"PHOTOCATALYTIC REACTIONS USING DYES AND SEMICONDUCTORS"

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[General Introduction]

The conversion of solar energy to chemical energy has been actively investigated over the last ten years originating from the so-called "First Energy Crisis ". Fujishima and Honda reported in 1972 that n-type titanium dioxide (TiO_2) single crystals show a photovoltaic effect in aqueous solution accompanying the decomposition of water into hydrogen and oxygen. This phenomenon has received much attention as the basis for a system to convert solar energy directly into stable fuels.

On the other hand, photochemical reactions, especially oxygen producion from water, making use of an electron-hole pair in the excited semiconductor powders such as titanium dioxide, zinc oxide (ZnO) and tungsten oxide (WO_3) had been reported by A.A.Krasnovski and his co-workers since 1962. In these cases, the semiconductor powders work as micro electrodes. In the mid-1970's, Tamura and Yoneyama showed that water is decomposed to hydrogen and oxygen quantitatively by the irradiation of an aqueous suspension of strontium titanate ($SrTiO_3$). Subsquently it was reported by several researchers independently that the water splitting reaction proceeds more efficiently by using a metal or metal oxide-loaded semiconductor powder. In 1981 Kawai and Sakata reported hydrogen-producing systems in which various organic compounds were used as electron donors instead of water. They found that the quantum efficiency of hydrogen production is 10~3000 times larger than that of water alone. Organic compounds are oxidized finally into carbon dioxide via various oxidation products which react with water when a semiconductor having strong oxidizing power (of the deep valence band) is used. The reaction processes are not known well, but they suggest the possibility of a new method for organic synthesis by isolating the intermediates.

In 1977 A.E. Shilov and his co-workers reported a homogeneous water splitting method in which a dye works as the light absorber. At this point in time a lot of similar research results were also reported. However most systems used only $Ru(bipy)_3^{2+}$ or water-soluble zinc porphyrins as the sensitizer. The final purpose of these studies is the complete decomposition of water, that is, the simultaneous production of hydrogen and oxygen. In 1979 M. Grätzel and his co-workers reported the complete decomposition using $Ru(bipy)_3^{2+}$, methylviologen, colloidal Pt and colloidal RuO_2 as the sensitizer, electron relay, reduction catalyst and oxidation catalyst, respectively. However no laboratory has been able to reproduce their results. Most reliable results are obtained only for the half decomposition of water, that is, hydrogen production in the presence of a reducing agent or oxygen production in the presence of an electron acceptor.

These dyes and semiconductor powders work catalyically as the energy carrier to water, and were called photocatalysts. Their reactions are called photocatalytic reactions.

In the present study, we investigated new methods of hydrogen production from water using various dyes as photocatalysts (Chapter I, Chapter II), and photocatalytic reactions of aliphatic and aromatic hydrocarbons with water using a semiconductor powder as the photocatalyst (Chapter III).

In Chapter I, section 1 we describe hydrogen production from water with visible light based on the dye-sensitization process of a semiconductor powder. Most semiconductors which are stable in an electrolyte solution have wide band-gaps, so that only UV light can be absorbed. However, from the viewpoint of solar energy conversion, the utilization of material which can absorb visible light is indispensable. Dye-sensitization of a semiconductor is known to be one of the ways of extending the wavelength of light available into visible region in a photoelectrochemical cell. The method described here is an application of this method to a powdered semiconductor photocatalyst. Most systems reported before contains methylviologen as an electron relay. In the present system, however, it is not necessary because the semiconductor powder serves as an electron carrier. I was able to observe hydrogen production based on this process and estimate the quantum yields of both hydrogen production and electron transfer. Moreover the possiblity of an efficient hydrogen production system based on this process could be shown. In section 2 the dynamic process of dye-sensitization is studied by a spectroscopic method. That is, $Ru(bipy)_3^{2+}$ is used as a sensitizer and is adsorbed on some semiconductors or micro crystalline methylviologen which is known to be a good electron accepter. The luminescence decay and time resolved spectra were measured. The results were compared with those obtained for the dye in aqueous solution and for the dye adsorbed on an insulator (SiO_2). Based on these results, the electron transfer rate and the spectral shift derived from the different adsorption sites are discussed.

In chapter II the hydrogen-producing method using dyes and platinized titanium powder is also described. However the reaction process is quite different from that described in Chapter I. In section 1 I demonstrate that several halogenated fluorescein derivatives also serve as very efficient sensitizers in addition to $Ru(bipy)_3^{2+}$ and water-soluble zinc porphyrin. These systems are efficient in the high pH region. Usually the photocatalytic reaction using a dye is possible only in acidic solution (pH = 5). However the system described in this chapter works well in the high pH region of 11~13. This is the first example using a dye in which hydrogen production is possible in the high pH solution. In section 2 the dynamic process of this system is studied by spectroscopic and photoelectrochemical measurements in order to elucidate the reaction mechanism. As a result, it was shown that the dye molecules are photo-reduced in the bulk solution to a very stable semi-reduced dye whose lifetime is more than 15 seconds, and this radical diffuses to the surface of a reduction catalyst initiating the electron transfer. This transferred electron is used for the hydrogen production. This process is the same as that of a photogalvanic cell in photoelectrochemical processes. Thus I named this a photogalvanic type hydrogen-producing system.

In Chapter III I describe the photocatalytic reactions of water with organic compounds using a semiconductor powder as the photocatalyst. First, hydrogen production from water with some aliphatic hydrocarbons and aromatic compounds were studied in section 1 as a part of the hydrogen-producing system I had studied in which organic compounds served as the reducing agent to water. Moreover, as an extention of this subject, some fossil fuels such as coal, tar-sand and pitch were chosen as the organic compounds. These fossil fuels, which exist in large quantities on the earth, have been of interest as energy sources after oil is no longer readily available. Many methods have been reported which are related to the gasification or liquefaction of fossil fuels, especially for coal. All the methods are based on thermal reactions. In the present photocatalytic method, however, light energy is used instead of heat and the reaction proceeds around room temperature. The present method can be thought of as the new gasification method for fossil fuels. In section 2 the photocatalytic oxidation processes of a linear saturated hydrocarbon and benzene in aqueous mixtures were studied by detecting the oxidation products in gaseous and aqueous media. It is characteristic in these reactions that carbon dioxide is produced even at an early stage in the irradiation. This property is quite different from that of the alcohol-water system in which carbon dioxide is produced only after prolonged irradiation. Hence, the details of the reaction, especially the mechanisms of carbon dioxide production are discussed.

Chapter I

Hydrogen Production in Dye-Sensitized Semiconductor Systems.

§1 Hydrogen Production

[Abstract]

Hydrogen was produced from water by exciting various organic dyes on TiO_2 or Pt/TiO_2 with visible light in the presence of reducing agent. The quantum efficiency of hydrogen production was estimated to be in the order of 10^{-1} for $Ru(bipy)_3^{2+}$ with EDTA as the reducing agent. It is postulated that hydrogen is produced by the reduction of water through dye-sensitized process.

[Introduction]

The photo-induced water splitting reaction in which TiO_2 or $SrTiO_3$ is used as a photocatalyst has been investigated by many researchers.[1-7] Hydrogen production has also been reported in the photocatalytic reaction of water with various organic compounds in which powdered semiconductors are used.[8-11] However, most semiconductors which are stable under irradiation in an electrolyte solution have wide band-gaps. They absorb mainly UV light. The utilization of dye-sensitization appears to be a promising means of extending the effective wavelength into the visible region. There have also been many reports of hydrogen production with visible light using dyes such as $Ru(bipy)_3^{2+}$ or water soluble zinc porphyrin in a homogeneous system.[12] In such a system, an electron relay such as methylviologen plays an important role in charge separation. We here report a system for hydrogen production by dye sensitization of a semiconductor (TiO_2) in which an electron relay is not necessary; rather, excited dye molecules near the semiconductor powder inject electrons to the conduction band. Grätzel et al. reported the complete water splitting reaction with the same electron relay free system by using $Ru(bipy)_3^{2+}$ analogues[12-j] or $Ru(bipy)_3^{2+}$[12-l] as sensitizer.

[Experimental]

As a semiconductor, very fine powdered TiO_2 (anatase, average grain size: 300 Å, Aerosil P-25) with a large surface area, 50 m^2/g, was used. Pt was deposited photochemically on the surface of TiO_2. Powdered TiO_2 (3g) suspended in a water-ethanol solution (20 % aq. soln, 100 ml) of K_2PtCl_6 (0.3 g) was illuminated with a 500W-Xe lamp (Ushio, UXL500).[13] The particle size of platinum on TiO_2, which is prepared with this photochemical method, is known to be about 20-100 Å.[11,14] $Ru(bipy)_3Cl_2$, various water soluble porphyrins and some other organic dyes served as sensitizers. EDTA or methanol was the reducing agent.

In the liquid phase experiment, platinized TiO_2 powder (0.1 g) was suspended in an aqueous solution of each dye (10^{-4} M, 50 ml) with a reducing agent (EDTA : 5×10^{-2} M or methanol : 50 vol %) in a 280-ml Pyrex glass flask. The pH of the solution was adjusted to 5 with HCl or NaOH. After deaeration the flask was irradiated from the bottom with visible light (500W-Xe lamp : a Toshiba sharp cut filter eliminated UV light). After irradiation for several hours, gaseous reaction products were trapped at -196°C or -40°C, and was analysed by a quadruopole mass spectrometer (Anelva, AGA-360).[8] The mass-spectrometric analysis of the gaseous products which could not be trapped at -196° C showed that hydrogen was the main component. The quantity of hydrogen gas produced was determined from the pressure using a sensitive manometer (Data metrics INC., barocel pressure sensor).

In the vapor phase experiment, $Ru(bipy)_3Cl_2$ was adsorbed as follows. The TiO_2 powder was soaked in a methanol solution of the dye and the solvent was evaporated by evacuation ($Ru(bipy)_3Cl_2/TiO_2$: 0.01 wt %). This semiconductor-dye photocatalyst was put into the flask described above and methanol-water vapor was introduced from a side glass flask. For the measurement of the apparent quantum yield of hydrogen production in $Ru(bipy)_3^{2+}$-TiO_2/Pt, monochromatic light at 460 nm, provided by a 500W Xe lamp and a monochromator (Nikon G250), was used to excite only the dye molecules. The photon number was determined by using a thermopile (Eppley Inc.).

The amount of $Ru(bipy)_3^{2+}$ adsorbed on the TiO_2 powder was estimated by measuring the change of the absorption intensities of the solution before and after addition of the TiO_2 powder. The absorption spectra were measured on a Hitachi 556 spectrometer. In order to avoid scattered light effects, the spectrum of the solution to which TiO_2 was added was measured after the powder was removed by using an ultracentrifuge (40000 rpm, 30 min. Beckmann Co.).

[Results and discussion]

In Table I are shown the results of the liquid phase experiments. When methanol was used as the reducing agent, the hydrogen production rate did not increase upon addition of $Ru(bipy)_3^{2+}$ into the solution [Run Nos. 12,13]. However, when EDTA was used as the reducing agent, the rate in the presence of $Ru(bipy)_3^{2+}$ was about 8 times larger than that in the absence of the dye [Nos. 9,10]. When D_2O was used instead of H_2O, D_2 was 90 % of the evolved hydrogen gas, DH 5 % and H_2 5 %. This result indicates that hydrogen is generated through the reduction of protons from water in this Dye-Pt/TiO_2 system as well as in Pt/TiO_2 systems in which band gap irradiation of the semiconductor is employed.[8,9,15] Small amounts of hydrogen could be produced in the presence of Pt/TiO_2 even without dyes [Nos. 8,13], probably becasue of the absorption of visible light by the surface states of TiO_2. Besides $Ru(bipy)_3^{2+}$, several dyes in Table I were found to be effective for hydrogen production. The hydrogen production rate was increased by more than a factor of 10 [Nos. 1-8]. Since it is known that they are able to sensitize semiconductor electrodes (ZnO, SnO_2 and TiO_2),[16] the present results suggest that hydrogen is produced via a dye-sensitization effect.

For dye-sensitization, the reaction scheme of hydrogen

Table I. – Rate of hydrogen production on Dye-Pt/TiO_2 system in the liquid phase. Light source: 500 W Xe lamp. (*) Pt/SiO_2 instead of Pt/TiO_2.

Run	Dye	Red. agent	Rate (μmol/h)	Light
1	Zn-TPPS	EDTA	1.6	λ>480 nm (filter Y-48)
2	Pd-TPPS	EDTA	<0.4	
3	H_2-TPPS	EDTA	<0.4	
4	Safranine T	EDTA	3.4	
5	Rhodamine B	EDTA	1.0	
6	Rhodamine 6G	EDTA	3.0	
7	Rose Bengal	EDTA	5.6	
8	none	EDTA	0.4	
9	Ru(bipy)$_3^{2+}$	EDTA	4.6	λ>440 nm (filter Y-44)
10	none	EDTA	0.6	
11	Ru(bipy)$_3^{2+}$ (*)	EDTA	0.0	
12	Ru(bipy)$_3^{2+}$	methanol	<0.5	
13	none	methanol	0.5	
14	none	EDTA	220	white light (no filter)
15	none	methanol	270	

production is written as,

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^{*} \tag{1}$$

$$\text{Dye}^{*} \longrightarrow \text{Dye}^{+\cdot} + e^{-}(\text{TiO}_2) \tag{2}$$

$$e^{-}(\text{TiO}_2) + \text{H}^{+} \xrightarrow{\text{Pt on TiO}_2} 1/2\text{H}_2 \tag{3}$$

$$\text{Dye}^{+\cdot} + \text{Red} \longrightarrow \text{Dye} + \text{Red}^{+\cdot} \tag{4}$$

$$\text{Red}^{+\cdot} \longrightarrow \text{Oxidation products} \tag{5}$$

Here $e^{-}(\text{TiO}_2)$ and Red represent an electron in the conduction band of TiO_2 and a reducing agent, respectively. Figure 1 illustrates the hydrogen production process resulting from dye sensitization of the TiO_2 semiconductor. This process is quite similar to that of the dye-sensitized semiconductor electrode in a photoelectrochemical cell.[16] Another mechanism of hydrogen production is possible. It involves reductive quenching of the excited dye as follows:

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^{*} \tag{6}$$

$$\text{Dye}^{*} + \text{Red} \longrightarrow \text{Dye}^{-\cdot} + \text{Red}^{+\cdot} \tag{7}$$

$$\text{Dye}^{-\cdot} + \text{H}^{+} \xrightarrow{\text{Pt or Pt/TiO}_2} \text{Dye} + 1/2\text{H}_2 \tag{8}$$

$$\text{Red}^{+\cdot} \longrightarrow \text{oxidation products} \tag{9}$$

This possibility is ruled out especially for Ru(bipy)_3^{2+}-EDTA in Table I for the following reasons. Firstly, hydrogen was not produced when Pt/SiO_2 was used instead of Pt/TiO_2 as seen in No. 11 of Table I. If the mechanism of reductive quenching, i.e. eqs. 6-9, is true in this case, hydrogen should be produced even for Pt/SiO_2. Actually, for fluorescein derivatives, which are reduced according to eq. 7 with treithanolamine (TEOA) as a reducing agent,[17] hydrogen is produced very efficiently with colloidal Pt or Pt/SiO_2 (hydrogen evolution rate: 320 μmol/h for dibromofluoresceine), since hydrogen production is possible without a semiconductor in this case, which is shown in Chapter II. This fact indicates that the dye sensitization is indispensable for $Ru(bipy)_3^{2+}$-EDTA-Pt/TiO_2.

