CHEMISTRY LETTERS, pp. 107-110, 1979. Published by the Chemical Society of Japan

PHOTOCHEMICAL ELECTRON TRANSPORT FROM WATER LAYER TO ORGANIC LAYER VIA SODIUM ANTHRAQUINONE-2-SULFONATE BY STEPWISE TWO PHOTON EXCITATION[1)]

Haruo INOUE and Mitsuhiko HIDA
Department of Industrial Chemistry, Faculty of Technology,
Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

An irreversible electron transport from hydroxide ion to organic molecules via sodium anthraquinone-2-sulfonate was observed in a reversed micellar system by stepwise UV (λ= 365 nm) and visible light (λ>450 nm) irradiations.

It is well known that anthraquinones are readily photoreduced by an electron transfer from hydroxide ion to produce the corresponding radical anion ($AQ^{\overline{\cdot}}$) as a stable product.[2,3)] It is expected that the succesive visible light irradiation to the resultant radical anion ($AQ^{\overline{\cdot}}$) may raise the reductive power of $AQ^{\overline{\cdot}}$ itself. From these points of view, we attempted to construct the electron transport system including anthraquinones as carrier of electron in non-micellar, micellar, or reversed micellar systems by stepwise two photon excitation and found that an effective irreversible electron transport from the water layer to organic layer could be attained in the reversed micellar system.

Sodium anthraquinone-2-sulfonate (**1**) (1×10^{-4}mol/dm^3) in the presence of hydroxide ion (NaOH = 6×10^{-2}mol/dm^3) in 1:1 ethanol-water mixture was irradiated by the monochromatic light of λ= 365 nm under nitrogen atmosphere. The radical anion ($AQ^{\overline{\cdot}}$) alone was produced during the initial irradiation for 90 s (Process A). On prolonged irradiation the radical anion disappeared, along with the formation of the dianion of **1** ($AQ^{=}$) (Process B). The spectral changes in the process A and B had different isosbestic points. These results indicated that the dianion ($AQ^{=}$) was produced by the further irradiation of the light (λ = 365 nm) to the radical anion ($AQ^{\overline{\cdot}}$). The radical anion ($AQ^{\overline{\cdot}}$) was stable against the selective excitation of itself by the further visible light irradiation (λ> 450 nm). However, the dianion ($AQ^{=}$) produced from the radical anion ($AQ^{\overline{\cdot}}$) was reversibly reconverted to the radical anion ($AQ^{\overline{\cdot}}$) by the visible light irradiation (λ> 450 nm), that is, the photochemical ejection of electron from the dianion ($AQ^{=}$) was observed. This reverse change of $AQ^{=}$ to $AQ^{\overline{\cdot}}$ was accelerated by the addition of 1,4-dicyanobenzene (DCB) as an electron acceptor and the similar tendencies, even though to a less extent, were also observed by the addition of cyanobenzene, pyridine, and bromobenzene etc, respectively. As a whole, three photons were concerned with the reaction in 1:1 ethanol-water mixture. When **1** (1×10^{-4}mol/dm^{3}) in a cationic cetyltrimethylammonium bromide (CTAB) micelle was irradiated by the light of λ= 365 nm under nitrogen atmosphere, effective simultaneous productions of both the radical anion of **1** ($AQ^{\overline{\cdot}}$) and the dianion of **1** ($AQ^{=}$) were observed with the irradiation. In a cetyltrimethylammonium hydroxide system in which the micellar surface was thought to be covered with hydroxide ion, the reaction was promoted by a factor of *ca*. 20. When anthraquinone, which was supposed to be incorporated in the micellar interior, was used in place of **1**, the photoreduction was hardly observed. CTAB formed 1:1 complex with **1** to precipitate at the concentration below its cmc. These results indicated that an electron might be transfered effectively from the hydroxide ion concentrated at micellar surface to the excited **1** located in the surface area of the cationic micelle. The production of the radical anion was not affected at all by the addition of $Cu(en)_2^{2+}$ (3×10^{-4}mol/dm^{3}) that has lower reduction potential (E_o = -0.35 Volt *vs*. NHE) than that of **1** (E_o = -0.004 Volt), but was completely supressed by the addition of $CuSO_4$ (2×10^{-4}mol/dm^{3}) that has higher reduction potential (E_o = 0.159 Volt) than that of **1**. This strongly suggested the presence of the electron transfer such as $OH^{-} \longrightarrow AQ \longrightarrow Cu^{2+}$ through the micellar surface. When DCB (1×10^{-2}mol/dm^{3}) as an acceptor molecule was added to the micellar system, the photochemical ejection of electron from the dianion ($AQ^{=}$) was also observed to be accelerated, indicating that an irreversible electron transport from hydroxide ion to an acceptor molecule via **1** or reduced **1** might take place by the stepwise UV (λ= 365 nm) and visible light ($\lambda > 450$ nm) irradiations. In search of the more effective electron transport system, the reaction in a reversed micellar system was attempted, in which the solvent itself was expected to act as an acceptor. **1** (1×10^{-4}mol/dm^{3}) in the presence of cetyldimethylbenzylammonium hydroxide (1×10^{-2} mol/dm^{3}) and water (0.5 Vol %) in cyanobenzene was irradiated by the monochromatic light of λ= 365 nm. After the sufficient formation of the radical anion ($AQ^{\overline{\cdot}}$) was observed, the selective excitation of the radical anion by the visible light

