Photocatalysis through Excitation of Adsorbates. 3. Effect of Electron Acceptors on the Efficiency of Interfacial Charge Separation

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Charge separation in photoexcited rhodamine B–CdS–electron acceptor systems was investigated photochemically and photoelectrochemically, by using acceptors with different standard reduction redox potentials (E°_{red}) . The formal quantum efficiency (FQE) of N-deethylation of the dye after photoinduced electron injection into CdS (in photochemical suspension systems) and sensitized photocurrents flowing through a single-crystal CdS membrane separating the dye from an acceptor (in photoelectrochemical systems) were measured as a function of concentration of acceptors. Both FQE and sensitized photocurrents reflect the efficiency of charge separation between the dye and acceptors. Results indicate that charge separation occurs only in the presence of CdS and its efficiency rises as E°_{red} of the acceptor is more positive. The effectiveness of the present systems for photoinduced charge separation is discussed.

Introduction

The importance of charge separation at an interface has recently been given attention especially in the field of light energy conversion. Quite recently, Calvin¹ has summarized the importance of the charge transfer across a membrane in photosynthesis. Quantum conversion of green plants is performed on a membrane possessing an oxidation side and a reduction side, and an electron is transported from one side to other. The charge separating characteristics of the membrane suppress charge recombination and render the photosynthesis efficient.¹ Many studies have, therefore, been made on micelles,²⁻⁵ microemulsion,^{6,7} vesicles,^{8,9} semiconductor electrodes,¹⁰⁻¹⁹ and other artificial membranes²⁰⁻²² as simplified charge-transfer membranes.

In the previous paper we showed that N-deethylation of rhodamine B (RhB), initiated by electron abstraction from the dye, occurs through excitation of the dye adsorbed on suspended CdS particles.²³ Methylene blue whose energy level for electron donation from an excited state lies below the bottom of conduction band of CdS is, however, inactive under similar illumination conditions.²⁴ This fact implies that electron injection from excited RhB into the conduction band of CdS causes the reaction, which corresponds to the electron transfer mechanism of spectral sensitization.

The injected electron has to be removed from the semiconductor particle, otherwise the resulting electrostatic field prevents further charge transfer. Therefore, the coexistance of an appropriate electron acceptor such as oxygen is indispensable.²³ Since the acceptor should have a standard reduction redox potential (E°_{red}) situated below the conduction band of CdS, an electron transfer from excited RhB to the acceptor is energetically possible even in a homogeneous solution. In a homogeneous solution with oxygen as an acceptor, however, practically no reaction occurs upon excitation.²³ On the other hand, the dye can easily be N-deethylated photochemically on the surface of CdS with a quantum efficiency of at least 0.5. This is certainly due to the effectiveness of heterogeneous interface for charge separation. Most studies reported so far on the photoinduced charge separation with semiconductors are related to the charge transfer at a semiconductor electrode/electrolyte solution interface where either oxidation or reduction occurs. The present system is charcaterized by the simultaneous occurrence of oxidation and reduction on a common surface. Application of these

systems to conversion of light energy into other forms of energy requires more knowledge of interfacial charge separation. It would be of interest to examine the effect of acceptors other than oxygen on the charge separation in these systems.

We report here the effect of a series of acceptors on the efficiency of photoinduced charge separation in RhB-CdS-acceptor systems. For this purpose, two different approaches have been made: the measurement of photochemical N-deethylation of the dye in CdS-suspended systems on one hand, and the measurement of sensitized photocurrents in an electrochemical cell on the other hand. The latter measurement, conducted by using a singlecrystal CdS membrane electrode which can spatially separate the dye from an acceptor, is expected to provide information concerning only the interfacial charge transfer steps occurring in the suspension.