Secondly, the luminescence of $Ru(bipy)_3^{2+}$ is quenched by TiO_2[18,19] as well as by MV^{2+} [12(d),(i),19] through an electron transfer process from the excited dye to these electron acceptors, although it is not quenched by EDTA,[12(d)(i)] which is shown in §2. This means that the rate of reduction of $Ru(bipy)_3^{2+*}$ is very slow compared with oxidative quenching. The mechanism of reductive quenching of excited dye can also be distinguished from the dye sensitization mechanism by using an electrochemical method, since the reductive quenching corresponds to a photogalvanic process in which electroactive species are accumulated in the bulk solution. For instance, in a photoelectrochemical cell with fluorescein derivatives and TEOA, the rise and decay time of the short circuit current and open voltage are quite slow (several ten seconds to several minutes) and depend on the thickness of the solution layer between a glass window and the metal (Pt) or semiconductor (ZnO, TiO_2) electrode.[17] This slow response can be explained by a gradual accumulation and diffusion of long-lived electroactive species which are generated by a photochemical redox reaction in the homogeneous solution. On the other hand, the rise time of the photocurrent in a photoelectrochemical cell based on dye sensitization is very rapid.[16,20,21] Such a rapid response was observed for an electrochemical cell with $Ru(bipy)_3^{2+}$-H_2O and Rose Bengal-hydroquinone, I_2 or EDTA. These results are shown in Chapter II. All these facts indicate that the hydrogen production from $Ru(bipy)_3^{2+}$-EDTA-Pt/TiO_2 occurs through a dye sensitization process. The hydrogen production by dye sensitization seems to be applicable also to the cases with other dyes (Nos. 1,4,5,6,7 in Table I), since it is well known that all these dyes are able to sensitize semiconductor electrodes (ZnO, SnO_2, TiO_2) in electrochemical cells.[16] Generally speaking for the systems using dyes which are soluble in an aqueous medium, hydrogen is produced more efficiently for the photogalvanic cases than for dye sensitization of semiconductor. This is because in the former cases the reduced species, responsible for hydrogen production, are formed in the bulk solution, whereas, in the latter cases, only the dyes near the semiconductor surface are involved in the electron transfer to the semiconductor.

Besides $Ru(bipy)_3^{2+}$, Rose Bengal, Safranine T and Rhodamine 6G showed rather a good effect (Nos. 4,6,7 in Table I). Rose Bengal, however, was not stable under long-time irradiation. The hydrogen production rate decreased gradually and became zero after 10 to 20 hours irradiation. Safranine T and Rhodamine 6G were relatively stable compared to Rose Bengal, but the rates also decreased gradually. $Ru(bipy)_3^{2+}$ was very stable and the rate did not change after more than 40 hours irradiation. For Pd-TPPS and H_2-TPPS, the effect was negative (Nos. 2 and 3 in Table I). It suggests that it is difficult for these dyes to sensitize TiO_2 and that the number of photons absorbed by the surface states of TiO_2 is decreased by the absorption by these dye molecules.

Since a hydrogen production rate of 0.1 μmol/hour corresponds to 5.3 μA of photocurrent in a photochemical cell, the rate for Rose Bengal-Pt/TiO_2 given in Table I, 5.6 μmol/hour, corresponds to a photocurrent of 300 μA. This value is quite large compared to even the largest photocurrent in a dye-sensitized semiconductor photochemical cell.[16] On the other hand, the hydrogen production rates achieved by dye-sensitization of platinized TiO_2 powder are about a hundred times smaller than those achieved by band gap excitation of platinized TiO_2 powder [Nos. 14,15]. The apparent quantum efficiency of hydrogen production (2 X the number of H_2 molecules produced/the number of the incident photons) in the dye sensitization system listed in Table I is quite small, in the order of 10^{-3}. It was measured to be $1.7 \cdot 10^{-3}$ for $Ru(bipy)_3^{2+}$-TiO_2/Pt by using monchromatic light at 460 nm, where $Ru(bipy)_3^{2+}$ shows an absorption maximum. However, this low value does not mean that the actual quantum yield of hydrogen production (2 X the number of H_2 molecules produced/the number of photons which were absorbed by the dye molecules involved in the dye-sensitized electron transfer reaction) is much smaller than that achieved by direct excitation of TiO_2, because only a relatively small number of dye molecules are able to participate in hydrogen production and only a small fraction of the incident light is absorbed by these molecules.

Actually the quantum yield for the $Ru(bipy)_3^{2+}$-TiO_2/Pt system is probably larger than 0.3. This value was estimated as follows. As was outlined in the Experimental section, the amount of $Ru(bipy)_3^{2+}$ adsorbed on the powdered TiO_2 was estimated by measuring the change of the absorption intensities of the solutions before and after addition of the powdered TiO_2. The change of absorbance in the dye solution ($1.0 \cdot 10^{-4}$ M, 50 ml) was less than 0.005 after addition of powdered TiO_2 (1.0 g, 50 m^2/g surface area). This value correponds to less than $2.5 \cdot 10^{-8}$ mol of adsorbed dye, and constitutes a 1/4000 monolayer on TiO_2. Here we assumed that

$Ru(bipy)_3^{2+}$ was a sphere with a radius of 5Å. In our hydrogen production experiment, it is less than $2.5 \cdot 10^{-9}$ mol since 0.1 g of TiO_2 was used. The absorbance of these adsorbed molecules can be calculated with the aid of the Beer-Lambert equation (eq. 10).

$$\log(I_0/I) = \varepsilon c d, \ \varepsilon = 10000 \ \mathrm{cm}^{-1} \mathrm{l}^{-1} \qquad \text{(at 460 nm)} \qquad (10)$$

The concentration (c mol/l) is given by eq. (11), in which it is assumed that the dye molecules are uniformly distributed in the total volume of TiO_2 powder (V cm^3). The path length (d cm) is calculated from eq. (12).

$$c = N_{ad.}/(10^{-3} \cdot V) = (2.5 \cdot 10^{-9})/(10^{-3} \cdot V) \qquad (11)$$

$$d = V/A = V/20 \qquad (12)$$

Here, $N_{ad.}$(mol) and A(cm^2) represent the number of adsorbed dye molecules and the irradiated surface area (20 cm^2), respectively. Using these equations the absorbance of adsorbed dye is calculated to be below $1.3 \cdot 10^{-3}$, so that less than 0.3 % of the incident light is absorbd by the adsorbed molecules. In addition to these adsorbed molecules, it is possible for exci~~a~~ted molecules in the bulk solution to inject electrons into the semiconductor by diffusing to the surface during their lifetime. Since the excited state of $Ru(bipy)_3^{2+}$ has a relatively long lifetime ($\tau = 6.0 \cdot 10^{-7}$ s [22]), this contribution cannot be neglected. It can be estimated as follows. The diffusion length (L cm) of the excited molecules is given by $L = \sqrt{\tau \cdot D}$ (D:diffusion coefficient), and is calculated to be $2.5 \cdot 10^{-6}$ cm by assuming $D = 10^{-5}$ $cm^2 s^{-1}$. The absorbance of this layer is calculated to be $1.0 \cdot 10^{-3}$ from eq. (10) assuming that the concentration and the path length are given by eq. (13) and eq. (14).

$$c = \frac{1}{6} c_1 \ {}^{23} = 10^{-4}/6 \qquad (mol/l) \tag{13}$$

$$d = LS/A = (2.5 \cdot 10^{-6})(5 \cdot 10^{4})/20 \qquad (cm) \tag{14}$$

Here, c_1 and S represent the concentration of the solution ($1.0 \cdot 10^{-4}$ M) and the surface area of TiO_2 powder ($5 \cdot 10^4$ $cm^2/0.1$ g TiO_2), respectively. Consequently, the ratio of light absorbed by the dye molecules that are involved in the electron transfer to the incident light is given by

$$\log(I_0/I) < 1.3 \cdot 10^{-3} + 1.0 \cdot 10^{-3}, \qquad I/I_0 > 0.995 \tag{15}$$

The quantum yield is given by

$$Q.Y. = (I_0/I_0 - I) \cdot Q.Y._{apparent} > 0.3 \tag{16}$$

These results suggest that the efficiencies of electron transfer from the excited state dye to the semiconductor and the hydrogen production are high. This value is close to the yield of electron transfer in dye sensitized photochemical cells. Memming et al. reported that the quantum yield of transferred electrons to absorbed photons was 0.15 in a monolyer of $Ru(bipy)_3^{2+}$ analogues on the SnO_2 electrode.[20]

In order to investigate this effect further, hydrogen production in the gaseous phase was carried out using $Ru(bipy)_3Cl_2$ and methanol as sensitizer and reducing agent, respectively. The result is shown in Table II. A comparison with the rates obtained without dye or TiO_2, clearly indicates that hydrogen production in the TiO_2-$Ru(bipy)_3^{2+}$ system results mainly from the sensitization effect of $Ru(bipy)_3^{2+}$.

Table II. – Sensitization effect on hydrogen production from saturated methanol-water vapor by $Ru(bipy)_3Cl_2$ on powdered TiO_2. Light source: 500 W Xe lamp with filter Y-44 ($\lambda > 440$ nm) (*) 30 hours irradiation. (**) White light from Xe lamp. Dye concentration: 0.01 wt/wt % (1/600 monolayer).

Photocatalyst	Quantity of H_2 (μmol) (*)
TiO_2	2.1
TiO_2-$Ru(bipy)_3Cl_2$	26
SiO_2-$Ru(bipy)_3Cl_2$	0
TiO_2 (**)	340

The rate is about ten times smaller than that resulting from direct band gap excitation of TiO_2 in the gas phase experiment. It is interesting that methanol is effective as a reducing agent in the gas phase.[24]

Hydrogen production with visible light where $Ru(bipy)_3^{2+}$ or Zn-TPPS was used as a photocatalyst has been reported.[12] This method is, however, based on the reaction in a homogeneous system in which methylviologen is necessary as an electron relay. The principal reaction scheme may be written as

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^* \tag{17}$$

$$\text{Dye} + MV^{2+} \longrightarrow \text{Dye}^{\dot{+}} + MV^{\dot{+}} \tag{18}$$

$$MV^{\dot{+}} + H^+ \xrightarrow{Pt} MV^{2+} + 1/2H_2 \tag{19}$$

$$\text{Dye}^{\dot{+}} + \text{Red} \longrightarrow \text{Dye} + \text{Red}^{\dot{+}} \tag{20}$$

$$\text{Red}^{\dot{+}} \longrightarrow \text{oxidation products.} \tag{21}$$

Here MV^{2+} is methylviologen.

The system reported in this paper is quite different from this system as mentioned before. The dye is used as a sensitizer of semiconductor powders and electrons are transferred from excited dye molecules to the conduction band of the semiconductor.

One of the characteristic features to which attention should be given is weak oxidizing power of the dye. As illustrated in Figure. 1, the valence orbital of the sensitizing dyes is at a higher energy than the valence band of the semiconductor. Oxidation of a reducing agent such as EDTA or methanol in the dye sensitization process may therefore be more difficult than oxidation by direct excitation of TiO_2. Furthermore, the rate of hole consumption by the reducing agent may decrease as a result of the weak oxidizing power of these oxidized dyes, resulting in an increased recombination. Actually the hydrogen production rate with methanol as a reducing agent was much smaller than the rate with EDTA in the case of the dye sensitization system [Table I Run Nos. 9,12], whereas in the case of direct excitation of TiO_2 the rates achieved with methanol and EDTA were almost equal [Nos. 14,15].

The hydrogen production rates listed in Tables I and II are rather small. As described previously, these small rates result from the fact that only a small portion of the incident light is absrobed by the dyes near the semiconductor in the liquid phase. In the vapor phase, the concentration of reacting molecules is small and some dye molecules such as $Ru(bipy)_3^{2+}$ are not attached closely to the semiconductor surface under the presence of water vapor.[19] Therefore, highly efficient hydrogen production would be possible under the following conditions:

(1) The sensitizing dye molecules should be adsorbed tightly

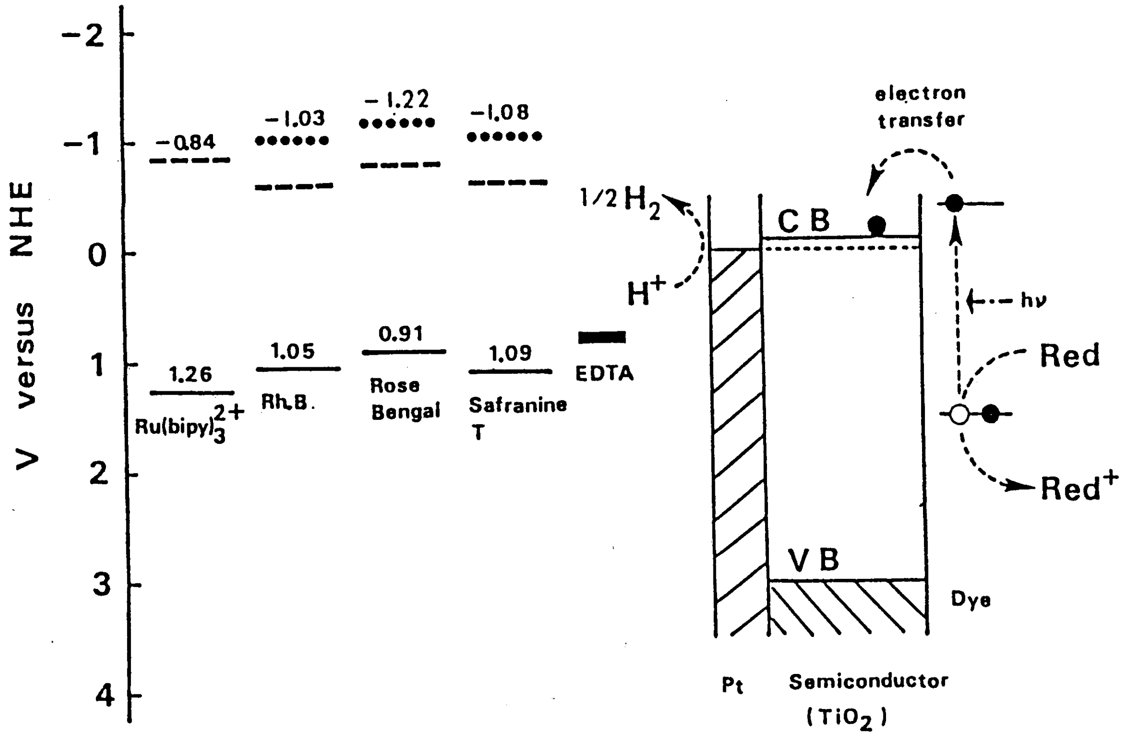

Figure. 1. Schematic mechanism of dye sensitization of semiconductor and the oxidation potentials of the ground state and the first excited state dyes.
——— D^+/D (the ground state) [25, 26];
. . . $D^+/^1D^*$ (the first excited singlet state) [27];
--- $D^+/^3D^*$ (the excited triplet state) [28, 29]. The TiO_2 energy level diagram is also drawn according to the scale at the lhs.

on the semiconductor surface with a consequent increase in the electron transfer interaction and in the amount of light absorbed by the dye molecules participating in hydrogen production.

