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Photo-induced Intramolecular Electron Transfer of Viologen with Hexacyanoferrate(II) Ion

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The charge-transfer band of 1,1'-diamyl-4,4'-bipyridinium hexacyanoferrate(II) varied by the kind of solvent and its absorption was enhanced by photo-induced intramolecular electron transfer via radical-ion complex.

Photo-induced reduction of viologens was found to take place in polar aprotic media in spite of large differences of redox potentials between bipyridinium and halides as counter anions.1) In order to evaluate the photochromism of viologen, this paper describes a peculiar behavior concerning the photo-induced intramolecular electron transfer within the viologen molecule bearing the metal-complexed counter anion, which possesses relatively low redox potential.

The colored complexes of 1,1'-diamyl-4,4'-bipyridinium dichloride (V^{2+}) with metal halides2) decomposed in water or in methanol (MeOH), and the solutions became colorless. While a charge-transfer (CT) band appeared in a mixture of ethanol (EtOH) and MeOH (e.g. V^{2+} -$FeCl_4$, λmax , 450 nm in 1:4-solution of MeOH-EtOH), irradiation with UV-light revealed no spectral change in the 410-1000 nm region.3) The complex with the hexacyanoferrate(II) ion having a low redox potential compared with those of metal halides exhibits CT-absorption peak at 586 nm in 50% aq. EtOH.4,5) The band of V^{2+}-$[Fe(CN)_6]^{4-}$ shifted to longer wavelengths with higher EtOH content in solution. The linear relationship between the Z-values of aq. EtOH6) and absorption wavelengths indicates that the complex exists in the π - δ structure.7)

The pale purple-colored aqueous soln. of 10^{-3} M (1 M = 1 mol dm^{-3}) of V^{2+} and $2x10^{-3}$ M of $[Fe(CN)_6]^{4-}$ turned intense violet upon irradiation of UV-light, and there is

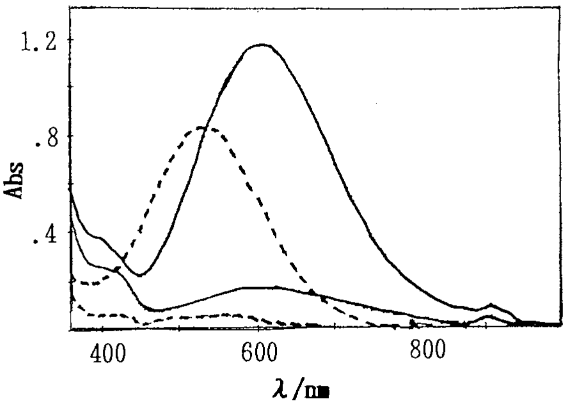
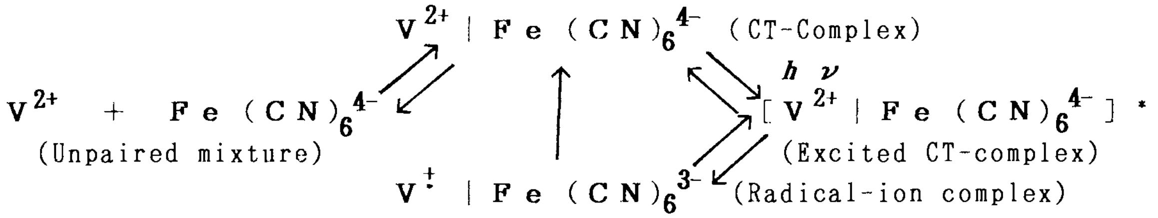


Fig. 1. Electronic spectra of a mixture of $V^{2+}(10^{-3}M)$ and $[Fe(CN)_6]^{4-}(2x10^{-3}M)$ before and after irradiation.
- - - - in water, ——— in 80% EtOH

no absorption peak around 398 nm characteristic of radical cations ($V^{+\cdot}$) alone,8) indicating that the concentration of CT-complex was increased with irradiation. The absorption increment slowly decreased in the dark, more rapidly by heating, and reached the original absorption finally.9) In the case of 80% aq. EtOH solution, the extent of the CT-complex formation after irradiation of UV-light was larger and the rate of formation of the complex was faster, compared with respective values in water.10) Cyclic voltamograms indicated that the half-redox potential value for the V^{2+} - $V^{+\cdot}$ transformation in 80% aq. EtOH was 160 mV higher than that in water. This might mean the V^{2+}-complex in EtOH is liable to be reduced to $V^{+\cdot}$ than the complex solvated strongly with water.11)

The following is proposed to account for the reversible reaction in solution.



Thus a radical-ion complex might generate from the ground-state CT-complex through an excited state by the application of UV-light. The radical-ion complex bearing $[Fe(CN)_6]^{3-}$ in solution may be so unstable8,12) that it brings about the intramolecular electron-transfer readily to form the CT-complex, which, upon standing in the dark, reaches an equilibrium with the unpaired mixture, or it is oxidized by air oxygen. In the absence of air, the reversible electron transfer can be repeated; the color fading is accelerated by heating and also possible by electrochemical oxidation-reduction of the hexacyanoferrate ion.

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3) Irradiation of 330 nm light for 2 min by using a 75w-Hg lamp at 25 °C.
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5) λ max: 532 nm in water; 616 nm in 50% aq. N-methyl-2-pyrrolidone.
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9) Half recovery time in water: 55 min at 25 °C, 50 s at 60 C.
10) The plot of absorption maxima against time (Abs/t) gives a straight line within 2 min. Abs/t (min^{-1}) : 0.48 in 80% aq. EtOH; 0.42 in water.
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