Experimental Section

All chemicals used were reagent grade. An aqueous solution of RhB containing ferric sulfate, cupric sulfate, cobaltous sulfate, or p-benzoquinone (p-BQ) as an acceptor was adjusted to pH 2.0 by sulfuric acid to avoid hydroxylation of metal ions. The solution (50 mL) and 0.5 g of CdS were introduced into a Pylex photochemical reaction cell. After deoxygenation of the cell by oxygen-free nitrogen, the suspension was illuminated with light from a 1-kW xenon lamp through an interference filter (Koshin Kogaku, 40% average peak transmittance, 10-nm halfband width). Analysis of the reaction mixture was performed with an ultraviolet and visible spectrophotometer (Shimsdzu, Model MPS-5000) and a high performance liquid chromatograph (JASCO, Model FLC-A700). A detailed procedure of the photochemical measurement is described elsewhere.23

For electrochemical measurements, the cell illustrated in Figure 1 was used. A CdS single crystal about 1 mm in thickness and with a cross section of 1 cm² was polished by alumina powder, etched with concentrated hydrochloric acid for 5 s, and washed with water. The crystal was fixed in the cell so as to separate the two compartments, I and II. Two electrolyte solutions containing 1.5×10^{-2} M sodium sulfate were adjusted to pH 2.0 and were introduced into the compartments. Two KCl agar bridges connected to SCE were immersed into the electrolyte solutions. A zero shunt ammeter (Nikko Keisoku Model NZ-1) was



Figure 1. A cell for photoelectrochemical measurement: (A) singlecrystal CdS membrane electrode; (B) agar bridges; (C) saturated calornel electrodes (SCE); (D) ammeter; (E) gas inlets for nitrogen bubbling; (F) quartz window for illumination. RhB is introduced into compartment I and an acceptor into II.

joined to the SCE. Under magnetic stirring and nitrogen bubbling, the cell was kept in the dark for 1 h, and then the blank photocurrent was measured with the same light source as in the photochemical measurements. After RhB was added to compartment I, the base photocurrent was measured. Measurements of effect of acceptors were performed after the addition of an appropriate amount of an acceptor to compartment II. It should be noted that the light incident on the electrochemical cell passes first through the acceptor solution without any attenuation and then through the CdS crystal before reaching the adsorbed RhB.

Adsorption of RhB on CdS was determined as follows: A RhB aqueous solution adjusted to pH 2.0, containing an appropriate amount of an acceptor and the same proportion of CdS as in the photochemical measurements, was mixed and kept in the dark for 0.5 h. Then the mixture was centrifuged and the absorbance of the supernatant solution was measured with the ultraviolet visible spectrophotometer to determine the amount of dye adsorbed on CdS.

Fluorescence quenching of RhB by the acceptors was measured with a fluorescence spectrometer (Hitachi Model MPF-4).

Results and Discussion

As was preliminally reported in the previous paper,²⁴ the Fe^{3+} ion promotes the photochemical N-deethylation of RhB in the presence of CdS and gives a FQE (formal quantum efficiency, the number of deethylated dye molecules per one incident photon) spectrum having a shape similar to that in the case of oxygen as an acceptor (Figure 2). The peak around 600 nm is ascribed to the excitation of RhB adsorbed on CdS, and the wavelength region shorter than 520 nm corresponds to absorption by CdS. Since our main interest is in the longer wavelength region where the excited dye injects an electron into the conduction band of CdS, experiments at 590 nm are mostly described hereafter.

In a homogeneous solution, the Fe³⁺ ion does not cause the photochemical reaction, which suggests that the charge separation between the excited dye and the acceptor is effective only through the intermediary of the conduction band of CdS. As with oxygen and the Fe³⁺ ion, acceptors whose E°_{red} are situated below the conduction band of CdS are expected to be effective for photochemical reaction. Furthermore, it is expected that the efficiency of charge



Figure 2. FQE spectrum of photochemical *N*-deethylation of RhB for the dye-CdS-Fe³⁺ system: initial dye concentration, 2.4×10^{-4} M; CdS suspended, 0.5 g/50 mL; deoxygenation for 3 h; illumination for 10 min. The solution pH was not controlled.



Figure 3. An energy diagram for RhB–CdS–electron acceptor systems at pH 2.0. Standard oxidation redox potentials of excited ($E^{\circ}(D^*/D^+)$) and ground state RhB ($E^{\circ}(D/D^+)$) have been determined previously.²³

transfer steps depends on $E^{\circ}_{red.}$ of the acceptor. The value of FQE for the *N*-deethylation of the dye should reflect this efficiency.