(2) The dye should have an intrinsically long excited state lifetime, so that the probability of photo-redox reactions in the excited state is increased.

(3) The electron energy in the excited state of the dye should be higher than the conduction band of the substrate semiconductor, and the valence orbital of the dye should be low enough to oxidize reactants such as organic compounds or water (or OH^-).

(4) Good catalysts for hydrogen production and also for the oxidation reaction are used.

[References and Notes]

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§2 Dynamics of Electron Transfer from Dye to Semiconductor.

[Abstract]

The dynamic spectroscopic properties of excited state of $Ru(bipy)_3^{2+}$ adsorbed on powdered semiconductors (TiO_2, SnO_2, $SrTiO_3$ and ZrO_2), a powdered insulator (SiO_2) and microcrystalline methylviologen chloride have been investigated by using a pulsed dye laser (6 ns, 450 nm) or a YAG laser (25 ps, 530 nm) as an exciting light source. The time resolved luminescence spectra of $Ru(bipy)_3^{2+}$ adsorbed on oxide-semiconductors were found to be classified into two components: One is blue-shifted compared with the normal spectrum and originates from the tightly bound $Ru(bipy)_3^{2+}$ whose excited state decays with a lifetime of 12-20 ns depending on the substrate. The short lifetime can be explained by an electron transfer interaction between the excited $Ru(bipy)_3^{2+}$ and the oxide semiconductor. The other originates from loosely bound $Ru(bipy)_3^{2+}$ whose luminescent state has a longer lifetime (40-3500 ns) than that of the tightly bound $Ru(bipy)_3^{2+}$. The excited $Ru(bipy)_3^{2+}$ on microcrystalline methylviologen chloride decays very fast with a lifetime of 3.3 ns, indicating a strong electron transfer interaction.

[Introduction]

$Ru(bipy)_3^{2+}$ and related complexes have been intensively investigated as photocatalysts for water splitting reaction.[1] In §1 we showed the hydrogen-producing system by making use of photosensitization by several dyes adsorbed on the powdered TiO_2 photocatalysts. A photochemical cell based on electron transfer quenching of the excited state $Ru(bipy)_3^{2+}$ gives both H_2 and a photocurrent.[2] Ru(II) complexes have also been used as photosensitizers of semiconductor electrode.[3] In the dye-sensitization of semiconductor, the electron transfer between the excited dye and the semiconductor has been believed to be the initial process.[3,4] Memming and Shroppel investigated electron transfer reactions of excited Ru(II) complexes in monolayer assemblies at the SnO_2 electrode by using photoelectrochemical methods.[3-(a)] The photocurrent was interpreted by an electron tranfer from the Ru(II) complexes, excited to its triplet state, to the conduction band of SnO_2. They suggested an efficient oxidation of water by Ru(III) complex generated in that reaction. Clark and Sutin performed a detailed photoelectrochemical study of sensitization of n-type TiO_2 electrodes by polypyridineruthenium(II) complexes and showed that the electron transfer from excited states of these complexes can occur efficiently.[3-(b)] The quenching processes involving the excited states of $Ru(bipy)_3^{2+}$ in solution have been well studied by the Stern-Volmer analysis of luminescence intensity and also by flash photolysis experiments.[5] However, transient spectroscopic analysis of quenching of excited $Ru(bipy)_3^{2+}$ by solid material has not been reported to authors' knowledge. These experiments, we think, can significantly contribute to the understanding of dye sensitization process of semiconductors because it may be possible to obtain direct data for the rate of electron transfer between the excited dye and the semiconductor that are free from complications caused by various diffusion processes inevitable for experiments using solutions. In the present study under vacuum, methylviologen (MV) and oxide semiconductors (TiO_2, SnO_2, $SrTiO_2$, and ZrO_2) were chosen as the electron acceptor. Since the luminescence of the $Ru(bipy)_3^{2+}$ monolayer adsorbed on the single crystal of these acceptor materials was too weak for the present apparatus to give reliable data, fine powders with large effective surface were used as substrates. SiO_2 was used as a reference substrate. Fine powdered semiconductors are also interesting because of the photocatalytic effects for hydrogen evolution which have been extensively investigated.[6] Here the hydrogen evolution was also investigated by making use of photosensitization by $Ru(bipy)_3^{2+}$ adsorbed on the powdered TiO_2 photocatalysts.

[Experimental]

$Ru(bipy)_3Cl_2$ was purchased from Stream Chemicals, Inc. and was purified by several recrystallization from water. It was sometimes used without purification and no significant difference was observed in the results. Methylviologen was purchased from SIGMA Chemical Co. and was used without further purification. TiO_2, SnO_2, ZrO_2, and $SrTiO_3$ powders of 99.9 or 99.99 % purity were purchased from Furuuchi Chemical Corp. and were used as received or after reduction under H_2 atmosphere.

One mg or less amount of $Ru(bipy)_3Cl_2$ was dissolved in small amount of pure water or pure methanol and the solution was mixed with the known amount of substrate powder. The mixture was dried under air at room temperature or at somewhat higher temperature and then, in most cases, dried completely by dehydration under the vacuum of about 10^{-3} mmHg. The dried sample was placed between two quartz plates and was mounted on the sample holder of an Oxford optical cryostat. Figure 1 shows the schematic diagram of the apparatus. A Molectron DL-II dye laser pumped by Molectron UV-22 N_2 laser was used as the excitation source. The excitation wavelength was 450 nm throughout the experiment, and the half width of the excitation pulse was 6 ns. The intensity was 0.5-1 mJ/pulse

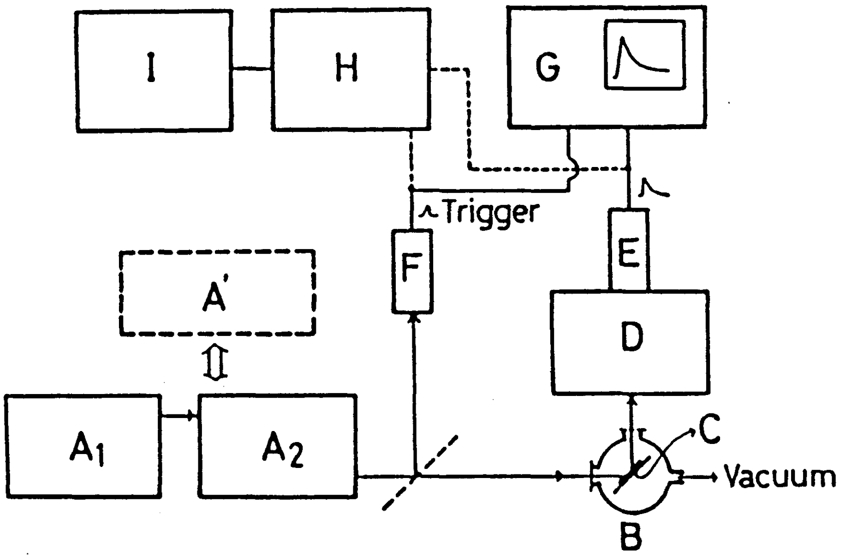


Figure 1. Schematic diagram of experimental apparatus: (A_1) N_2 laser, (A_2) dye laser, (A′) YAG laser, (B) cryostat, (C) sample, (D) monochromator, (E) photomultiplier, (F) biplanar phototube, (G) oscilloscope, (H) boxcar integrator, (I) recorder.

and the repetition rate was several tens per second.

The Hamamatsu TV R-955 or R-636 photomultiplier was used and the decay curve drawn on a CRT of Sony-Tektronix 7104 (1 GHz) or 7904 (500 MHz) was photographed with a polaroid type 410 (ASA 10000) film. The overall time constant of the detecting system was restricted by the rise time of the photomultiplier to 2.6 ns. A Quantel YG-500 YAG laser (the second harmonics, 530 nm) and Hamamatsu TV R-1294U (rise time 350 ps) were also used as a light source and a photomultiplier, respectively. The overall time constant of this system was several hundred picoseconds. The decay characteristics of the luminescence obtained by using this did not show any significant difference with those obtained by using the nanosecond system except for the case of $Ru(bipy)_3Cl_2$/MV system which showed a fast decay component. Measurements were performed at room temperature (25 °C) and at liq. N_2 temperature under a vacuum of $\sim 10^{-3}$ mmHg. The transient phosphorescence spectra of adsorbed $Ru(bipy)_3Cl_2$ were also obtained by use of a boxcar detector PAR 162, or reconstructed from the decay curves at different wavelengths.

[Results and Discussion]

$Ru(bipy)_3Cl_2$ in pure water showed a single exponential decay under air at room temperature. The lifetime was about 400 ns and was similar to the value reported for the solution of 50 % H_2SO_4.[7] The decay of the phosphorescence of $Ru(bipy)_3Cl_2$ adsorbed on the substrate powders was apparently much faster and was more complicated (see Figure 2). It could be expressed as a sum of exponential decays.

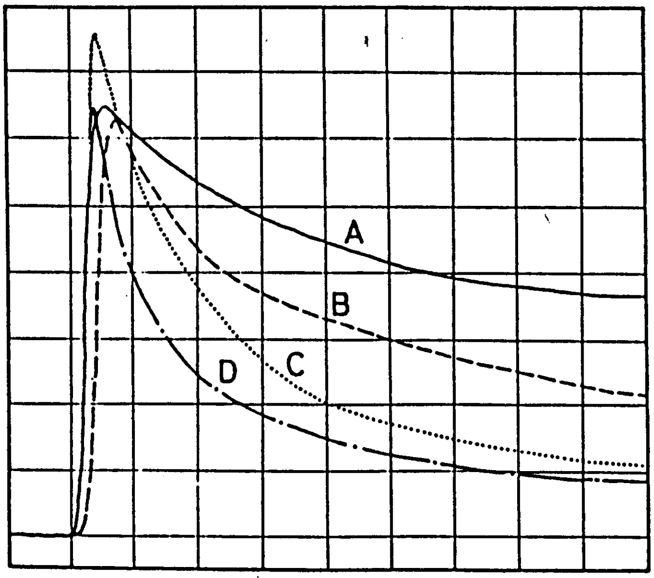


Figure 2. Phosphorescence decay curves of $Ru(bpy)_3Cl_2$ adsorbed on various oxide powders. Dye laser excitation, 6 ns, 450 nm. Observed at 620 nm, at 25 °C and under vacuum of 10^{-3} mmHg: (A) SiO_2, (B) ZrO_2, (C) TiO_2, (D) $SrTiO_3$.

$$I(t) = \sum_{i=1}^{N} I_i e^{-t/\tau_i} \qquad \cdots\cdots(1)$$

The slowest decay component (with the largest τ_i) was determined at first, because when t is large enough I(t) can be expressed by a single exponential decay as $I_N\exp(-t/\tau_N)$, where τ_N is the largest among τ_i's. Then the other components were successively determined in order of the magnitude of τ_i, by subtracting the already determined components from I(t). This process is illustrated in Fig. 3 for the case of $Ru(bipy)_3Cl_2/TiO_2$. The preexponential factors depended on the wavelength of the monitored light. Figure 4 shows the typical transient spectra of $Ru(bipy)_3Cl_2$.

The luminescence seems to be composed of at least two components with different decay constants.

