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# Photochemical Electron Transport from Water Layer to Organic Layer *via* Sodium Anthraquinone-2-sulfonate by Stepwise Two Photon Excitation[†]

Haruo Inoue* and Mitsuhiko Hida
*Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University,*
*Fukazawa, Setagaya-ku, Tokyo 158*

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Photochemical electron transport from hydroxide ion to organic acceptor molecule *via* an anthraquinone derivative as an electron carrier was investigated in homogeneous, cationic micellar, and cationic reversed micellar systems. In homogeneous alkaline aqueous ethanol, the photochemically generated radical anion of sodium anthraquinone-2-sulfonate (**1**) was stable against further irradiation with visible light ($\lambda > 450$ nm), while the dianion of **1** was reversibly converted to the radical anion by visible light irradiation. The reversible conversion was accelerated by the addition of an organic acceptor molecule such as 1,4-dicyanobenzene. In a cationic hexadecyltrimethylammonium micellar system, an effective photoreduction of **1** by an electron transfer from hydroxide ion concentrated on the micellar surface to the excited **1** located in the surface area of the micelle was observed. In a reversed micellar system an electron was effectively transported from the water layer to the organic layer; an electron was transfered from hydroxide ion in the water layer incorporated in a benzylhexadecyldimethylammonium reversed micelle to **1** at the micellar surface by irradiation with light of $\lambda = 365$ nm. Successive visible light irradiation ($\lambda > 450$ nm) caused an electron ejection from the radical anion of **1** to benzonitrile as a bulk phase solvent. The possibility of the incorporation of carbon dioxide into the acceptor cycle of the electron transport system was also examined. In pyridine solution, carbon dioxide caused the disappearance of the reduced species of **1** on visible light irradiation ($\lambda > 450$ nm). Trace amounts of dihydropyridinedicarboxylic acid derivatives were obtained.

Recently many intensive studies have been made on photochemical electron transport systems in relation to the photochemical conversion of solar energy.[1] Considerable attention has been paid to the photochemical splitting of water into hydrogen and oxygen using semiconductors,[2] metal complexes,[3] and chlorophylls.[4] Photochemical reductions of carbon dioxide[5] and nitrogen[6] have also been examined. Various different approaches to the photochemical electron transport system including water molecules are required in order to achieve more effective conversion of solar energy.

It is of interest to investigate the photochemical redox reactions including the water molecules as an electron donor and some quinone as an electron carrier with a view to approaching artificial photosynthesis. It is well known that anthraquinones are readily photoreduced by an electron transfer from hydroxide ion to produce the corresponding radical anion ($AQ^{\cdot -}$) as a stable product.[7,8,19] Then, it may be possible to formulate an electron transport system as depicted in Fig. 1; that is, light irradiation of the anthraquinones would evoke the oxidation of hydroxide ion equilibrated with water and successively the electron would be transfered from the radical anion ($AQ^{\cdot -}$) to another molecule step by step. The successive visible light irradiation of the resultant radical anion ($AQ^{\cdot -}$) is expected to raise the reductive power of $AQ^{\cdot -}$ itself and this photoredox system may cover a wide range of redox potential by stepwise two photon excitation. On the basis of this view point, we attempted to construct an electron transport system including anthraquinones as carrier of electron in homogeneous, cationic micellar, and cationic reversed micellar systems. The photoreduction by an electron transfer through the cationic micellar surface was actually observed to take place and an effective irreversible electron transport from the water layer to the organic layer could be attained in the cationic reversed micellar system. Furthermore, the possibility of the incorporation of carbon dioxide into the acceptor cycle of the electron transport system was examined.

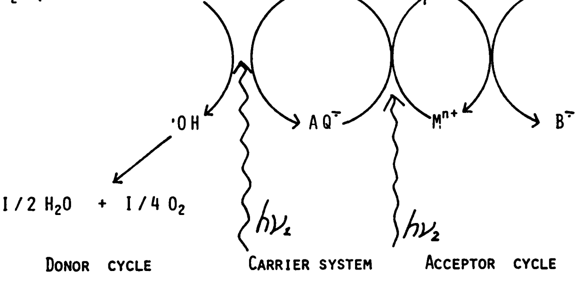

Fig. 1. Electron transport cycle including anthraquinone derivative (AQ) as a carrier and water as an electron donor by stepwise two photon excitation.

