Mechanism of Reversible Photochemical Color Change of Bis(triphenylimidazolyl) at Low Temperature

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We reported that a reddish-purple color of triphenylimidazolyl radical produced by irradiation of solutions of bis(triphenylimidazolyl) (I),[1] the photochromic isomer,[2] in benzene, *n*-hexane or EPA at room temperature gradually faded with diminishing temperature even under irradiation and finally disappeared at about −100°C.[3]

We found that the solutions of I mentioned above showed a bluish-purple color on irradiation with 365 mμ light in a rigid state at −196°C. The color persisted for many hours in the rigid state in the dark. It rapidly faded on raising temperature from −196°C to make the rigid solution fluid in the dark or even under irradiation. When the temperature of the faded solution was further raised above about −50°C, the reddish-purple color of triphenylimidazolyl radical appeared again in the dark or under irradiation.

While a degassed solution of I in EPA showed an absorption maximum at 277 mμ in the rigid state at −196°C, the bluish-purple rigid solution produced on irradiation at −196°C showed new absorption maxima at 352, 540(sh) and 575 mμ with decrease of the absorbance at 277 mμ. Although the feature of the spectrum of the colored solution was similar to that of triphenylimidazolyl radical, the absorption maxima of the colored solution were slightly shifted from the maxima 345, 526(sh) and 551 mμ of the radical, respectively, and the colored rigid solution showed a weak broad absorption band at about 700 mμ besides the maxima mentioned above. On making the rigid media fluid by raising temperature, the new bands rapidly disappeared with bleaching of the color. From these facts it is likely that the bluish-purple substance is a cation radical produced from I by photolytic loss of one electron and the weak band at about 700 mμ is attributed to the ejected electrapped in the rigid solvent.

Whereas no ESR signal was shown in the unirradiated solutions of I at −196°C, an ESR signal appeared with the coloration by irradiation with 365 mμ light at −196°C, showing formation of a free radical which is presumably the cation radical. The intensity of the signal increased with time of irradiation. The rate of formation of the radical by irradiation was proportional to the intensity of the light. This fact is likely to show that the cation radical is formed by a one-step photoionization mechanism. The ESR spectrum showed a strong line (g=2.00) at 3280 gauss, three pairs of lines at 3120—3375 gauss and a line of a half field transition at 1750 gauss, showing existence of a triplet state. The intensity of these lines did not diminish at −196°C on ceasing irradiation, but rapidly diminished by raising temperature from −196°C in the dark or under irradiation, and also by irradiation of infrared light at −196°C.

A degassed solution of I in EPA showed phosphorescence of a life-time of 0.5 sec at −196°C and the spectrum showed maxima at 495 and 512 mμ. The intensely colored rigid EPA solution produced by irradiation at −196°C showed a weak after-glow by raising temperature to make the rigid media fluid. The color of the after-glow was similar to that of the phosphorescence.

From these observations it is likely that the reversible color change of solutions of I on irradiation in the rigid state at or near −196°C is due to formation of a cation radical produced by photolytic loss of an electron from a nitrogen atom in the imidazole ring of I, the electron being trapped by the rigid solvent, and that the weak after-glow and bleaching of the bluish-purple color observed on raising temperature from −196°C are attributed to recombination of the trapped electron with the cation radical to I through a triplet state of I.

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[1] T. Hayashi and K. Maeda, This Bulletin, **33**, 556 (1960); T. Hayashi, K. Maeda and M. Morinaga, *ibid.*, **37**, 1567 (1964).

[2] D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 3825 (1966).

[3] T. Hayashi and K. Maeda, This Bulletin, **36**, 1052 (1963).