The origin of the photoluminescence of ruthenium(II) complexes has been assigned to three closely spaced charge transfer levels, $d\pi^*(a_2);A_2$, $d\pi^*(a_2);E$, and $d\pi^*(a_2);A_1$ of rather singlet nature by Crosby and coworkers.[7-(a),(b),(c)] They assumed that Boltzmann distribution between these three levels holds down to 1.6K owing to strong spin-orbit coupling. On the basis of this assumption, they could successively analyse the temperature dependence of lifetime and quantum yields of the photoluminescence of $Ru(bipy)_3Cl_2$ in polymethylmethacrylate film between 77K and 4.2K and derived the following characteristics of the above mentioned three

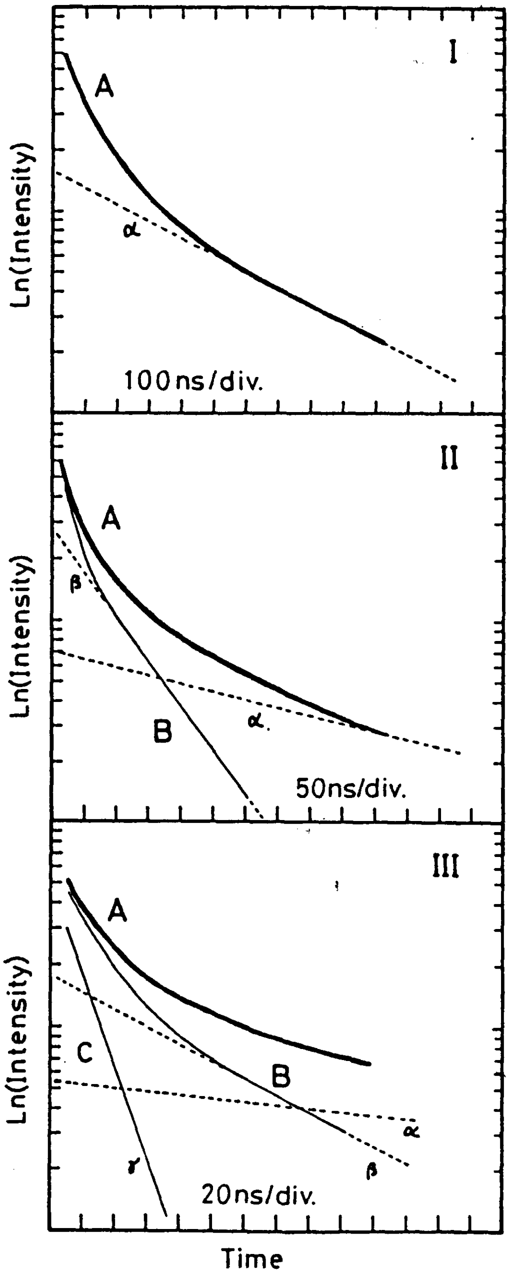


Figure 3. Typical decay curves and decomposition to components. Luminescence decay of $Ru(bpy)_3Cl_2$ on TiO_2 powder observed at 620 nm at liquid-N_2 temperature. See Table I. A: Observed decay curves with different time scales, which are decomposed as described in the text in the order I, II, and III. α 530-ns lifetime component. β = 100-ns lifetime comonent. γ = 20-ns lifetime component If we express the intensity of A by A and so on, $B = A - \alpha$ and $C = B - \beta = \gamma$. Absolute intensities are not the same for I, II, and III, and B, C, α, β, and γ are normalized relative to A.

levels. The A_1 level is energetically the lowest and both the radiative lifetime (τ_r) and nonradiative lifetime (τ_{nr}) are very large; $\tau_r = 1091.5\ \mu s$ and $\tau_{nr} = 183.1\ \mu s$. The A_2 level is energetically the highest and is located at 61.2 cm^{-1} above the A_1 level. Though thermodynamically unfavarable, this A_2 level is most important decay channel of the excited $Ru(bipy)_3^{2+}$ both radiatively and non radiatively due to its relatively short lifetimes; $\tau_r = 1.69\ \mu s$, $\tau_{nr} = 0.68\ \mu s$. Thus this level contributes more than 90 % of the luminescence intensity at 77K. The degenerate E level is located at 18.8 cm^{-1} above the A_1 level and contributes about 10 % of the luminescence intensity a 77K; $\tau_r = 81.7\ \mu s$ and $\tau_{nr} = 18.8\ \mu s$. Allsopp and coworkers gave evidence that the multiple state model described above holds also in H_2O, D_2O and other solvents at temperatures above 77K.[7-(e)] They showed that the location of the A_2 level relative to the A_1 level (E_2 of reference 7-(e)) is slightly dependent on the solvent. For example, it was 2.64 kJ/mol (221 cm^{-1}) in H_2O in the temperature region from 273 to 373 K, 1.90 kJ/mol (159 cm^{-1}) in 9M $LiCl-H_2O$ in the temperature region from 178 to 373 K, and 0.63 kJ/mol (52.7 cm^{-1}) in the temperature region from 77K to the glass transition temperature (143 K). Unfortunately, the data reported by Allsopp et.al. are insufficient to determine the relative contributions of three levels to the intensity of luminescence at temperatures above 77K. However, if we assume the decay rates reported by Crosby et. al. are not significantly dependent on solvent, the contribution of the A_2 level is calculated to be not less than 91 % at temperatures between 77K and 373K. Crosby and coworkers have also reported that the temperature dependence of the luminescence band contours is not significant under 77K and that vibrational structures of the luminescence spectra originating from these three levels must be similar except for slight difference in relative intensities of vibrational bands. This observation can be reasonably explained by postulating that the vibrational structure of the luminescence is, according to the Franck-Condon principle, governed by the change of vibrational states of ligand molecules induced by charge transfer excitation, which should be similar for the three levels. When temperature is raised from 77K to room temperature, The luminescence spectrum broadens and red shifts.[7-(f),(g)] The studies described previously have shown that the A_2 level is the predominant emitting state at temperature above 77K, which precludes the possibility to ascribe the temperature dependence of the spectrum above 77K to alteration of the emitting level. Thus it seems reasonable to say that this temperature change is caused by the change in the vibrational modes of ligands and consequently to the change of Franck-Condon factors.

All the time-resolved spectra observed in the present study and shown in Figures 4 and 5 fall in the same region as the low temperature spectra and room temperature spectra of $Ru(bipy)_3^{2+}$ reported by Van Houten and Watts[7-(f)] and

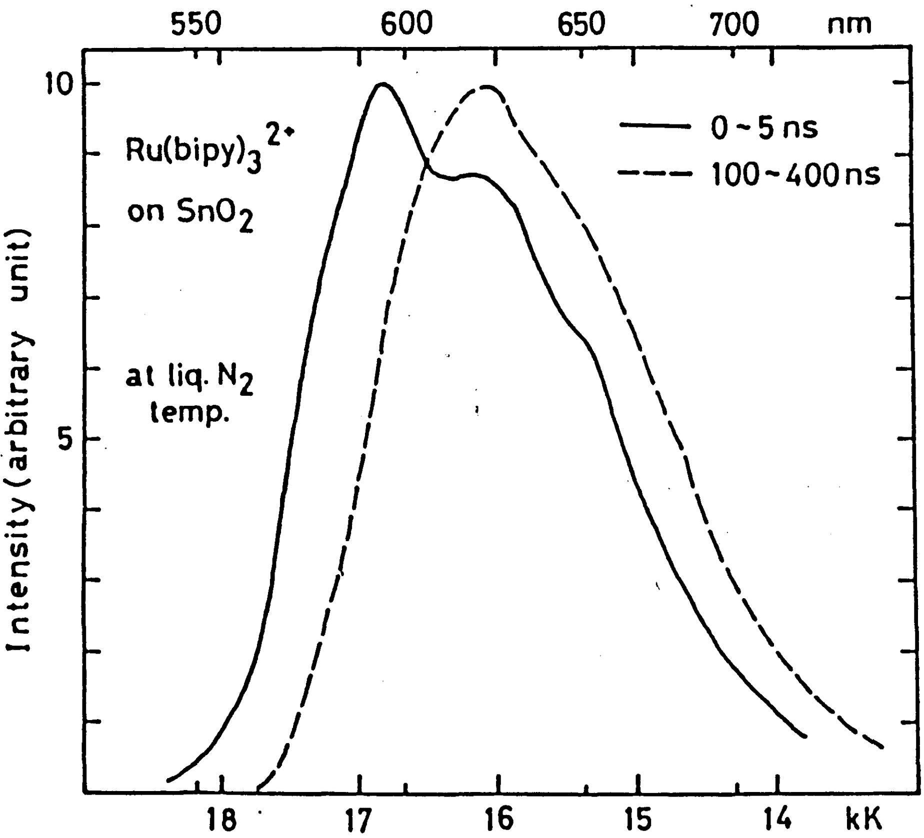


Figure 4. Transient spectra of $Ru(bpy)_3Cl_2$ on SnO_2 detected by boxcar integrator. Light source: pulsed dye laser, 6 ns, 450 nm. Time window of boxcar integrator: (—) 0–5 ns from the instant that the short-wavelength region of the spectra began to decrease; (- - -) 100–400 ns after the excitation pulse. Each spectrum has been normalized to its maximum for comparison of the spectrum shape. The spectra are not corrected for sensitivity of the detecting system.

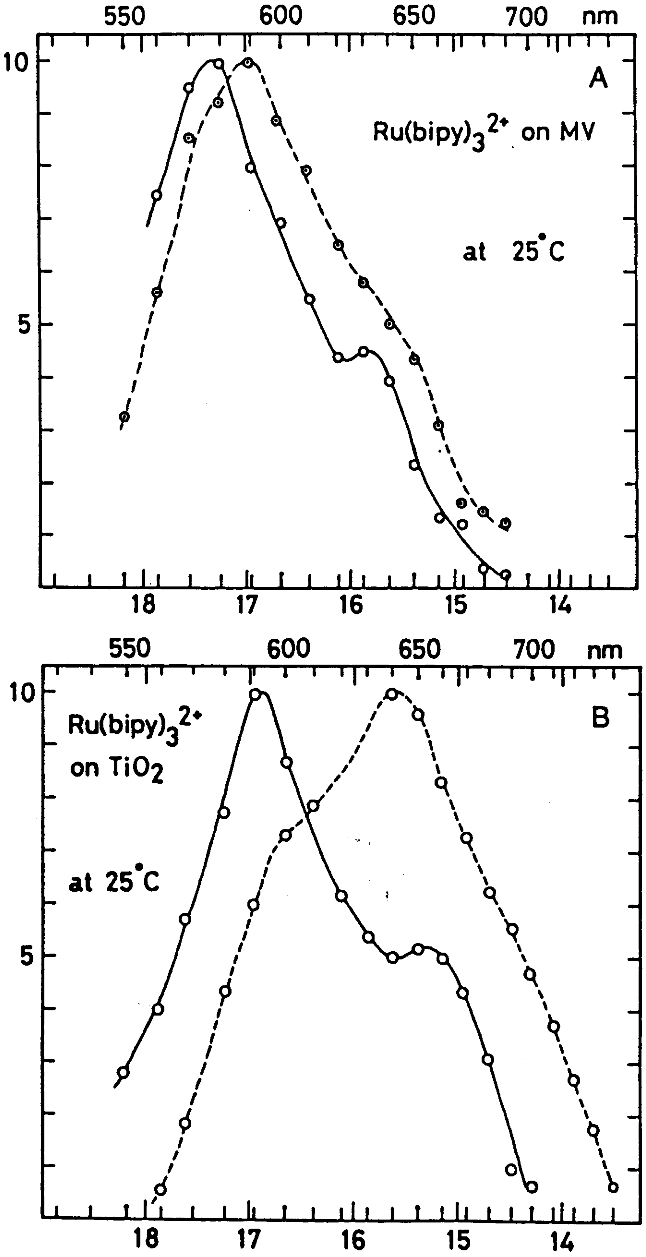


Figure 5. Normalized spectra of respective phosphorescence decay components of Ru(bpy)$_3$Cl$_2$. The spectra have been constructed from decay data at various wavelengths. They are not corrected for wavelength dependence of sensitivity of the detecting system. (A) Ru(bpy)$_3$Cl$_2$ (1/1000 w/w) on methylviologen: (—) component of 3.3-ns lifetime; (---) component of 13-ns lifetime. (B) Ru(bpy)$_3$Cl$_2$ (1/1000 w/w) on TiO$_2$: (—) component of 18-ns lifetime; (- - -) component of 64- and 280-ns lifetime.

other authors.[7-(g)] The band contours observed in this study are also similar to those reported by these authors. Thus we think it is reasonable to conclude that the origins of the time-resolved spectra are all the same, that is, a mixture of more than 90 % A_2 level and less than 10 % E level, and that difference in the band contour is due to difference in circumstances around the ligands. The spectral components that decay rapidly are located at relatively short wavelength region and their band contours resemble more or less the spectrum of $Ru(bipy)_3^{2+}$ in a low temperature solution. On the basis of a forementioned discussion on the band contour we tentatively assign these components to molecules which are rather firmly attached to the surface of the substrate where the molecular motion of ligands are somehow hindered. Hereafter we will call the corresponding spectrum as the F-spectrum (the spectrum of firmly attached species). Similarly, the time-resolved components with long lifetimes can be ascribed to more or less loosely held molecules. We will call the corresponding spectrum as L-spectrum (the spectrum of loosely attached species). The F-spectrum is blue-shifted compared with the L-spectrum as seen in Figure 5. The firmly attached $Ru(bipy)_3^{2+}$ would be stabilized near the ionic atmosphere of the oxide or methylviologen chloride surface. The stabilization would be larger in the ground state than in the excited state, because the adsorbed molecule in the ground state locates the position of minimum energy on the surface. That must be the reason of the blue shift of the F-spectrum. The above interpretations agree with the proposal that the relaxation channel responsible for the fast decay is the electron transfer process from the excited $Ru(bipy)_3Cl_2$ to the substrate, because the probability of this process should depend on the overlap of the wavefunctions of the donor and the acceptor, which is strongly dependent on the distance between the two. Heavy atom effect must be not important because Ru itself is a heavy atom.[7-(c)] The decay characteristics are summarized in Table I.

It may seem an attractive conjecture as an alternative interpretation of the different time-resolved spectra that different lifetimes are due to difference in the electron transfer rate from each level of the multiplet (A_2, E and A_1), and that the different emitting level gives the different spectrum. However, this interpretation seems to contradict to Crosby and coworkers' observation that thermal equilibration process between the three levels is rather raid due to strong spin-orbit coupling.[7-(a),(b),(c)] If any one of three levels has very large electron transfer rate, it must greatly shorten lifetimes of other levels through the rapid thermal equilibration process. The wide range of observed lifetimes indicates that the conjecture stated above does not apply to the present case.

TABLE I: Lifetime of Decay Component and Relative Weight

substrate	concn, w/w	temp	lifetime (rel wt),[d] ns
MV[a]	1/1000	room temp	3.3 (0.81), 13 (0.19)
		liq-N_2 temp	3.1 (0.81), 14 (0.17), 130 (0.02)
TiO_2	1/10000	room temp	18 (0.52), 64 (0.32), 280 (0.16)
		liq-N_2 temp	21 (0.64), 100 (0.28), 530 (0.07)
SnO_2	1/10000	room temp	14 (0.63), 65 (0.30), 260 (0.07)
		liq-N_2 temp	15 (0.59), 140 (0.31), 1000 (0.10)
$SrTiO_3$	1/10000	room temp	12 (0.58), 40 (0.22), 130 (0.13), 500 (0.06)
		liq-N_2 temp	12 (0.50), 60 (0.26), 280 (0.17), 1200 (0.07)
ZrO_2	1/10000	room temp	17 (0.35), 130 (0.38), 530 (0.27)
		liq-N_2 temp	20 (0.25), 240 (0.29), 810 (0.45)
SiO_2	1/10000	room temp	50 (0.33), 420 (0.36), 1200 (0.31)
		liq-N_2 temp	50 (0.25), 1300 (0.26), 3500 (0.60)
in ethanol-methanol (5:1) soln[b]		290 K	0.89 μs
		80 K	4.0 μs
in 50% H_2SO_4 [b]		290 K	0.70 μs
		80 K	2.7 μs
in ethanol-methanol (4:1) soln[c]		77 K	5.12-5.37 μs

[a] YAG laser (25 ps, 530 nm) was also used as an exciting light source (see text). [b] Reported by Lytle and Hercules (ref 7g). [c] Reported by Demas and Crosby (ref 14). [d] The precision of the obtained values has not been statistically determined but the rough estimate is ±10% for lifetime and ±5% for relative weight.