## Experimental

*Materials.* Sodium anthraquinone-2-sulfonate (**1**),[19] sodium 1-aminoanthraquinone-2-sulfonate (**2**),[9] and 2-piperidinoanthraquinone (**3**)[19] were purified as reported elsewhere. Anthraquinone (**4**) (Sumitomo Chemical Co.) was passed through silica-gel column and recrystallized repeatedly from benzene; mp 285—286 °C, Found: C, 80.58%; H, 3.78%. Calcd for $C_{14}H_8O_2$: C, 80.76%; H, 3.87%. Sodium 1-amino-4-butylaminoanthraquinone-2-sulfonate (**5**) was obtained by the photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulfonate with butylamine.[10] 1-Acetylaminoanthraquinone (**6**) was prepared by acetylation of 1-aminoanthraquinone with acetic anhydride and was purified by

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[†] A part of this study was presented in *Chem. Lett.*, **1979**, 107.

repeated recrystallization from 1 : 1 toluene–ethanol mixture; mp 220—221 °C; Found: C, 72.42%; H, 3.95%; N, 5.27%. Calcd for $C_{16}H_{11}NO_3$: C, 72.47%; H, 4.15%; N, 5.28%. 1-Lauroylaminoanthraquinone (**7**) was prepared by the reaction between 1-aminoanthraquinone and lauroyl chloride in pyridine solution and was purified by passing through a silica, gel column and the repeated recrystallization from 2 : 5 benzene–ethanol; mp 132.5—133.5 °C; Found: C, 76.96%; H, 7.79%; N, 3.38%. Calcd for $C_{26}H_{31}NO_3$: C, 77.01%; H, 7.71%; N, 3.45%. Hexadecyltrimethylammonium bromide (CTAB) (Tokyo Kasei, EP) was recrystallized twice from water. Hexadecyltrimethylammonium hydroxide (CTAH) (10% in methanol; Tokyo Kasei) and benzylhexadecyldimethylammonium hydroxide (CDBAH) (10% in methanol; Tokyo Kasei) were used without further purification. Bis(ethylenediamine)copper(II) sulfate was prepared from copper(II) sulfate and ethylenediamine.[11] 1,4-Dicyanobenzene (Tokyo Kasei; G. R.) was used without further purification. Benzonitrile was dried with phosphorus pentoxide and fractionally distilled under a nitrogen atmosphere before use. Pyridine was refluxed with potassium hydroxide and fractionally distilled under a nitrogen atmosphere. Ion exchanged neutral water was used for the preparations of micellar solutions except where otherwise stated.

*Procedures.* Each sample of non-micellar and cationic micellar solution was degassed in a quartz cell by repeated freeze-thaw procedures. The reversed micellar reaction mixture was prepared by the following procedures; an appropriate amount of CDBAH methanol solution was placed in a Schlenck flask and the methanol was evaporated completely. Benzonitrile and **1** were added to the flask and the mixture was stirred vigorously. The suspension of the mixture was brought into solution by adding small amount of water ($\approx$0.5 v/v%). The dissolved oxygen was removed by bubbling with nitrogen for at least 30 min or by the repeated freeze-thaw procedures. Monochromatic light of $\lambda$=365 nm and visible light of $\lambda$>450 nm were generated by a 500 W high pressure mercury lamp (USHIO USH-500D) through UV-DIA (Toshiba) and VY-45 (Toshiba) glass filters, respectively. The visible and UV absorption spectra of the irradiated reaction mixtures were measured by a Shimadzu UV-200 spectrophotometer. GC-Mass spectra were measured by a JMS D-100 (JEOL) mass spectrometer equipped with Thermon-100 and SE-30 columns.