Values of FQE for the reaction were compared as a function of $E^{\circ}_{red.}$ of selected acceptors Fe^{3+} , Cu^{2+} , Co^{2+} , and p-BQ. The positions of $E^{\circ}_{red.}$ of the acceptors and those of standard oxidation redox potential E°_{ox} of excited and ground state RhB are shown in Figure 3 together with levels of the conduction and the valence band of CdS. The bottom of the conduction band is situated between $E^{\circ}_{red.}$ of the acceptors and E°_{ox} of the excited dye in all cases. This suggests that all acceptors employed can trap the conduction band electron.

All experiments except for the one shown in Figure 2 were done at pH 2.0 to avoid hydroxylation of the metal ions. Without any pH control or additives RhB aqueous



Figure 4. Dependence of the FQE on the concentration of acceptors; (O) Fe^{3+} , (\bullet) Cu^{2+} , (\times) Co^{2+} , and (Δ) p-BQ: initial dye concentration, 10^{-4} M; CdS suspended, 0.5 g/50 mL; illumination at 590 nm for 20 min. Prior to the illumination, the solution pH was adjusted to 2.0 and the solution was deoxygenated by nitrogen bubbling for 3 h.

solution shows a pH value around 4-5. It should be noted that the FQE of the reaction depends on the pH of the dye solution. In the pH region lower than about 6, FQE is nearly constant. As the pH increases from 6, FQE decreases and approaches 0 at pH 12. This pH dependence was found to result from the pH-dependent adsorption of the dye on CdS.

The dependence of the values of FQE on the concentration of the acceptors is shown in Figure 4. This experiment was performed with 10^{-4} M RhB solutions and a 590-nm light. The value of FQE decreases with deoxygenation of the suspension, but probably because of the insufficiency of deoxygenation, FQE values at lower acceptor concentrations remain 0.02–0.03. As expected, the three metal ions can promote to some extent the photochemical N-deethylation of RhB on CdS. On account of changes of the CdS surface (deposition of sulfides of acceptor ions or reduced metals), however, Co^{2+} and Cu^{2+} tend to suppress the reaction at higher concentrations. The peak value of FQE increases, nevertheless, as E°_{red} . becomes positive in the order of Co^{2+} , Cu^{2+} , and Fe^{3+} .

Contrary to expectation, p-BQ, whose E°_{red} lies between those of Fe³⁺ and Cu²⁺, seems inhibitive. Photochemical N-deethylation of RhB is actually suppressed, but it was confirmed spectrophotometrically that p-BQ provokes a photochemical bleaching of the dye in the presence of CdS. In a homogeneous solution p-BQ loses the ability to promote the bleaching reaction; this suggests that the reaction is also the result of electron transfer from excited dye to p-BQ via CdS. On the surface of a CdS particle, coexistence of the dye with the acceptor is capable of bringing about various interactions of unspecified nature which seem to cause the bleaching reaction.

Changes in adsorption equilibrium by the addition of acceptors will affect the value of FQE since only the light absorption by the adsorbed dye is effective for the *N*deethylation. The adsorbed amount of RhB on CdS is shown in Figure 5 as a function of concentration of acceptors. The initial dye concentration is 10^{-4} M and the amount of CdS is 0.5 g in 50 mL of solution. The variation of the adsorbed amount has no clear relation to E°_{red} of acceptors (see Figure 3). Moreover, a comparison of Figures 4 and 5 indicates that the influence of the acceptors on the adsorption characteristics of RhB on CdS does not



Figure 5. Amount of RhB adsorbed on CdS in the dark as a function of acceptor concentration; (O) Fe³⁺, (\bullet) Cu²⁺, (\times) Co²⁺, (Δ) p-BQ; initial dye concentration, 10⁻⁴ M; CdS suspended, 0.5 g/50 mL.



Figure 6. Photocurrent spectra measured in the electrochemical cell with oxygen as an acceptor (the electrolyte solution in compartment II was saturated with air): (O) photocurrent spectrum in the presence of 10^{-4} M RhB in compartment I; (\bullet) base photocurrent spectrum without dye. Both spectra have been corrected for the number of incident photons.

directly affect the photochemistry of the dye within the experimental conditions employed.