Van Houten and Watts,[7-(f)] and Allsopp et al.[7-(e)] have shown that a certain set of levels which is located about 3600 - 4000 cm^{-1} above the emitting multiplet works as a significant decay channel at temperatures above 173 K. This set of levels was originally proposed by Van Houten and Watts[7-(f)] as being of d-d parentage to explain the temperature dependence of luminescence lifetime and quantum yield between 0 °C and 100 °C. They reported that it is important for photochemical reaction involving ligand displacement. Apparently, it cannot be a candidate for the origin of our spectra, because not only the position of the level is too high but also it is not luminescent.

On Methylviologen

On the surface of microcrystalline powder of methylviologen chloride, $Ru(bipy)_3Cl_2$ showed a fast decay, which are composed of two components with about 3 ns and about 13 ns lifetime. The decay curve of the former component was unambiguously observed by using the picosecond system. Figure 5a shows the spectra corresponding to the two components. They both belong to the F-spectrum. No significant difference was observed between the decay curves at room temperature and at liq. N_2 temperature, except that a small amount (2 %) of a slowly decaying component was observed at liq. N_2 temperature. It may be conjectured that the molecules which give the long lifetime component at liq. N_2 temperature have some freedom of movement at room temperature and can take a position where fast electron transfer is possible.

On TiO_2 and other oxide semicondutors

On the TiO_2 powder (99.9 %, anatase, the surface area of ca. 50 m^2/g, Nippon Aerosil Co.), the decay has three components and the lifetimes of these components are 16 ~~ns~~, 60 ~~ns~~ and 280 ns at room temperature and 21 ~~ns~~, 100 ~~ns~~ and 520 ns at liq. N_2 temperature. The fastest decay component is dominant and shows the F-spectrum, and the slowest decay component shows the L-spectrum. The intermediate decay component seems to belong to the L-specturm, and Figure 5b shows the F- and L-spectrum constructed from the decay curve data at various wavelengths. The relative magnitude of the pre-exponential factors of the fast, the intermediate and the slow decay component is not significantly dependent on temperature. This naturally leads to the conclusion that each decay component originates from different kinds of sites and the electron transfer rate from the excited $Ru(bipy)_3Cl_2$ molecule at the respective sites should be one of important factors that determine the lifetime, especially in the case of F-spectrum. It is probable that thermal reorientational motion of the loosely attached molecules enhance the electron transfer, which may be partly responsible for the rather large temperature dependence of the lifetime of the long lifetime component.

We performed some experiments on samples loaded with different amounts (1/1000 w/w and 1/100000 w/w) of Ru(bipy)$_3$Cl$_2$. Contrary to our expectation, these experiments could not give any significant information. When the quantity of Ru(bipy)$_3$Cl$_2$ was 1/1000 w/w, inspection by sight apparently showed that uniform mixing was not attained, and resultant aggregation of Ru(bipy)$_3$Cl$_2$ molecules obstructed rational analysis of observed decay curves. A further discussion will be given later on the luminescence decay curve of crystalline powder of Ru(bipy)$_3$Cl$_2$. On the other hand, when the quantity of Ru(bipy)$_3$Cl$_2$ was 1/100000 w/w or less, the luminescence intensity was so small that signal to noise ratio of our present apparatus was not sufficient for acquisition of data that can be used for reliable analysis. A rough estimate showed that relative weights of time resolved components for 1/100000 w/w Ru(bipy)$_3$Cl$_2$ on TiO$_2$ were not significantly different from those in Table I. This did not seem to support our expectation that the relative weight of firmly attached species might be larger at lower concentration of Ru(bipy)$_3$Cl$_2$. However, we think this result is not fatal to the F-, and L-spectrum interpretation, because the ratio of molecules of various kinds of adsorption states might be mainly governed by the ratio of different adsorption sites on the surface of oxide rather than the concentration of $Ru(bipy)_3Cl_2$ at these low concentrations, considering that 1/10000 w/w $Ru(bipy)_3Cl_2$ on the surface of TiO_2 whose surface area is 50 m^2/g corresponds to a mean surface area per one $Ru(bipy)_3^{2+}$ molecule of 5×10^4 A^2 which is much larger than the value for monolayer adsorption (1/600 monolayer).

On SnO_2, $SrTiO_3$ and ZrO_2 surfaces, similar results were obtained, and the lifetime of the fastest decay component was similar to the value for TiO_2. However, in the case of ZrO_2, the weight of the decay component with long lifetime is larger than those for other oxide semiconductors.

<u>On SiO_2</u>

On SiO_2 (99.99 %, the surface area of ca. 50 m^2/g, Nippon Aerosil Co.), the components with long lifetimes, 420 ns and 1200 ns at room temperature and 1300 ns and 3500 ns at liq. N_2 temperature are dominant. These values are similar to the values in alcoholic solution or in its rigid glass solution.[7] It is noticeable that there is a component with a very long lifetime up to 1200 ns at room temperature. It is longer than those in the solutions as shown in Table I. It seems to indicate a smaller radiationless process due to the inhibited movement of ligands on the surface. Figure 6 shows the energy levels of the conduction and valence bands for the oxides in solution at pH 7, together with the redox

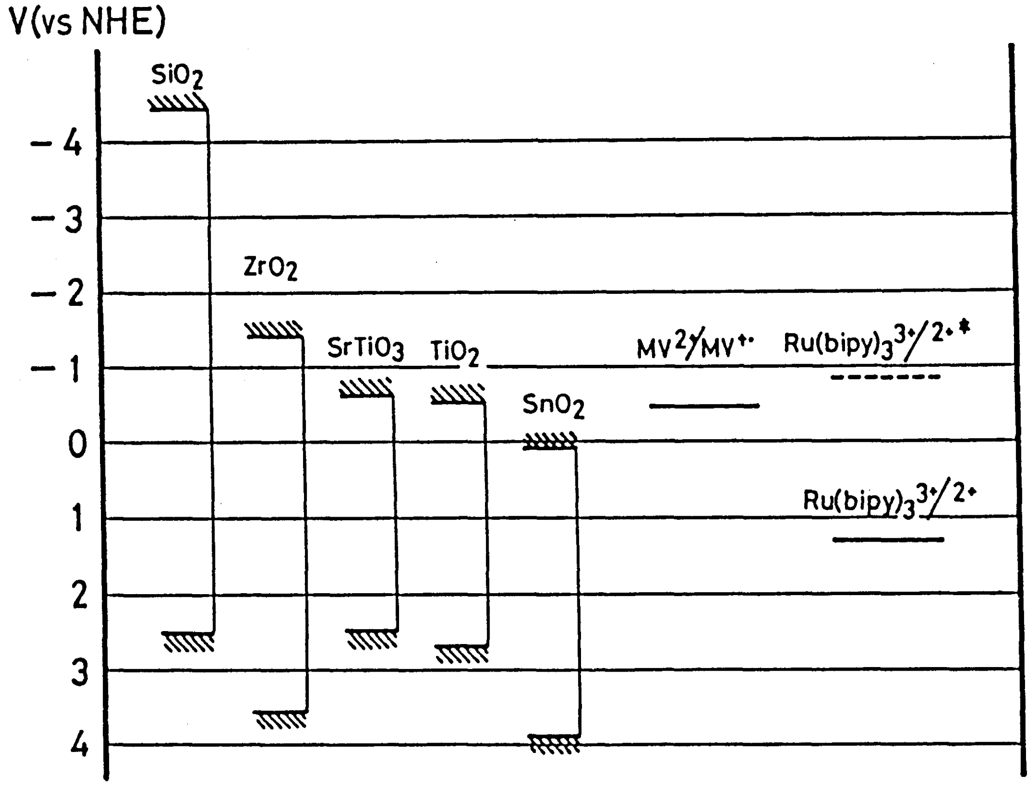


Figure 6. Band energies of oxides at ph 7 and redox potentials of methylviologen and $Ru(bpy)_3Cl_2$: (—) redox potential for ground state; (- - -) redox potential for excited state. See text and ref 8-11.

potentials of methylviologen and $Ru(bipy)_3^{2+}$.[8,9,10] Since our experiments were carried out in the gas phase (10^{-3} mmHg), not in the aqueous medium, the energy levels in the gas phase should be used. Moreover, for the redox potential of $Ru(bipy)_3^{2+}$, the values at the oxide surface and also in the gas phase are necessary for a rigorous discussion. However, those data are not available at present. Thus the energy diagram described in Figure 6 should be understood as a rough measure for the present discussion. The position of the conduction band of SiO_2 is estimated by using Scaife's equation[11] and the band gap of 6.9 eV. From this figure the electron transfer from the excited $Ru(bipy)_3^{2+}$ to the conduction band is conjectured to be possible for SnO_2, TiO_2 and $SrTiO_3$. This is supported by the large weight of the fast decay components as seen in Table I. Clark and Sutin[3-(b)] estimated the reorganization parameter λ, the energy required to change the environment of the reduced form to that which exist around oxidized form at equilibrium for $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+*}$ couple in water to be about 0.25 eV. In the present case of $Ru(bipy)_3^{2+}$ on the surface of oxide powder under vacuum, the value of λ must be much smaller, since polar molecules of solvent do not exist around $Ru(bipy)_3^{2+}$. The small value of λ favors the electron transfer from excited $Ru(bipy)_3^{2+}$ to oxides.

On the other hand, for SiO_2, the decay characteristics are quite different from those for the other oxides: The dominant decay components have very long lifetimes. In the case of ZrO_2, the decay characteristics look intermediate between those of SiO_2 and those of the other three oxides, i.e. SnO_2, TiO_2 and $SrTiO_3$ as seen in Figure 2 and Table I. The weight of the decay component with a short lifetime (17 ns at room temperature) is smaller than those for other oxide semiconductors. This is expected from the fact that the conduction band of ZrO_2 is located, in the aqueous medium, higher than those of $SrTiO_3$, TiO_2 and SnO_2 as shown in Figure 6. In this case, the existance of a considerable amount of a fast decay component (17-20 ns lifetime) as shown in Table I might be explained by assuming that the relative positions of the energy bands of the oxides and the energy levels of $Ru(bipy)_3^{2+}$ are different from those in solution at pH 7. Another explanation would be possible by assuming surface states which interact with the excited $Ru(bipy)_3^{2+}$ through the electron or energy transfer processes and reduce its lifetime.

The component with 50 ns in the case of SiO_2 is also controversial, because the electron transfer from the excited $Ru(bipy)_3^{2+}$ to the conduction band is quite difficult as shown in Figure 6. One possible explanation would be the surface states interacting with $Ru(bipy)_3^{2+*}$ similar to the case of ZrO_2. On the other hand, the following decay channels would not be neglected, if aggregates of $Ru(bipy)_3Cl_2$ are formed on the surface of SiO_2.

$$2\ Ru(bipy)_3^{2+*} \longrightarrow Ru(bipy)_3^{1+*} + Ru(bipy)_3^{3+} \qquad (2)$$

$$Ru(bipy)_3^{2+*} + Ru(bipy)_3^{2+} \longrightarrow Ru(bipy)_3^{1+} + Ru(bipy)_3^{3+} \qquad (3)$$

Indeed, crystalline powder of $Ru(bipy)_3Cl_2$ gave a decay curve which was a superposition of several decays just as those for $Ru(bipy)_3Cl_2$ on SnO_2, TiO_2 and $SrTiO_3$, and the lifetime of the fastest component reached sometimes as low as about 20 ns. However, the decay curve showed more complicated characteristics, that is, large temperature dependence in the preexponential factors, than the case of oxide semiconductors. The preexponential factors were also significantly affected by sample conditions that could not be controlled. If we assume rapid random movement of excitation and spatially uniform energy transformations in the crystal, the processes (2) and (3) and ordinary first order radiative and nonradiative processes will give a rate equation like

$$dx/dt = -\alpha x^2 - \beta x \qquad (4)$$

where α is the rate constant for process (2) and β is the sum of rate constants for other processes. By integrating Eq. (4), we obtain

$$1/x = (\alpha/\beta + 1/x_0)e^{\beta t} - \alpha/\beta \qquad (5)$$

where x_0 is the initial (t=0) value of x. The three solid lines in Figure 7 exhibits the observed 1/x versus $\exp(\beta t)$ curves that are expected when Eq. (5) holds, depending whether the chosen value of β is appropriate, large or small.

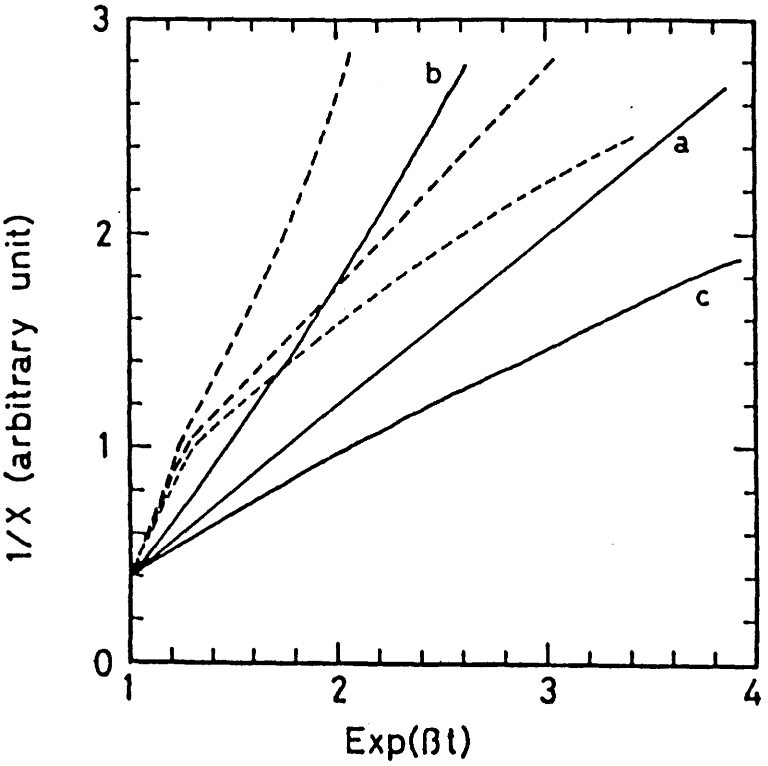


Figure 7. Phosphorescence decay characteristics of $Ru(bpy)_3Cl_2$ crystalline powder compared to general second-order decay curve. (—) The decay that obeys eq 2: (a) $\beta = \beta_0$, (b) $\beta < \beta_0$, (c) $\beta > \beta_0$ where β_0 is the appropriate value of β. (---) observed decay for crystalline powder of $Ru(bpy)_3Cl_2$, monitored at 620 nm at liquid-N_2 temperature, excited by a dye laser. Three lines correspond to relatively large, medium, and small values of β, respectively. Similar decay characteristics were also observed at room temperature.