## Results and Discussion

*Photochemical Electron Transport in Aqueous Alcohol.* Sodium anthraquinone-2-sulfonate (**1**) ($1.0\times10^{-4}$ mol/dm$^3$) in the presence of hydroxide ion (NaOH=$6.0\times10^{-2}$ mol/dm$^3$) in 1 : 1 ethanol–water mixture was irradiated with monochromatic light of $\lambda$=365 nm under a nitrogen atmosphere. The visible absorption spectra of the reaction system are shown in Fig. 2. The radical anion ($AQ^{\cdot-}$) of **1** alone was produced during the initial irradiation for 90s (Process I in Fig. 2). On prolonged irradiation the radical anion disappeared, along with the formation of the dianion of **1** ($AQ^{2-}$) (Process II in Fig. 2). The radical anion ($AQ^{\cdot-}$) and dianion ($AQ^{2-}$) produced were stable for several hours in the dark. The spectral changes in the processes I and II had different isosbestic points. These results indicated that the dianion ($AQ^{2-}$) was produced by the further irradiation with light ($\lambda$=365 nm) to the radical anion ($AQ^{\cdot-}$). Contrary to our expectation the radical anion ($AQ^{\cdot-}$) was stable against its selective excitation by further visible light irradiation ($\lambda$>450 nm) even in the presence of an acceptor molecule, such as 1,4-dicyanobenzene (DCB) ($1\times10^{-2}$ mol/dm$^3$). However, the dianion ($AQ^{2-}$) was reversibly reconverted to the radical anion ($AQ^{\cdot-}$) on visible light irradiation ($\lambda$>450 nm) with the same isosbestic points in process II. Thus,

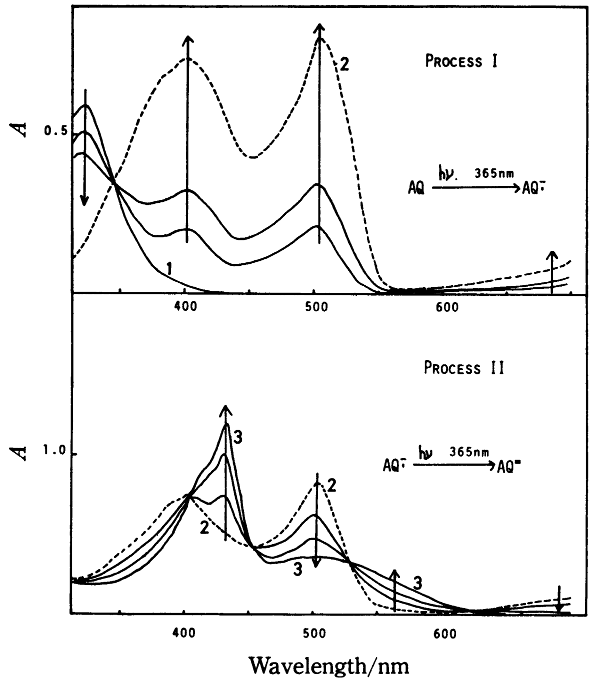


Fig. 2. Absorption spectra of the reaction system of the photoreduction of **1** under nitrogen atmosphere; [**1**]: $1.0\times10^{-4}$ mol/dm$^3$ in 1 : 1 ethanol–water mixture; [OH$^-$]: $6.0\times10^{-2}$ mol/dm$^3$; irradiation light: $\lambda$=365 nm; 1: 0 s; 2: 90 s; 3: 30 min.

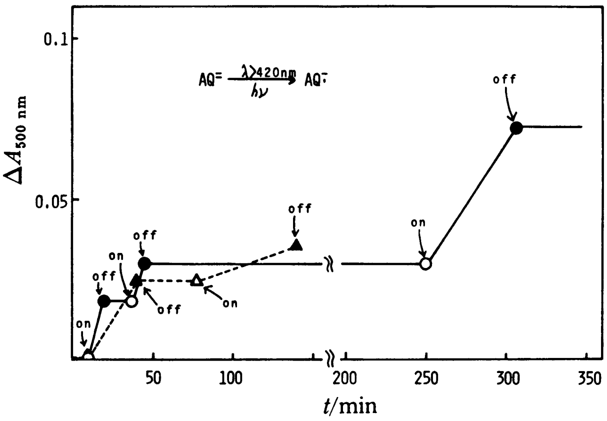


Fig. 3. Effect of the irradiation of visible light ($\lambda$>420 nm) on the reversible reconversion from the dianion ($AQ^{2-}$) to the radical anion ($AQ^{\cdot-}$) of **1**; the amount of the reconversion was monitored at $\lambda$=500 nm; "on": light is on; "off": light is off;

| | [1] mol/dm$^3$ | [OH$^-$] mol/dm$^3$ | [CN-⌬-CN] mol/dm$^3$ |
|---|---|---|---|
| —○—●— | $1.0\times10^{-4}$ | $6.0\times10^{-2}$ | $1.0\times10^{-2}$ |
| ---△---▲--- | $1.0\times10^{-4}$ | $6.0\times10^{-2}$ | 0 |

