$M) in deaerated neutral methanolic solutions is bleached by γ-irradiation by way of the primary reaction represented as:

$$E + CH_2OH\cdot \longrightarrow EH\cdot + CH_2O \qquad (1)$$

No stable absorption associated with semireduced eosin (EH·) is observed. In basic methanolic solutions, however, the intensity of a stable absorption band at 406 nm. increases as the intensity of eosin absorption decreases; no shift of the eosin absorption band is observed *in the dark*. The 406 nm. peak can be assigned, on the basis of the photochemical results,[3-7] to basic semireduced eosin ($E^{\overset{\cdot}{-}}$), which is stabilized in basic solutions due to the formation of a symmetrical tri-anion.[8] The e.s.r. spectrum of the semi-reduced eosin is shown in Figure 1.

Upon excitation of the semi-reduced eosin with 406 nm. light, the absorption peak shows a gradual hypsochromic shift as the intensity decreases. Correspondingly, the e.s.r. spectrum grows more complex until ultimately it is superimposable on that of semi-reduced uranin (U$^{\bar{\cdot}}$) (Figure 1). These results indicate that upon irradiation semi-reduced eosin undergoes a debromination leading ultimately to semireduced uranin.

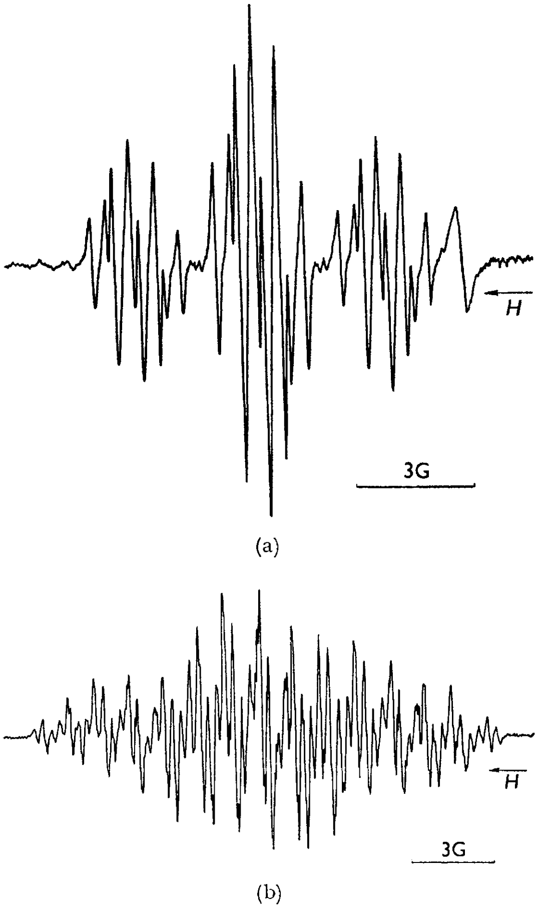


FIGURE 1. (a) *Electron spin resonance spectrum of semireduced eosin produced by* γ*-irradiation in* 80 *vol-%* MeOH *containing* 0·2M-NaOH. (b) *Electron spin resonance spectrum after irradiation by* 406 *nm. light superimposable upon that of semireduced uranin*).

Concurrent with the change in the 406 nm. absorption band, a new absorption band appears at shorter wavelength than the peak wavelength of eosin (522 nm.); this shifts until it attains the wavelength corresponding to the peak wavelength of uranin (494 nm.). Absorption bands appearing between 522 and 494 nm. are due to the formation of dyes in which there is replacement of bromine by hydrogen. Actually the absorption band of 4,5-dibromouranin has a peak at 506 nm.[2]

It should be noted, in Figure 2, that the absorption band of the remaining eosin disappears as the intensity of the absorption band due to debrominated dye increases. This result is explained by electron transfer from semi-reduced debrominated dye to eosin, the latter having an electron affinity higher than the former. When semi-reduced uranin (λ_{max} on 392 nm.) produced by γ-irradiation of uranin in basic methanolic solution is mixed with eosin *in vacuo* and in the dark, the absorption peak at 392 nm. shows a bathochromic shift; the

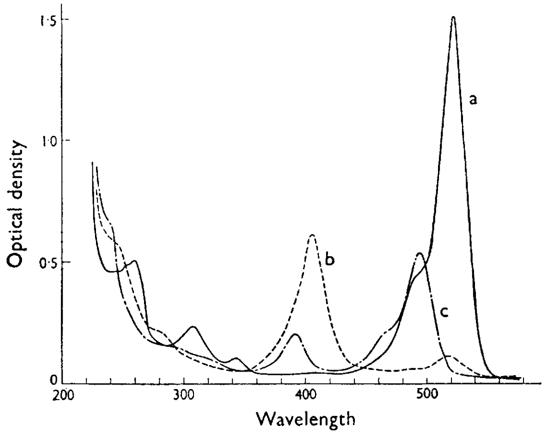


FIGURE 2. *Absorption spectra in* 98 *vol-%* MeOH *containing* 0·2M-NaOH. (a) *Eosin.* (b) *After* γ*-irradiation* (*semireduced eosin*). (c) *After irradiation of semireduced eosin by* 406 *nm. light.*

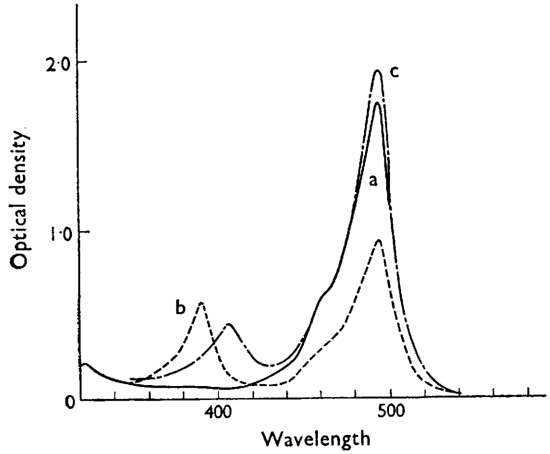


FIGURE 3. *Absorption spectra in* 98 *vol-%* MeOH *containing* 0·4M-NaOH. (a) *Uranin.* (b) *After* γ*-irradiation* (*semireduced uranin*). (c) *Mixture of* (b) *and eosin* in vacuo *and in the dark.*

absorption band of eosin disappears and that of uranin increases as shown in Figure 3. This result evidently indicates that the electron transfer

$$U^{\overline{\cdot}} + E \longrightarrow U + E^{\overline{\cdot}} \qquad (2)$$

does occur.

In conclusion, debromination takes place in basic solution *via* photoexcited semi-reduced dyes, and proceeds in a stepwise fashion by electron transfer between brominated dyes and semi-reduced debrominated dyes.

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