The observed decay curve is shown by dashed lines for various values of β and it is obvious that Eq. (5) is not a good approximation. The initial fast decay can not be reconciled with the posterior slow decay by Eq. (5). Thus we have to assume some nonuniform processes in the crystal. It may involve a few kinds of special sites where the molecules are arranged in configurations that are, in various degrees, favorable for charge separation by processes like (2) and (3). The diffusion velocity of molecular excitation must be sufficiently slow and the charge separation may occur rapidly in the vicinity of these sites in comparison with other regular sites. These special sites may involve impurities, defects and surface traps, which are not easily controlled and are well known as the important factors that affect the photoelectric process of solid. Accordingly, the present data about crystals can only suggest that processes (2) and (3) are quite probable, though the latter might be unfavorable with regard to free energy change. Further details are beyond the scope of the present work. Anyway, the aggregate formation seems to be a factor that decreases the lifetime of $Ru(bipy)_3^{2+*}$ on SiO_2, and possibly on ZrO_2. The spectrum of the 50 ns component seemed to be F-type, but we could not perform the unambiguous decomposition because the weight of this component was relatively small.

The electron transfer rate from $Ru(bipy)_3^{2+*}$ to SnO_2, TiO_2, $SrTiO_3$ and possibly to ZrO_2 is deduced to be about 5×10^7 s^{-1} (=1/20 ns) from the results and discussion so far described. Although this value is not large compared to those for other systems; e.g., for rhodamine B/anthracene, 2.9×10^{10}

s^{-1} 12), and for Zn-porphyrin/SnO_2, $7.5x10^9$ s^{-1} 13), it is sufficient for effective electron transfer, because the rates for the other deactivation channels are small, if the mutual charge separation processes (2) and (3) are not important. The photoinduced electron transfer from a sensitizing molecule to a semiconductor can be confirmed easily by measuring a photocurrent of the semiconductor electrode immersed in an electrolyte solution of a sensitized dye.[4] Although, such a measurement is impossible for a powdered semiconductor in a gaseous medium. We showed the hydrogen evolution with $Ru(bipy)_3^{2+}$-TiO_2 powder in vapor phase due to the dye sensitization effect in §1 (Table II). The result demonstrates the electron transfer from $Ru(bipy)_3^{2+*}$ to TiO_2. It indicated clearly the sensitization effect to the hydrogen evolution, although the efficiency was not good. Since the hydrogen evolution rate of 1 μmol/10 h corresponds to 5.3 μA of photocurrent, the evolution rate, 26 μmol/30 h, for TiO_2-$Ru(bipy)_3^{2+}$ in Table II in §1 corresponds to the photocurrent of 46 μA. The efficiency was rather low contrary to our expectation.

One important reason of this low efficiency seems to be that $Ru(bipy)_3Cl_2$ molecules are not closely attached to the surface of the semiconductor powder under the conditions of the present photocatalytic reactions. The concentration of 1/10000 w/w $Ru(bipy)_3Cl_2$ on TiO_2 is much less than that of monolayer adsorption (∽1/600 monolayer) as was previously mentioned. Yet, the pre-exponential factor of the fastest component for this case is only about 60 % as is given in Table I. This implies that TiO_2 is not a good adsorbent of $Ru(bipy)_3Cl_2$. This has been suggested by the observation that fast decay components with less than 100 ns lifetimes decreased extremely when the $Ru(bipy)_3Cl_2/TiO_2$ sample is only slightly wetted by water.

Another reason of the low efficiency may be the recombination of the electrons injected into the conduction band of the semiconductor with the oxidized dyes. This process is considered to be important because of following characteristics which are common for simple sensitization process. As shown in Figure 6, the redox potential of $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+}$ is located higher than the valence band of TiO_2. It means that the oxidation power of $Ru(bipy)_3^{3+}$ is weaker than that of the holes in the valence band of TiO_2. Thus, oxidation of methanol-water by visible irradiation of $Ru(bipy)_3^{2+}/TiO_2$ may be more difficult than the oxidation by direct excitation of TiO_2. This increases the probability of the recombination process. Furthermore, the band bending of TiO_2 is considered to be small under conditions of hydrogen evolution, and this is also unfavorable for charge separation of injected electrons.

[Conclusion]

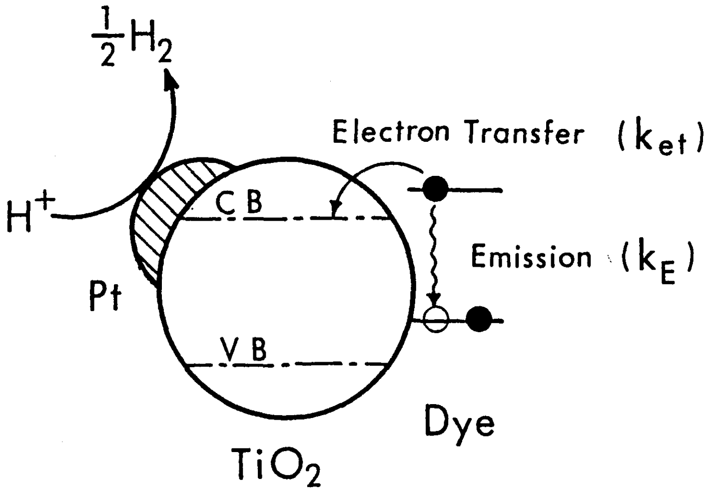
We have obtained time resolved luminescence spectra of $Ru(bipy)_3^{2+}$ which have characteristic features depending on the interaction on the surfaces. Although the decay characteristics are not so simple as we had expected, the origin of more than two decay components of different lifetimes would be mainly assigned to different electron transfer rates depending on the relative position of $Ru(bipy)_3^{2+}$ on the solid surface. The concentration quenching and the electron and energy transfer to the surface states seem also to contribute to the deactivation process of $Ru(bipy)_3^{2+*}$, though further work is necessary to prove and clarify the details of these mechanisms. Anyway, the electron transfer to the conduction band must be the main deactivation channel for $Ru(bipy)_3^{2+}$ giving the fast decay component with less than 21 ns lifetime, by the following reasons.

i) There is a good correlation between the relative weight of the fastest decay component and the energy of the conduction band edge of the substrate semiconductor relative to the redox level of $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+*}$

ii) The spectrum of the fastest decay component can be assigned to $Ru(bipy)_3^{2+}$ molecules firmly attached to the surface of semiconductors.

iii) A photosensitization effect to the hydrogen evolution has been observed for $Ru(bipy)_3^{2+}/TiO_2$ system.

Thus, the present study confirms that $Ru(bipy)_3Cl_2$ has a considerable potential ability for sensitization of oxide semiconductors. However, close contact between the sensitizer and the semiconductor surface must be realized and the recombination of injected electrons with the oxidized sensitizer must be somehow prevented to achieve a high overall efficiency for sensitization. The schematic illustration of these processes are shown in Figure 8.



$$\frac{1}{\tau_E} = k_E + k_n + \underline{\underline{k_{et}}}$$

Figure 8. Schematic illustration of the electron transfer from a dye to a semiconductor.

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Chapter II

Hydrogen Production in Photogalvanic Type Systems.

§1 Hydrogen Production

[Abstract]

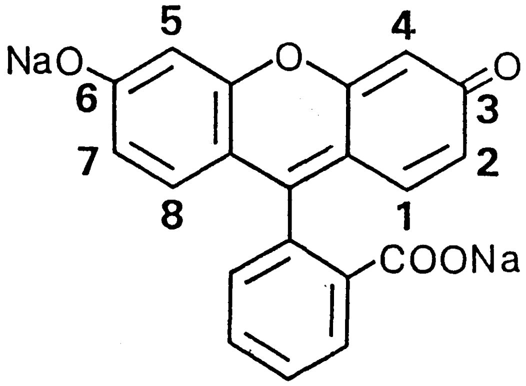
Various halogenated fluorescein derivatives are found to serve as efficient photocatalysts for hydrogen production with visible light in the presence of a reducing agent. These dyes are stable and the reaction is efficient in the high pH region. The quantum yields of hydrogen production for erythrosin are 12 % and 0.15 % with triethanolamine (TEOA) and ethanol as the reducing agents, respectively.

[Introduction]

Photochemical and photoelectrochemical energy conversion has been actively investigated over the last years in connection with solar energy utilization. Especially, the photocatalytic water-splitting reaction is well studied.[1] However only a limited number of dyes and semiconductors such as $Ru(bipy)_3^{2+}$ [2], water soluble zinc porphyrins[3] and CdS[4] have been used as efficient photocatalysts for visible light.

In chapter I we showed that several other dyes can also serve as sensitizers of the hydrogen production system based on dye-sensitization of a semiconductor, in which excited dye molecules are quenched by electron transfer to the semiconductor. The efficiencies of hydrogen production, however, were not high since only a relatively small number of dye molecules adsorbed on the semiconductor or located in the distance of diffusion length of the excited-state dye were able to participate in the electron transfer. Consequently, a strong adsorption or a long excited-state lifetime is necessary for an efficient system based on the dye-sensitized semiconductor method.[5,6]

Here we showed that fluorescein and its halogenated derivatives also serve as efficient photocatalysts for hydrogen production in the presence of a reduction catalyst and a reducing agent.[7] The absorption peaks in the visible region of these dyes are situated around 500 nm and shift to longer wavelength with substituting heavier halogen atoms. This hydrogen production system is also a so-called two-component system, i.e.,non-electron relay system,[8] but the reaction is not based on the dye sensitization of semiconductor.



Fl : 1,2,4,5,7,8-H
$FlCl_2$: 2,7-Cl
$FlCl_2(OCOCH_3)_2$: 2,7-Cl, 3,6-$OCOCH_3$
$FlBr_2$: 4,5-Br
$FlBr_2Hg$: 2,7-Br, 5-Hg
$FlBr_2(NO_2)_2$: 2,7-NO_2, 4,5-Br
$FlBr_4$: 2,4,5,7-Br
FlI_4 : 2,4,5,7-I

Figure 1. Chemical Structures of halogenated fluorescein derivatives.

[Experimental]

The dyes (fluorescein, dichlorofluorescein, dichrolofluorescein diacetate, dibromofluorescein, mercurochrome, eosin B, eosin Y and erythrosin) were obtained either from Eastman Kodak Co. Organic Chemicals or from Aldrich Chemical Company,Inc. and were used without further purification. Hereafter, these dyes are reffered to as Fl, $FlCl_2$, $FlCl_2(OCOCH_3)_2$, $FlBr_2$, $FlBr_2Hg$, $FlBr_2(NO_2)_2$, $FlBr_4$ and FlI_4, respectively. The dyes except $FlCl_2(OCOCH_3)_2$ were employed as the sodium salts. Fl, $FlCl_2$ and $FlBr_2$ were available only in the acid form so that in these cases the sodium form was prepared by dissolving the dye in aqueous NaOH solution. The chemical structures of these dyes are shown in Figure 1.

As the reduction catalyst, platinized TiO_2 powder or colloidal Pt was used. Pt was deposited on the surface of the TiO_2 powders (Nippon Aerosil Co.,LTD.) photochemically as described in Chapter I. The colloidal Pt catalyst was stabilized with polyvinylpyrrolidone (PVP).[9] Other regents were at least commercial special grade and used without further treatments.

An aqueous solution of each dye ($5x10^{-3}$M, 10 ml) with a reducing agent (TEOA, triethylamine (TEA), ethylenediamine-tetra-acetic acid (EDTA), or phenol : $5x10^{-1}$ -

10^{-2}M, or 30 vol% ethanol) and a reduction catalyst (300 mg of Pt/TiO_2 or 4 mg of Pt for colloidal Pt/PVP) in a 280-ml Pyrex flask was evacuated. The pH of the solution was adjusted to 8 - 13.5 with HCl or NaOH. The flask was irradiated from the bottom with visible light from a 500-W Xe lamp(Ushio, UXL500) filtered with a Toshiba 470-nm sharp cutoff glass filter. After irradiation for about one hour, the gas produced was analysed by a quadrupole mass spectrometer and a manometer, as described in Chapter I. For the measurement of the quantum yields for $FlBr_2$ and FlI_4, monochromatic light at the wavelength of the absorption peak of each dye, provided by the 500-W Xe lamp and a interference filter (Vacuum Optics Corporation of Japan), was used as an exciting light whose photon number was determined by using a thermopile (Eppley Inc.). A hydrogen production rate of 87 ml/hour under white light illumination corresponded to a quantum yield of 1.0 with the present equippment. The spectral profiles of the other dyes are similar to those of $FlBr_2$ and FlI_4, so that from the hydrogen production rates under white light illumination we estimated the quantum yields for the other dyes.

[Results and Discussion]

It was found that fluorescein and its halogenated derivatives serve as good sensitizers for hydrogen production from water in the presence of Pt/TiO_2 and TEOA as the reduction catalyst and the reducing agent, respectively. When an aqueous solution of dye-Pt/TiO_2 -TEOA system was irradiated with visible light, the hydrogen gas produced was observed as streams of bubles. When D_2O was used instead of H_2O, D_2 was 79% of the produced gas, DH 19% and H_2 2%. This result suggests that hydrogen is produced from water. In Table I are shown rates and quantum yields of hydrogen production in these systems. Here the quantum yield, Φ_{H_2}, was defined as follows.

$$\Phi_{H_2} = 2 \times \frac{\text{(number of hydrogen molecules produced)}}{\text{(incident photon number)}}$$

Φ_{H_2} values for $FlBr_2$ and FlI_4 were determined directly to be 0.082 and 0.12, respectively, and those for the other dyes were estimated with the method described in the experimental section. Fluorescein itself can serve as the sensitizer with a low efficiency, $\Phi_{H_2} = 0.006$, but the efficiency of hydrogen production increases drastically with halogen atom substitution. Quantum yields of triplet formation (Φ_T) of these dyes in alkaline aqueous solution which were reported by

TABLE I: Quantum Yields of Hydrogen Production and Intersystem Crossing

Dye(a)	Abs. Peak (nm)(b)	H_2 Production(c) (ml/h)(d)	Q.Y.	Intersystem Crossing Q.Y.(e)
(1) Fl	490	0.62	$0.74x10^{-2}$	0.05 ± 0.02
(2) $FlCl_2$	503	1.4	$1.7\ x10^{-2}$	
(3) $FlCl_2(OCOCH_3)_2$	503	3.6	$4.3\ x10^{-2}$	
(4) $FlBr_2$	506	7.1	$8.5\ x10^{-2}$	0.49 ± 0.07
(5) $FlBr_2Hg$	506	7.1	$8.5\ x10^{-2}$	
(6) $FlBr_2(NO_2)_2$	518	0.019	$2.3\ x10^{-4}$	
(7) $FlBr_4$	518	7.8	$9.4\ x10^{-2}$	0.71 ± 0.1
(8) FlI_4	526	10.0	$12\ x10^{-2}$	1.07 ± 0.13

(a) Na salt, (b) pH=12.5 aq.soln., (c) Dye : $5x10^{-3}$ M, Pt/SiO_2, TEOA : 10^{-1} M, (d) reported by P.G. Bowers and G. Porter (10).