the photochemical ejection of an electron from the dianion ($AQ^{2-}$) was observed on the visible light irradiation. As indicated in Fig. 3, this reverse change from $AQ^{2-}$ to $AQ^{\overline{\cdot}}$ was accelerated by the addition of DCB as an electron acceptor; similar tendencies, though to a lesser extent, were also observed on the addition of benzonitrile, pyridine, and bromobenzene. Though it was revealed that under these conditions in 1 : 1 ethanol–water mixture the radical anion ($AQ^{\overline{\cdot}}$) was mainly produced by a hydrogen abstraction from ethanol rather than an electron transfer from hydroxide ion,[12] the dianion ($AQ^{2-}$) was also produced from the radical anion ($AQ^{\overline{\cdot}}$) in alkaline aqueous solution, indicating that hydroxide ion can also act as an electron donor in the process II. These results imply that an electron transport system including the reversible cycle $AQ^{\overline{\cdot}} \rightleftharpoons AQ^{2-}$ can be constructed under appropriate conditions (Fig. 4). As a whole three photons are concerned with the electron transport.

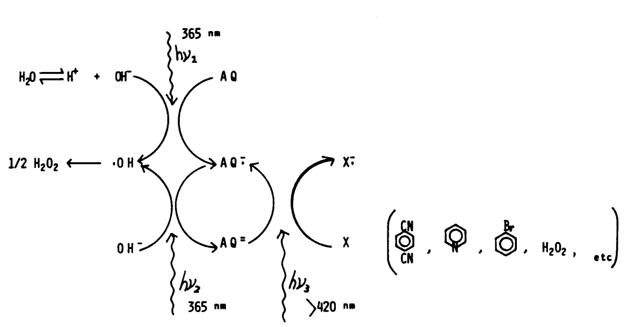


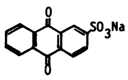
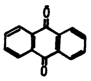
Fig. 4. Electron transport cycles including the reversible cycle of $AQ^{\overline{\cdot}} \rightleftharpoons AQ^{2-}$.

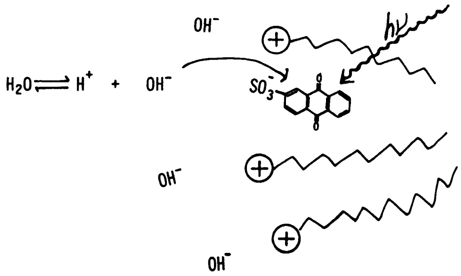
*Photochemical Electron Transport in Cationic Micellar System.* It is most important to establish a suitable donor system in Fig. 1 for an effective electron transport. Since cationic micelles are known to concentrate hydroxide ion on their surface[13] and may be preferable for charge seperation,[14] the reactions in a cationic micelle were examined. When **1** ($1.0 \times 10^{-4}$ mol/dm$^3$) was irradiated with light of $\lambda = 365$ nm in a cationic hexadecyltrimethylammonium bromide (CTAB) ($8.0 \times 10^{-3}$ mol/dm$^3$) micelle[15] in water (pH 5.70) under a nitrogen atmosphere, effective simultaneous productions of both the radical anion ($AQ^{\overline{\cdot}}$) and the dianion ($AQ^{2-}$) of **1** were observed on irradiation. On the other hand, the photoreaction in the same cationic micelle in phosphate buffer solution (pH 6.88) afforded the corresponding 9,10-anthracenediol ($AQH_2$) (Fig. 5). Since the equilibrium in Eq. 1 is well known to lie well over to the right in neutral and acidic media,[16] the difference between the reactions in water and phosphate buffer solution strongly indicated that the micro pH value around the micellar surface in phosphate buffer solution was kept neutral, while that in water was raised to that in an alkaline medium in spite of the bulk phase solvent being acidic. No hydroxylated compound

