BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (3), 1033—1034 (1975)

A Flash Photolytic Investigation of the Interaction between Halide Anions and the Triplet Eosin

Takeshi AKIYAMA,* Mamoru KAMIYA, and Yukio AKAHORI
Shizuoka College of Pharmacy, Oshika, Shizuoka-shi 421

(Received may 16, 1974)

Synopsis. The quenching effect of the iodide ion to the triplet eosin in oxygen-free aqueous solution was strongly enhanced at 10^{-1}—10^{-2} M, but the effects of bromide and chloride ions were negligibly small at 10^{-1}—10^{-4} M. The above-mentioned results were found directly by means of a flash photolytic method.

Halide anions work as typical quenchers of the fluorescence of an eosin aqueous solution. In this case, the quantity of the quenching rate constant suggests that the energy transfer from the photoexcited eosin to the halide anion is a diffusion-controlled process.[1] It has also been found that the iodide ion strongly quenches the dye phosphorescence in a viscous glycerol solution.[2] Hence, we can expect that the halide anion quenches the triplet eosin as well as the singlet eosin. This postulation is supported also by the intermolecular heavy-atom effect of the halogen atom.

Experimental

Commercial eosin-Y was purified chromatographically according to the method of Koch.[3] A 6.2 μM eosin solution was prepared using a 1/15 M phosphate buffer at pH=7.0. Sodium iodide, sodium bromide, and sodium chrolide (G.R.) were used without further purification. Repeated cycles of freezing and thawing under a high vacuum were adopted in order to degass the sample solutions. The flash irradiation source consisted of two xenon lamps, Ushio-103 type. The lamps were used at 2 μF and 6 kV. A cylindrical quartz cell 20 cm in length and 2 cm in diameter was used. The monitoring lamp was a 500-W xenon arc lamp, Ushio-UXL-500D. The changes in the optical density after the flash irradiation were followed by means of a 1P28 photomultiplier coupled to a Hitachi QV-50 spectrophotometer. The decay of the triplet eosin was followed by selecting the wavelength of 436 nm, according to the method of Zwicker and Grossweiner.[4] The kinetic data were taken only from the initial flash irradiation of a freshly-prepared solution.

Results

Figures 1 and 2 show the decay curves of the transient absorbance of the triplet eosin. The initial decays were well fitted by exponential decay curves, which gave first-order decay constants. Without the quencher, the decay constant is of the same order as that obtained by Zwicker and Grossweiner.[4] The origin of the irreversible absorbance change which is seen at the period of ms order after the flash irradiation is not known. We consider, however, that it can not necessarily be attributed to another transient product whose spectrum overlaps that of the triplet eosin, because a permanent increase in the absorbance in this wavelength region is observed. It is of interest to note that

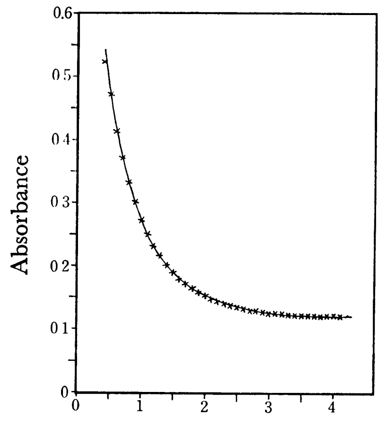

Fig. 1. Time-dependence of absorbance at 436 nm as measured by Flash-photolysis of eosin-Y in buffer solution (pH=7.0).
Concentration of eosin-Y: 6.19×10^{-6} mol/l.

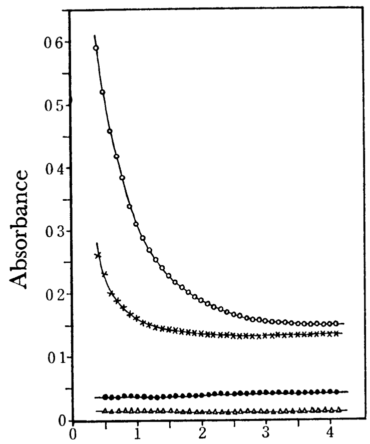

Fig. 2. Time-dependence of absorbance at 436 nm as measured by flash-photolysis of eosin-Y and quencher (NaI) in buffer solution (pH=7.0).
Concentration of eosin-Y: 6.19×10^{-6} mol/l.
Concentration of NaI
△: 1.03×10^{-1} mol/l ●: 1.08×10^{-2} mol/l
×: 1.08×10^{-3} mol/l ○: 1.06×10^{-4} mol/l

the quenching effect of the iodide ion is enhanced at 10^{-1}—10^{-2} M to such an extent that the triplet eosin can not be observed within ms time after the flash irradiation. The quenching effects of the bromide and chloride ions are negligibly small at 10^{-1}—10^{-4} M.

* Present address: Japan IBM Co. Inc., 2-6-1, Nishishinjuku, Shinjuku-ku, Tokyo 160.

The remarkable concentration dependence of the quenching effect of the iodide ion gives definitive evidence of a specific interaction between the triplet eosin and the iodide ion. This finding is in accord with the earlier suggestion of a charge-transfer interaction between the photoexcited eosin and the iodide ion.[5]

Table 1. The kinetic data of the decay constants of the triplet eosin

Quencher	Concentration of quencher (mol/l)	First-order decay constant (s^{-1})
None	—	406.5
NaI	1.03×10^{-1}	—
	1.08×10^{-2}	—
	1.08×10^{-3}	347.4
	1.06×10^{-4}	429.9
NaBr	1.00×10^{-2}	420.5
	1.02×10^{-3}	410.3
	1.05×10^{-4}	399.3
NaCl	1.69×10^{-1}	433.3
	1.08×10^{-3}	451.3
	1.11×10^{-4}	411.7

References

1) G. Oster and A. H. Adelman, *J. Amer. Chem. Soc.*, **78**, 913 (1956).
2) F. Perrin, *C. R. Acad. Sci. Paris*, **184**, 1121 (1927); S. Boudin, *J. Chem. Phys.*, **27**, 285 (1930).
3) L. Koch, *J. Assoc. Offic. Agr. Chemists*, **39**, 397 (1956).
4) E. F. Zwicker and L. I. Grossweiner, *J. Phys. Chem.*, **67**, 549 (1963).
5) J. Q. Umberger and D. K. LaMer, *J. Amer. Chem. Soc.*, **67**, 1099 (1945).