P.G.Bowers and G.Porter,[10] are also shown in the same table. Φ_T increases with heavier halogen substitution because of the heavy atom effect on intersystem crossing. Φ_{H_2} increases with Φ_T, suggesting that hydrogen is produced by way of the triplet states of these dyes.

Although the system with Pt/TiO_2 was efficient and the results reproducible, colloidal Pt also served as the reducing catalyst. This result suggests that although the components of the present hydrogen-producting systems are similar to those of the systems based on dye sensitization of semiconductors which are composed of a dye and Pt/TiO_2,[5,6] these reaction mechanisms are quite different from each other. Because in the system Ru(bipy)$_3^{2+}$ - Pt/TiO_2 - EDTA, the existsnce of TiO_2 is indispensable for hydrogen production as shown in Chapter I.

Another characteristic of the present systems is that the reaction is efficient and relatively stable in the high pH region. The maximum rate was obtained in the pH region, 11 - 13 as is shown in Figure 2. From an energetic point of view, the reduction of H_2O is much more difficult than that of protons, but the reaction rates for neutral and acidic solutions are lower and decrease faster than that for alkaline solution. This result suggests that the intermediate species of this reaction is stable and its formation yield is high in the alkaline region. On the other hand fluorescein and its halogenated derivatieves are known to be photo-reduced via the triplet state, forming very stable semi-reduced dyes in aqueous alkaline solution in the presence of a reducing agent.[11] All the results described above indicate that the reductive quenching of the excited triplet state dye is the first reaction step and forms the semi-reduced radical which plays the role of the intermediate in the present hydrogen production reaction. This will be discussed in §2.

Besides TEOA, several other sacrificial reducing agents such as TEA[12] and EDTA,[11-(a),13] and some organic compounds such as ethanol and phenol[11-(c)] are known to be able to reduce fluorescein derivatives to the semi-reduced radicals.

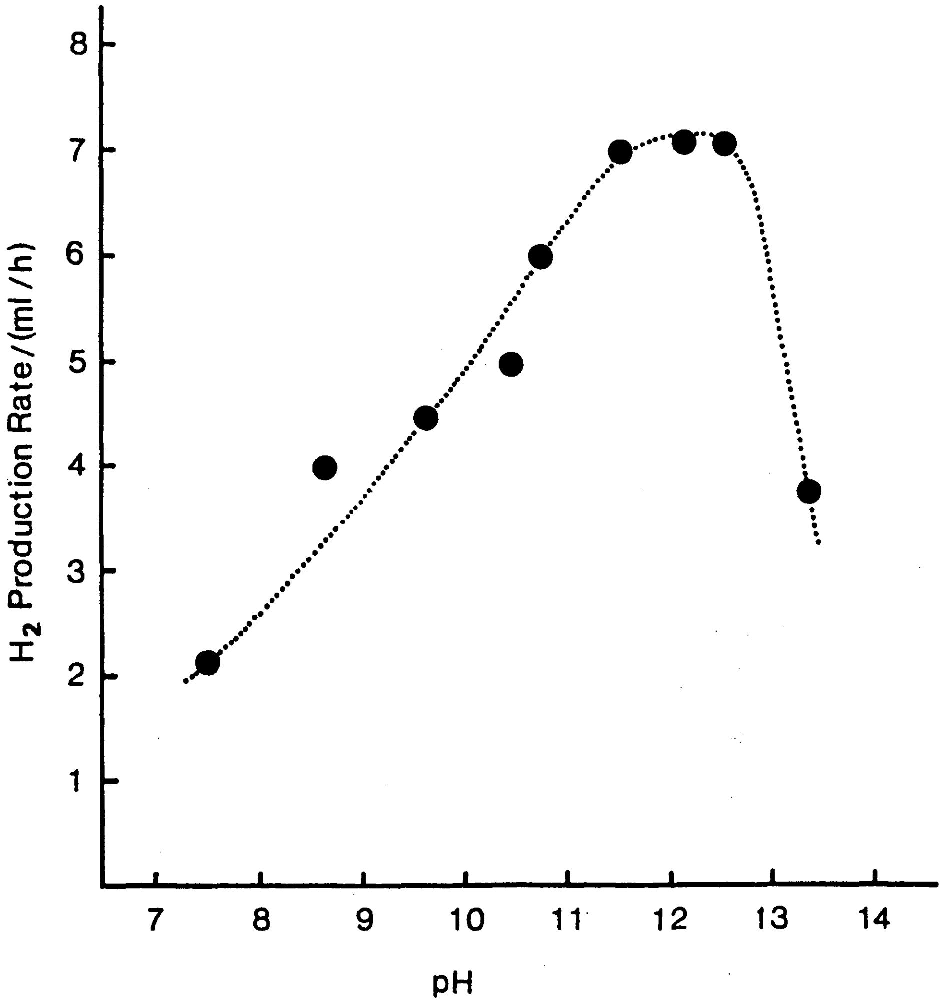


Figure 2. pH dependence of the initial rate of hydrogen production. $FlBr_2$:$5x10^{-3}$ M, Pt/TiO_2, TEOA:$5x10^{-1}$ M

In fact hydrogen can also be produced with these compounds instead of TEOA in the presence of a reducion catalyst, although the efficiencies are lower than that with TEOA. The rates and the quantum yields of the hydrogen production with $FlBr_4$ are shown in Table II. The result that ethanol and phenol also served as reducing agents indicates that the excited states of these dyes have relatively strong oxidating power.

The initial efficiency of hydrogen production with FlI_4 and TEOA is rather high compared to the other homogeneous systems. The photofading of dyes, however, occurs and the

TABLE II: Hydrogen Production with Eosin-Y ($FlBr_4$) and Various Reducing Agents

Red. Agent	H_2 Production	
	Rate (μl/h)	Q.Y.
TEOA(a)	7800	9×10^{-2}
TEA(a)	630	7×10^{-3}
EDTA(a)	1300	1.5×10^{-2}
Ethanol(b)	110	1×10^{-3}
Phenol(a)	1	1×10^{-5}
H_2O	0	0

(a) 10^{-1} M, (b) 50 vol %
Reduction catalyst: Pt/SiO_2

reaction rate decreases gradually during prolonged irradiation. Figure 3 shows the change in the hydrogen production rate and the turn-over number of the dye in the

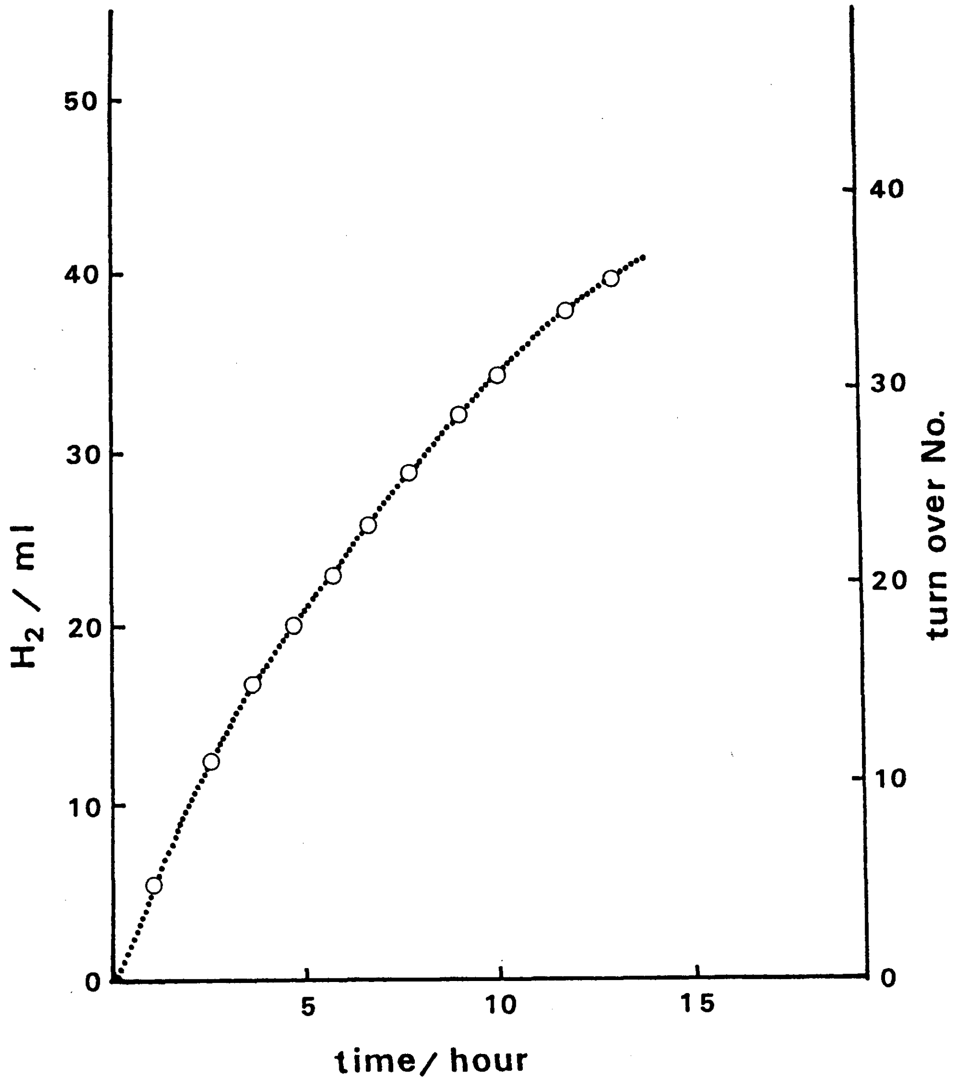


Figure 3. Overall hydrogen production and turn-over number of the dye in Eosin-Y ($FlBr_4$)-Pt/SiO_2-TEOA system as a function of the visible light illumination time.
Light source:500 W Xe lamp (λ>470 nm). $FlBr_4$:$5x10^{-3}$ M, TEOA:10^{-1} M, pH = 12.5 (10 ml aq. soln).

$FlBr_4$ -Pt/SiO_2-TEOA system. The rate after 10 hours of irradiation was about a half of the initial rate. The turn-over numbers of Fl, $FlBr_4$ and FlI_4 in the presence of Pt/SiO_2 and TEOA, were about 400, 120 and 30, respectively, showing the catalytic nature of these reactions and the tendency that the dyes substituted with heavier halogen atoms are more easily decomposed. These values, however, depend on various conditions such as light intensity, reduction catalyst and pH, so that these might be improved with better conditions.

Φ_{H_2} of the most efficient system studied (FlI_4) is 0.12 and is almost equal to that of one of the most efficient three-component systems, $Ru(bipy)_3^{2+}$ - MV^{2+}- Pt/PVA in the presence of EDTA, 0.13.[14] The other two-component systems were reported by several researchers, for instance, $Ru(bipy)_3^{2+}$-PtO_2,[15] proflavine-Pt/PVA[8] and chromium (III) complexes-Pt/PVA[16] in the presence of TEA, EDTA or TEOA, and EDTA, respectively. However, hydrogen production in the present system is more efficient than that in other relatively stable two-component systems. For instance, the rate for $FlBr_4$ is several times larger than that for proflavine. The quantum efficiency for the chromium complexes is almost the same as for $FlBr_4$, but the turn-over number of chromium complexes is very small, about 4. A comparison of these hydrogen production systems is summarized in Table III.

TABLE III: Comparison of Characteristics of Hydrogen-Producting Systems

Dye	Eosin-Y ($FlBr_4$)	Proflavine (b)	$Ru(bipy)_3^{2+}$ (c)	$Ru(bipy)_3^{2+}$ (d)
Absorption Peak (nm)	518	445	452	452
Electron Relay	—	—	MV^{2+}	—
Redox Catalyst	Pt/TiO_2	Pt-PVP	Pt-PVP	Pt/TiO_2
H_2 Production Rate(ml/h)(a)	7.8	2.4	2.9(e)	0.1
pH	12.5	7.0	5.0	5.0
Reducing Agent	TEOA	TEOA	EDTA	EDTA

(a) Visible light from a 500-W Xe lamp filtered with a 470-nm filter for the $FlBr_4$ system, a 390-nm filter for the proflavine system and a 440-nm filter for the $Ru(bipy)_3^{2+}$ systems, respectively.

(b), (c) The experimental conditions were the same as those of references (8) and (1-(g)), respectively.

(d) Dye-sensitized Pt/TiO_2 sytem.(5)

(e) See note (17).

[Conclusion]

Relatively efficient hydrogen-producting systems can be constructed by using halogenated fluorescein derivatives. These are the first examples of the hydrogen production system using dye which is efficient in the high pH region. This indicates that the intermediate radical has relatively strong oxidating power, because the reduction of H_2O, which is more difficult than that of H^+, proceeds under these conditions. Therefore, there might be the possibility of applying them to other reductive reactions, especially in alkaline solution. Moreover the spectral properties can be easily controlled by substitution, which is a characteristic feature of these kinds of organic dyes.

There are, however, still two serious problems to be solved. One is the instability of the dye. The other is the weak oxidating power of the dye in the excited state. If we can succeed in synthesizing a stable dye with a more positive reduction potential in the excited state, this method will become more promising.

[References and Notes]

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§2 Photocatalytic and Photoelectrochemical Processes of Fluorescein Derivatives.

[Abstract]

The mechanism of photocatalytic hydrogen production with fluorescein derivatives was studied by measuring the transient absorption spectrum and the time behavior of the intermediate species. First, these dyes are photo-reduced to stable semi-reduced dyes via the triplet state. The intermediate radical has a very long lifetime, more than ten seconds, so that these dyes can serve both as photo-sensitizers and electron relays. The radical formed in the bulk solution diffuses to the surface of the catalyst initiating the electron transfer in the hydrogen production system. These processes are very similar to those of a photogalvanic cell. In fact the photoelectrochemical cell composed of a fluorescein derivative shows a photo-response behavior typical to a photogalvanic cell. The open voltage and the quantum yield of the short circuit current for eosin Y as a sensitizer in the presence of TEOA are about 1 V and 21 %, respectively.

[Introduction]

In §1 we showed that several halogenated fluorescein derivatives serve as photocatalysts for hydrogen production in the presence of a reduction catalyst and a reducing agent. This hydrogen production system is a so-called two-component system, i.e .,non-electron relay system. The reaction was efficient in the high pH region, and colloidal Pt also served as the reduction catalyst.