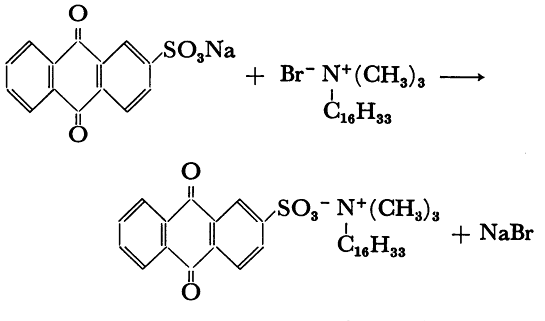
$$AQ^{2-} + 2H^+ \rightleftharpoons AQH_2 \qquad (1)$$

was observed in contrast to the reaction in aqueous solution.[17] The radical anion ($AQ^{\overline{\cdot}}$) and the dianion ($AQ^{2-}$) of **1** in aqueous ethanol were rapidly oxidized to **1** in the instant of introducing air to the reaction system, while they are reasonably stable in the cationic micelle for *ca.* 30 min even with the vigorous stirring under an air atmosphere. A similar apparent protective effect of a micelle against the oxidation of the reduced species had also been observed in an anionic micellar system.[18] In a hexadecyltrimethylammonium hydroxide (CTAH $2 \times 10^{-2}$ mol/dm$^3$) system in which the micellar surface is thought to be covered with hydroxide ion, the photoreduction was promoted by a factor of *ca.* 100 as compared with that in neutral aqueous solution (Table 1). When anthraquinone (**4**), which was assumed 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 quantitatively at the concentration below its cmc according to Eq. 2 (Found: C, 69.22%; H, 8.85%; N, 2.42%. Calcd for $C_{23}H_{49}NSO_5$: C, 69.31%; H, 8.64%; N, 2.45%). These results indicated that an electron might be transfered effectively from the hydroxide ion concentrated at a 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 addition of $Cu(en)_2^{+2}$ ($3 \times 10^{-4}$ mol/dm$^3$) that has lower reduction potential ($E_0 = -0.35$ V *vs.* NHE), but was completely suppressed by the addition of $CuSO_4$ ($2 \times 10^{-4}$ mol/dm$^3$) that has a higher reduction potential ($E_0$=through the micellar

Table 1. Photoreduction in aqueous solution

| | Surfactant | Product | Relative reactivity |
|---|---|---|---|
|  | None | $AQH_2$ | 1.0 |
| | CTAB ($8 \times 10^{-3}$ mol/dm) | $AQ^{\overline{\cdot}}, AQ^{2-}$ | 5.5 |
| | CTAH ($2 \times 10^{-2}$ mol/dm) | $AQ^{\overline{\cdot}}, AQ^{2-}$ | 100 |
|  | CTAB ($8 \times 10^{-3}$ mol/dm$^3$) | $AQH_2$ | $\ll 1.0$ |





$$\text{AQ-SO}_3\text{Na} + \text{Br}^- \, \text{N}^+(\text{CH}_3)_3\text{-C}_{16}\text{H}_{33} \longrightarrow \text{AQ-SO}_3^- \, \text{N}^+(\text{CH}_3)_3\text{-C}_{16}\text{H}_{33} + \text{NaBr} \qquad (2)$$