For the purpose of studying the photoinduced electron transfer processes to and from the semiconductor, the following electrochemical measurements were carried out with the electrochemical cell shown in Figure 1. A CdS single-crystal membrane separating two electrolyte solutions is a simplified model for a single CdS powder particle on which the electronic processes from an excited dye to the conduction band of CdS and from the latter to an acceptor may occur. Using this membrane electrode, we can detect a flow of electrons from one side of the membrane to the other as a photocurrent, if photoinduced charge transport really takes place.

Illumination of the system gives photocurrents whose action spectra are shown in Figure 6. Even when the



Figure 7. Dependence of photocurrent on the concentration of acceptors; (O) Fe^{3+} , (\bullet) Cu^{2+} , (X) Co^{2+} , and (Δ) p-BQ at pH 2.0: initial dye concentration, 10^{-4} M; illumination at 590 nm; under nitrogen bubbling.

electrolyte solutions contain neither dye nor acceptor, some photoresponse exists in this spectral region, but the addition of 10⁻⁴ M RhB into I results in a definite increase in the photocurrent around 590 nm (sensitized photocurrent) which further increases by the addition of acceptors into II. These results correspond to the electron injection from the excited dye molecules, adsorbed at the solution I-CdS interface, into the conduction band of the crystal and the capture of the electrons by acceptor molecules at the solution II-CdS interface. The decrease or even reversal of the photocurrent in the wavelength region shorter than 550 nm can be explained by the increase in the absorptivity of CdS. As the absorptivity increases, the penetration depth of light into CdS decreases and the photogeneration of carriers takes place near the illuminated side of the membrane. The photogenerated electrons and holes are, due to band bending, driven into the bulk and to the surface of CdS, respectively, thus giving rise to an electron flow from II through CdS to I.

The dependence of sensitized photocurrent ($\lambda = 590$ nm) on the concentration of acceptors is shown in Figure 7. The magnitude of the base photocurrent (without acceptors) depended on the pretreatment of CdS surface, while the blank photocurrent (without dye and acceptors) was almost the same for each measurement.

The results shown in Figure 7 demonstrate that the magnitude of the saturated photocurrent corrected for the base photocurrent is larger with an acceptor having a more positive $E^{\circ}_{red.}$ (see Figure 3). Similarly, the value of C_{A} at the rising point of photocurrent is smaller with an acceptor having a more positive E°_{red} . Regarding these behaviors, we find that p-BQ is no exception, in contrast to the photochemical results described above. This indicates that all acceptors used can readily capture electrons from the conduction band of CdS. In the electrochemical cell, the dye must be subjected to the same reaction regardless of the nature of acceptors because the surroundings of the dye (in I) remain unaffected by the addition of acceptors in II. The photochemical bleaching reaction which takes place readily in a RhB-CdS-p-BQ heterogeneous suspension does not occur in a homogeneous solution without CdS. Judging from these results, the bleaching reaction must involve a half-oxidized dye and a semiquinone, though a detailed mechanism remains to be clarified.

The saturated sensitized photocurrent corrected for the base photocurrent is plotted in Figure 8 as a function of



Figure 8. Saturated photocurrent as a function of standard reduction redox potential (E^{o}_{red}) of acceptors converted from Figure 7. The points correspond, from left to the right, to Co²⁺, O₂, Cu²⁺, p-BQ, and Fe³⁺.

 $E^{\circ}_{red.}$ of acceptors. The point for O_2 is the result of measurement with compartment II saturated with air. From the tendency in Figure 8, together with Figure 3, there seems to be a threshold for electron acceptability near the bottom of conduction band.

The results described above support the assumption that the conduction band of CdS mediates the charge separation between an excited RhB and an electron acceptor. For charge separation to proceed efficiently, E°_{red} of the acceptor must be more positive than E°_{ox} of the excited dye. Hence, even in a homogeneous solution containing RhB and an acceptor, electron transfer from the excited dye to the acceptor should be thermodynamically favorable. This may result in an oxidative quenching of excited state of the dye by the acceptor. It was confirmed by measuring the fluorescence quenching of RhB that the rate of fluorescence quenching increases in the order of Co²⁺, Cu²⁺ Fe^{3+} and the quenching is oxidative. No photochemical N-deethylation, however, occurs in a homogeneous solution with all acceptors studied. A reverse electron transfer, from the reduced acceptor to the resulting dye radical cation, may immediately follow the initial photoinduced transfer, since the dye molecule must exist close to the acceptor at the moment of homogeneous electron transfer.