($\lambda > 450$ nm) irradiation for about 3 minutes caused a rapid and complete disappearance of the radical anion itself. The radical anion again appeared by the 365 nm irradiation and disappeared by the visible light ($\lambda > 450$ nm) irradiation repeatedly. A trace amount of hydrogen peroxide, which was supposed to be derived from the hydroxide radical, was detected in the reaction system after the photoreaction, suggesting that the most part of the hydroxide radical produced in the reaction system might abstract a hydrogen atom from the surfactant molecule to produce water. These results strongly suggested that an effective irreversible electron transport was attained from the water layer incorporated in the reversed micelle to the organic layer cyanobenzene as solvent via **1** as a carrier by the stepwise two photon excitation. It was also demonstrated that the redox system including **1** as a carrier could cover a wide range of redox potential by stepwise two photon excitation (Fig.).

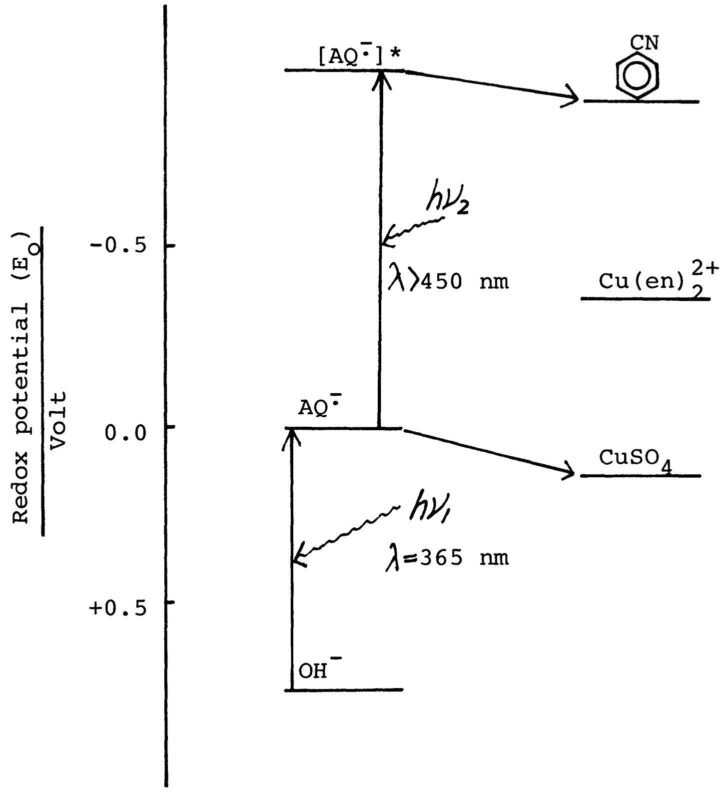

Fig. Flow of electron in the electron transport system including **1** as a carrier by stepwise UV and visible light irradiations.

References

1) This work was presented at the " 2nd International Conference on the Photochemical Conversion and Storage of Solar Energy " (Cambridge, August 1978).

2) V.A.Kuzmin and A,K,Chibisov, Chem. Comm., 1971, 1559.

3) H.Inoue, K.Kawabe, N,Kitamura, and M.Hida, Chem. Lett., 987(1977).

(Received November 2, 1978)