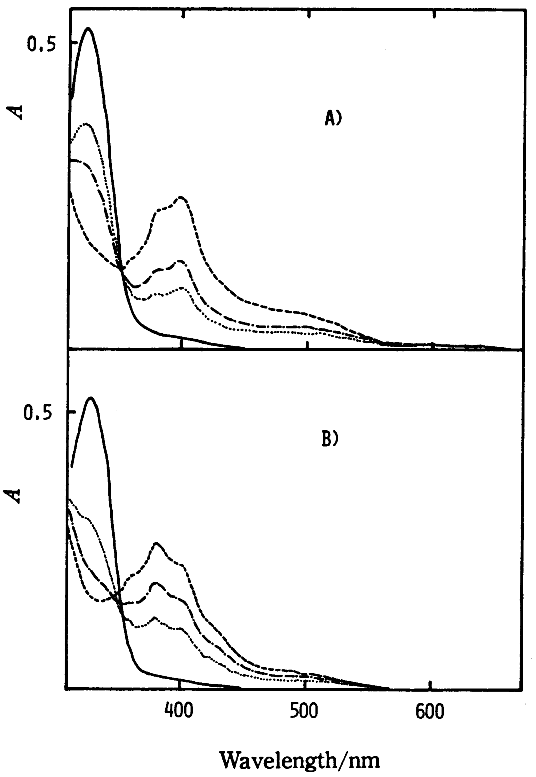


Fig. 5. Absorption spectra of the reaction system of the photoreduction of **1** in CTAB micelle; [**1**]: $1.0\times10^{-4}$ mol/dm$^3$; [CTAB]: $8.0\times10^{-3}$ mol/dm$^3$; irradiation light: $\lambda=365$ nm;
A) dispersed in aqueous solution (pH=5.70); irradiation time; (——): 0 min; (······): 10 min; (-·-·-·): 16 min; (------): 38 min; B) dispersed in phosphate buffer solution (pH=6.88); irradiation time; (——): 0 min; (······): 7 min; (-·-·-·): 13 min; (------): 23 min.

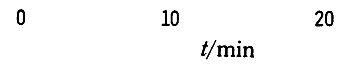
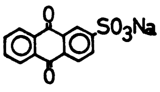


Fig. 6. Effect of cupric copper on the production of the radical anion (AQ$^{\overline{\cdot}}$) of **1** in the photoreduction in CTAB micelle; irradiation light: $\lambda=365$ nm; the amount of AQ$^{\overline{\cdot}}$ was monitored by the absorbance at $\lambda=400$ nm;

| | [1] mol/dm$^3$ | [CTAB] mol/dm$^3$ | [CuSO$_4$] mol/dm$^3$ | [Cu(en)$_2$]SO$_4$ mol/dm$^3$ |
|---|---|---|---|---|
| —●— | $1.0\times10^{-4}$ | $8.0\times10^{-3}$ | 0 | 0 |
| —○— | $1.0\times10^{-4}$ | $8.0\times10^{-3}$ | $2.0\times10^{-4}$ | 0 |
| —△— | $1.0\times10^{-4}$ | $8.0\times10^{-3}$ | 0 | $3.0\times10^{-4}$ |

0.159 V) (Fig. 6). This strongly suggested the presence of the electron transfer such as $\mathrm{OH^-}\rightarrow\mathrm{AQ}\rightarrow\mathrm{Cu^{2+}}$ surface. When DCB ($1\times10^{-2}$ mol/dm$^3$) was added to the micellar system as an acceptor molecule, the photochemical ejection of an electron from the dianion (AQ$^{2-}$) was accelerated, indicating that an electron was irreversibly transported from hydroxide ion to an acceptor molecule *via* **1** or reduced **1** by the stepwise UV ($\lambda=365$ nm) and visible light ($\lambda>450$ nm) irradiations. Since aminoanthraquinones are known to be photoreduced by an electron transfer from hydroxide ion in their upper excited n$\pi$* triplet states in homogeneous solution,[19] their photoreduction in CTAB and CTAH micelles were also examined. However, sodium 1-aminoanthraquinone-2-sulfonate (**2**), 2-piperidinoanthraquinone (**3**), sodium 1-amino-4-butylaminoanthraquinone-2-sulfonate (**5**), 1-acetylaminoanthraquinone (**6**), and 1-lauloylaminoanthraquinone (**7**) were all ineffective for photoreduction. The reason for those inactivities is not clear. Small differences of their solubilization sites in the cationic micelle from that of **1** may cause the differences of the reactivities.



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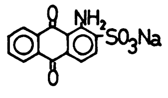

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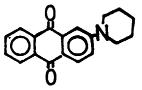

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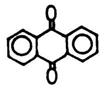

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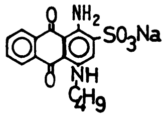

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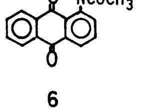

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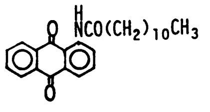

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*Electron Transport in Cationic Reversed Micelle.* It is well known that some surfactant molecules in nonaqueous solutions form reversed micelles which can solubilize considerable quantities of water and have inverse structures from those formed in water.[20] In search of a more effective electron transport system, the reaction in a reversed micellar system was attemped, in which the bulk phase solvent itself was expected to act as an acceptor in high concentration. **1** ($1\times10^{-4}$ mol/dm$^3$) in the presence of benzylhexadecyldimethylammonium hydroxide (CDBAH) ($1\times10^{-2}$ mol/dm$^3$) and water (0.5 v/v%) in benzonitrile was irradiated by the monochromatic light of $\lambda=365$ nm. After sufficient formation of the radical anion (AQ$^{\overline{\cdot}}$) was observed, the selective excitation of the radical anion by visible light ($\lambda>450$ nm) irradiation for about 3 min caused a rapid disappearance of the radical anion itself (Fig. 7). As indicated in Fig. 8, the radical anion again