In conclusion, the acceptors which possess $E^{\circ}_{red.}$ lying below the bottom of conduction band of CdS can capture electrons from the conduction band injected by excited RhB molecules, and the efficiency of the electron separation depends on $E^{\circ}_{red.}$ of acceptors. The efficiency is reflected in the FQE of the *N*-deethylation of the dye, and the FQE tends to increase as $E^{\circ}_{red.}$ of acceptors becomes positive.

The high efficiency of the photochemical *N*-deethylation of RhB in a CdS-suspended system compared with a homogeneous solution is ascribed to the effectiveness of CdS in separating electrons between the excited dye and acceptors. The space charge layer, existing near the surface of the semiconductor, enables an injected electron to leave the interface rapidly and prevents a reverse electron transfer. The conduction band can transmit the injected electron from one site to another, where the electron is captured by an acceptor. Hence a chemical reaction of the dye can proceed with high efficiency before charge recombination takes place.

The results of the present investigation demonstrate that a photoelectrochemical technique of using a membranetype semiconductor can provide valuable information concerning photoinduced charge separation processes occurring on a semiconductor particle suspended in a dye solution.

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Catalytic Conversion of Alcohols. 15. Alkene Selectivity from the Conversion of 2-Octanol over Hafnium-Zirconium Mixed Oxide Catalysts

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Publication costs assisted by Institute for Mining and Minerals Research

The substitution of Zr ions for Hf does not alter the 1-octene selectivity from that of pure HfO₂ until 0.70-0.85 mole fraction Zr, whereupon the selectivity abruptly changes to that of pure ZrO₂.

The catalytic activities and selectivities for hydrocarbons conversions vary among the group VIIIB metals.¹ In many cases, the catalytic parameters change uniformly with position within the group. They may be altered by alloying two or more of the metals^{2,3} even though the surface compositions may vary significantly from the bulk composition for some of the alloys.⁴ The purpose of this study was to look for catalytic activity and selectivity changes for oxide systems as a different metal ion is substituted for the metal atoms in a pure oxide.

Hafnium and zirconium mixed oxides should be an ideal system to carry out a study with mixed oxides that would parallel the studies with metal alloy catalysts. Our earlier study shows that zirconia⁵ forms greater than 90% 1-octene from the dehydration of 2-octanol while hafnia produces only 30-33% of the 1-octene isomer.⁶ The precipitation of the mixed hydroxide should not lead to surface enrichment since the solubilities are so similar that separation of the two elements is not possible by fractional precipitation of the hydroxide.⁷ The free energies of the oxides are so similar that surface enrichment should not occur after calcination.⁸ This, together with the same crystal structure and ionic size, should permit uniform solid solutions over the entire composition; this has been verified for mixtures after high temperature calcination.⁹ Furthermore, the same valence of the metal ions and the difficulty of reducing the oxides⁸ should eliminate the necessity of introducing a third ion to maintain electrical neutrality as is the case in some mixed oxides such as silica-alumina where the hydrogen ion imparts protonic acidity.

The pure and mixed metal hydroxides were prepared by precipitation from a rapidly stirred aqueous solution by the rapid addition of about a fivefold excess of concentrated ammonium hydroxide. The hafnium(IV) solution was prepared by dissolving the metal in hydrofluoric acid, precipitating the hydroxide, and then redissolving in the minimum amount of an approximately equal mixture of hydrofluoric and hydrochloric acids. The zirconium(IV) solution was prepared by dissolving zirconyl nitrate in water. Appropriate volumes of these solutions were mixed to give the desired Hf-Zr composition with a concentration of about 20 g of metal oxides per liter. The mixed hydroxide, after drying at 120 °C, was calcined at 600 °C in air for 18 h. The surface area for all oxides was in the range 18–35 m^2/g ; it increased uniformly from the