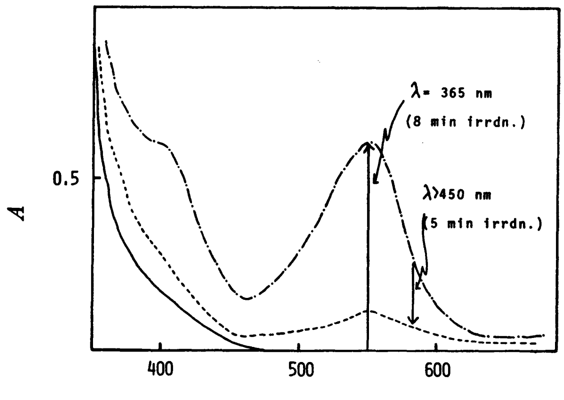

Fig. 7. Absorption spectra of the reaction system of the photoreduction of **1** in CDBAH reversed micelle dispersed in benzonitrile; [**1**]: $1.0\times10^{-4}$ mol/dm$^3$; [CDBAH]: $2.5\times10^{-2}$ mol/dm$^3$; [$H_2O$]: 0.5 v/v% in benzonitrile; (——): before irradiation; (-·-·-·): 8 min irradiation with the light of $\lambda=365$ nm; (------): 5 min irradiation with the light of $\lambda>450$ nm subsequently.

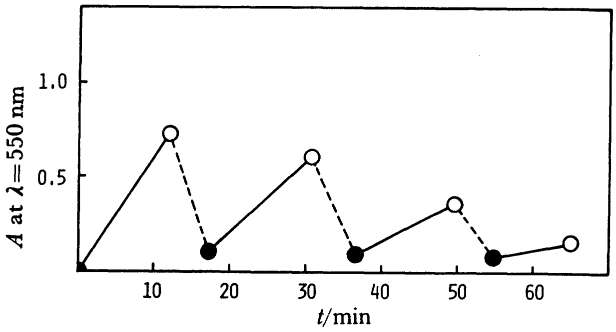

Fig. 8. Effect of the repeated irradiations of UV ($\lambda=365$ nm) and visible ($\lambda>450$ nm) light on the production of the radical anion ($AQ^{\overline{\cdot}}$) of **1** in CDBAH reversed micelle dispersed in benzonitrile; [**1**]: $1.0\times10^{-4}$ mol/dm$^3$; [CDBAH]: $2.5\times10^{-2}$ mol/dm$^3$; [$H_2O$]: 0.5 v/v % in benzonitrile; the absorbance at $\lambda=550$ nm was monitored; (●——): UV light ($\lambda=365$ nm) was irradiated; (○——): visible light ($\lambda>450$ nm) was irradiated.

appeared on 365 nm irradiation and disappeared on visible light ($\lambda>450$ nm) irradiation repeatedly. A small amount of hydrogen peroxide ($5.4\times10^{-5}$ mol/dm$^3$) was really detected in the reaction system after the photoreaction, suggesting that the greater part of the hydroxyl radical produced in the reaction system might abstract a hydrogen atom from the surfactant molecule. Moreover, a GC-Mass measurement (column; SE-30, 180 °C) of the irradiated reaction mixture indicated the presence of a trace amount of dihydrodimer (*m/e*; 208, 121, 103) and trimer (*m/e*; 309, 103) of benzonitrile which might be produced from the radical anion of benzonitrile as observed in electrochemical reduction.[21,22] 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 benzonitrile as solvent and that **1** acted as an electron carrier at the micellar interface by the stepwise two photon excitation. These conclusions are illustrated in Fig. 9. However, the electron transfer cycle lost its ability to transfer an electron in the repeated cycles as observed in Fig. 8, though repeated short time irradiations seemed to improve the apparent number of transfer cycles. Side reactions such as photohydroxylation[17] and photodesulfonation[23] of **1** may cause this fatigue-like phenomenon. However, the fact that no hydroxylated compound was detected in the reaction system, and **4** as a possible product in the case of desulfonation *via* the radical anion ($AQ^{\overline{\cdot}}$) of **1**, also acted as a carrier, ruled out the above possibilities. The main reason may be that the hydroxide ion in the water layer incorporated in a reversed mecelle is consumed during the photoreduction and the resultant acidification renders the system inactive. Hence we attempted the reaction in a two phase system, in which benzonitrile solution of **1** and CDBAH was placed over the water layer including potassium hydroxide. In this two phase system, it is expected that the water core of the reversed micelle in the benzonitrile organic layer is always washed with fresh alkaline aqueous solution by vigorous stirring and the system is refreshed. In accordance with the expectation, the apparent number of transfer cycles was greatly improved to more than twenty in the two phase system. Though more detailed studies are required, it will be useful to carry out the reaction in such a two phase system.

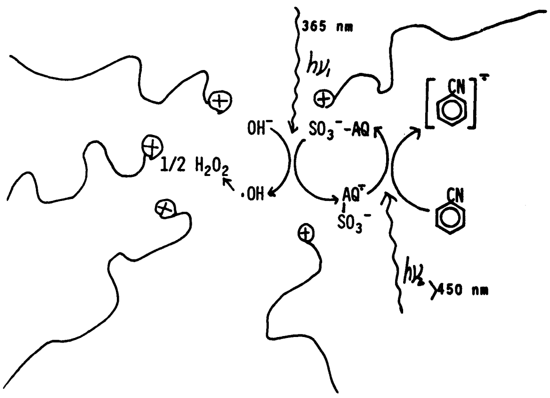

Fig. 9. Electron transport in reversed micellar system.

*The Possibility of the Incorporation of Carbon Dioxide into the Electron Transport.* Next we examined the possibility that carbon dioxide might be incorporated into the electron transfer cycle. In order to obtain a high concentration and activation of carbon dioxide, pyridine was used as solvent. **1** and CTAB or CTAH ($2.0\times10^{-2}$ mol/dm$^3$) with a small amount of water (0.5 v/v%) in pyridine were irradiated by light of $\lambda=365$ nm. The radical anion and dianion of **1** were produced on irradiation. Then, visible light of $\lambda>450$ nm was irradiated successively. When the pyridine solution had been saturated with carbon dioxide, the reduced species decreased with visible light irradiation. On the other hand, under a nitrogen atmosphere without carbon dioxide, no such tendency for the disappearance of the reduced species of **1** was observed. After the photoreaction under carbon dioxide, potassium hydroxide was added to the reaction mixture and the solvent was evaporated. The residual mixture was then

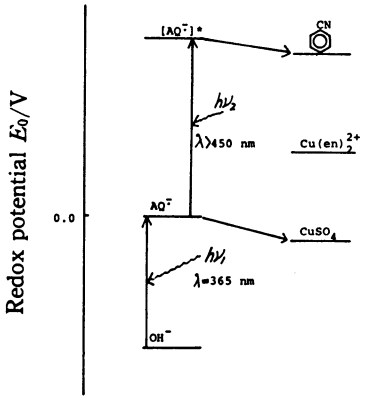

Fig. 10. Flow of electron in the electron transport system including **1** as a carrier by stepwise UV and visible light irradiations.

acidified with sulfuric acid and esterified with 1-butanol. GC-Mass spectra (column; Thermon 100, 150 °C) of the hexane solution extracted from the esterified reaction mixture indicated the presence of trace amounts of products (*m*/*e*; 281, 207, 57) which might be assigned to isomers of a dibutyl ester of dihydropyridinedicarboxylic acid. Since carbon dioxide did not affect the initial productions of the reduced species of **1**, carbon dioxide participated in the process after the photoreduction, that is, carbon dioxide could be incorporated in the acceptor cycle of the electron transport system to produce the addition products with pyridine.

In an attempt to establish an artificial photosynthesis which produces carbohydrate from water and carbon dioxide under illumination with sunlight, it is required to prepare a redox system which can cover a wide range of redox potential in order to carry an electron from hydroxide ion ($E_0$=2.0 V) to carbon dioxide ($E_0$ is in the neighborhood of −2 V) photochemically by one electron processes, if we use only organic materials without multi-electron conversion system such as semiconductors. As summarized in Fig. 10, the redox system including **1** as a carrier was demonstrated in this study to cover a wide range of redox potential (*ca.* 4 V) and may be useful for the purpose.

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