Here we studied this hydrogen-producting reaction in detail. As was described in §1 it is well known that xanthene and thiazine dyes are photo-reduced in the presence of a reducing agent under visible light illumination.[1] Especially, fluorescein and its halogenated derivatives are reduced to very stable semi-reduced dyes in the high pH region.[1,2] We can show evidences that these semi-reduced dyes play the role of intermeadiate species in the present system. The mechanism, based on reductive quenching of excited dyes, will be discussed and compared with that based on the dye sensitized semiconductor system. This process is very similar to that of a photogalvanic cell. In fact we also found that an efficient photogalvanic cell can be constructed by using these dyes and an irreversible reducing agent.

[Experimental]

(1) Hydrogen Production and Characterization of Intermediate Species.

Hydrogen production experiments were done with the same conditions with §1. As the reduction catalyst, several platinized semiconductor powders, platinized SiO_2 powder or colloidal Pt was used. Commercial semiconductor powders and SiO_2 powders were obtained either from Nippon Aerosil Co.,LTD. (TiO_2 : P-25 rutile, average grain size 0.3 μm, surface area 50 m^2/g, SiO_2 : Ox-50, 0.4 μm, 50 m^2/g) or Kojundo Kagaku Co.,LTD. (TiO_2 (anatase), SnO_2, $SrTiO_3$ ZrO_2, average grain size, several μm). Pt was deposited on the surface of the powders either with the photochemical,[10] or a conventional impregation method.

The absorption spectra were measured on a Hitachi 556 spectrometer with 1 mm path length cell. The measurements of the time behavior of the transient species were performed with a frequency-doubled (532 nm) YAG laser with a pulse width of 15 ns (Quanta-Ray Inc.) as the exciting light and a DC iodine lamp as the monitor light. The photomultiplier output was recorded and analysed with a 100 MHz transient digitizer (Iwatsu INC., DM901). The details were described elsewhere.[3]

(2) Photoelectrochemical Experiment

A commercial TiO_2 single crystal which was heated under hydrogen(300 torr) for 2 hours, a commercial SnO_2 coated glass plate and a ZnO sintered disk, which was prepared from ZnO powder moulded by compression and heated at 1300 °C for 2 hours in the air, were used as working electrodes. The electrochemical measurements were performed in a glass cell containing a working electrode, a Pt plate and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. The electrolyte solution contained the dye ($5x10^{-4}$M), TEOA (10^{-2}M) and K_2SO_4 (0.2 M). The pH of the sample solution was adjusted to 12.6 by adding NaOH solution. Nitrogen gas was bubbled into the solution for 10 min. before each measurement. The open voltage (V_{op}) and the short circuit current (I_{sc}) were measured on a digital voltmeter and a recorder under visible light illumination (λ>470 nm from the 500-W Xe lamp). For the measurements of the action spectrum, time response and quantum efficiency of I_{sc}, monochromatic light provided by the 500-W Xe lamp and a monochromator (Nikon G250) was used.

[Results and Discussion]

(1) Photocatalytic Properties

In §1 we suggested that the reaction mechanism for the present system is different from that for the dye sensitized semiconductor system, although both consist of the same components, that is, dye, Pt/TiO_2 and a reducing agent. Table I shows the relative activities of various kinds of reduction catalysts on hydrogen production in the $FlBr_2$-TEOA system. Here the rate for Pt/TiO_2 (Aerosil) was normalized to 100. Neither remarkable nor systematic changes depending on the energy levels of supporting semiconductors were observed. Moreover both Pt/SiO_2 and colloidal Pt can serve as reduction catalysts. The existence of semiconductor is dispensable in the present systems although that is necessary in the hydrogen production systems based on dye sensitization of semiconductors. The efficiency of hydrogen production in the present case might be determined mainly by the catalytic activity of platinum.

On the other hand fluorescein and its halogenated derivatieves are known to be photo-reduced via a triplet state, forming very stable semi-reduced dyes in aqueous alkaline solution in the presence of a reducing agent.[2] It can be expected that these semi-reduced dyes play the role of the

TABLE I: Effect of Reduction Catalysts on Hydrogen Production

Reduction Catalyst	Ratio of Initial Hydrogen Production Rates[c]
Pt/ZrO_2[a]	75
$Pt/SrTiO_3$[a]	90
Pt/TiO_2[a]	90
Pt/SnO_2[a]	80
Pt/TiO_2[b]	100
Pt/SiO_2[b]	95
colloidal Pt	85

Dye:$FlBr_2$ ($5x10^{-3}$ M), Reducing agent: TEOA (10^{-1} M), Powders of (a) and (b) were purchased from Kojundo Kagaku Co.,LTD. (grain size:several μm) and Nippon Aerosil Co.,LTD.(300 Å), respectively. (c) The rate for Pt/TiO_2 (300 Å) was normalized to 100. These values were averaged from sevetal experiments.

intermediate species in the present system, since the hyrogen-producting reaction is also efficient in the high pH region and becomes more efficient with a heavier atom substitution. Thus we have done spectroscopic experiments to confirm the above consideration. First we measured the absorption spectra of FlI_4 in the presence of TEOA. The dotted curve and the solid curve in Figure 1 represent the absorption spectra of FlI_4 in the absence of a reduction catalyst before irradiation and just after 10 seconds irradiation with the visible light from the 500-W Xe lamp. The intensity of the main peak decreases and a new peak emerges around 415 nm. This new peak is assigned to the semi-reduced dye.[2-(b),(c),(d)] Second, we measured the time behavior of these peaks with the flash photolysis technique. In Figure 2-(A) are shown the time course of the transient absorptions at 415 nm of the semi-reduced radical. In the absence of a reduction catalyst, this radical decayed very slowly (curve (a)) and the lifetime was estimated to be more than 15 seconds. Curves (b) and (c) are the decay curves in the presence of colloidal Pt. With increasing ~~the~~ concentration of colloidal Pt, the radical disappears faster. Figure 2-(B) represents the time behavior of the original ground state dye in the presence of colloidal Pt observed at 545 nm. From these curves, it can be seen that the amount of the original ground state dye decreased with excitation and the semi-reduced radical was formed. In the presence of Pt the radical disappeared and the original dye was recovered, although the radical has a very long lifetime in the absence of a reduction catalyst. Consequently, we can conclude that this semi-reduced dye is the intermediate species in the

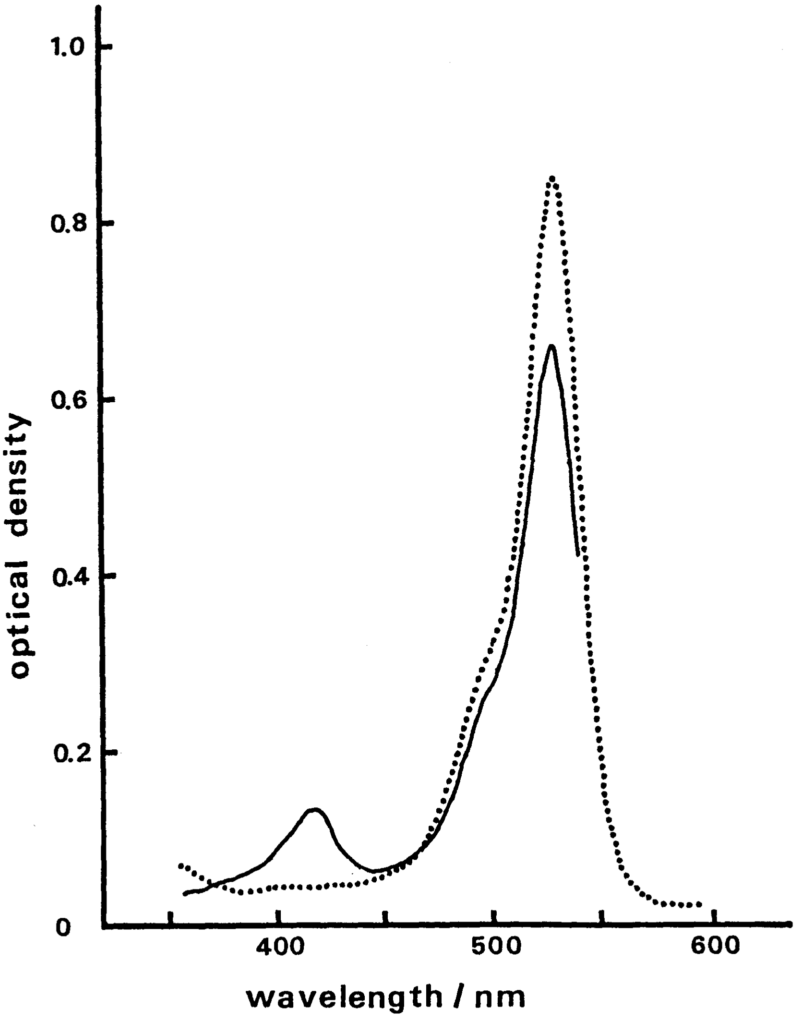

Figure 1. Absorption spectra of erythrosin (FlI_4) in the presence of TEOA.

Dotted curve : before irradiation, solid curve : after irradiation for 10 seconds in the absence of a reduction catalyst.

Light source : 500-W Xe lamp (λ>470 nm), FlI_4 : 9.5×10^{-6}M, TEOA : 10^{-3}M, pH = 12.5, path length of the cell : 1 mm.

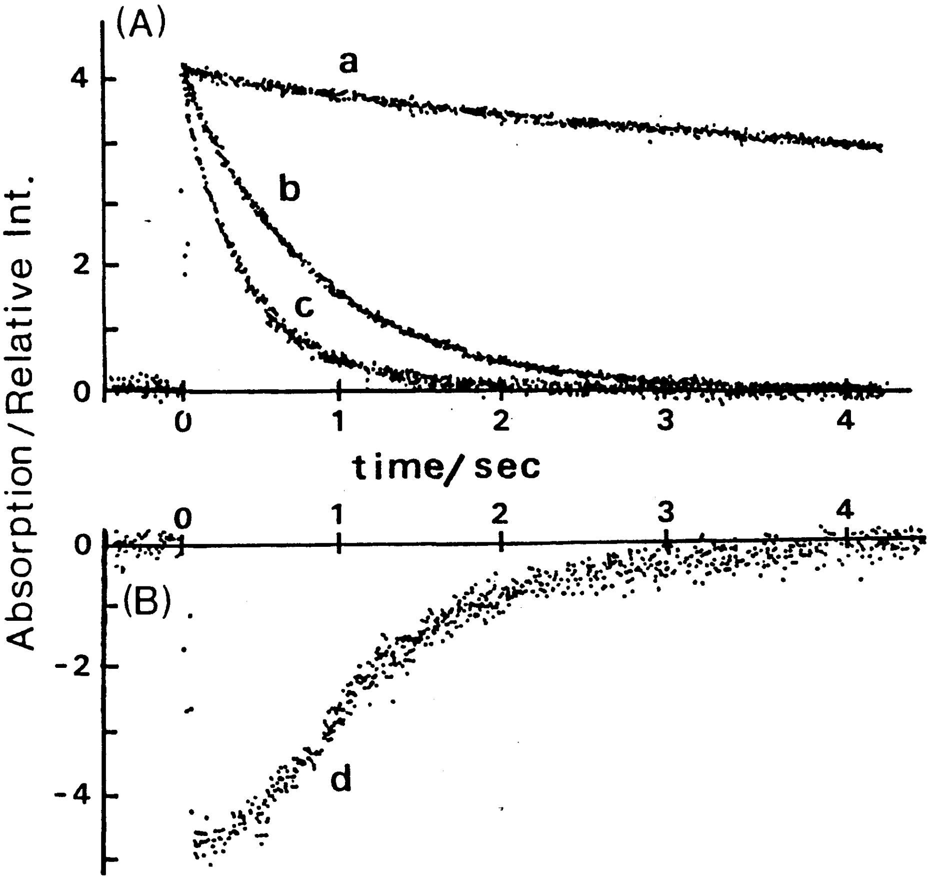

Figure 2. Transient abosrption of erythrosin (FlI_4) in the presence of TEOA.
(A) observed at 415 nm (semi-reduced dye).
(B) observed at 545 nm (ground state dye).
(a) in the absence of colloidal Pt.
(b), (c) and (d) in the presence of 10^{-4} M, $2x10^{-4}$ M and 10^{-4} M colloidal Pt, respectively.

present hydrogen production process and recovers to the original dye releasing an electron to the Pt catalyst on which hydrogen is produced.

(2) Photoelectrochemical Properties

We constructed relatively efficient photoelectrochemical cells by using the present fluorescein derivatives and TEOA. Interestingly, they showed very high photovoltages (V_{op}) amounting to 1 V, and the quantum efficiencies of the short circuit current ($\Phi_{I_{SC}}$) for monochromatic light, which are defined as follows,

$$\Phi_{I_{sc}} = \frac{\text{(number of electron flown in the cell)}}{\text{(incident photon number)}} \qquad (1),$$

were rather high, 0.01 - 0.20.

Photoelectrochemical cells using dyes can be roughly classified into two categories.[4] One is based on the sensitization effect of the dye adsorbed on the semiconductor electrode,[5] and the other is based on the photochemical reaction of the dye in the bulk solution,[6] the latter is called photogalvanic cell. The present systems seem to correspond to the latter case containing an irreversible reducing agent,[7,8] because the long-lived semi-reduced dye might play an important role in the current generation as well as in the hydrogen production system described previously. In fact, a platinum plate can also serve as the light electrode instead of semiconductors. This property is characteristic of a photogalvanic cell.[4]

Table II shows the values of V_{op} and Φ_{Isc} in the cell, <semiconductor or Pt (light) |$FlBr_4$-TEOA| Pt (dark)>, with various light electrode materials. Neither V_{op} nor Φ_{Isc} depends greatly on the kind of light electrode. Here, the following two points are to be noted. (a) Either a semiconductor or Pt can work as the electron acceptor from the semi-reduced dye, and the efficiency for the semiconductor is slightly better than that for platinum, probably because of a rectification effect of the semiconductor. (b) The photopotential of each light electrode is more negative than -1.0 V vs SCE. Actually the potential value of the anodic oxidation of the semi-reduced radical for $FlBr_4$ was measured to be more negative than -1.2 V vs SCE under the same conditions.[9]

TABLE II: Dependence of Light Electrode Materials on Open Voltage and Short Circuit Current

Electrode	Open Voltage (V)	V vs SCE	Q.Y. of I_{sc}
TiO_2	0.95	-1.12	0.14
ZnO	1.02	-1.19	0.18
SnO_2	0.99	-1.16	0.21
Pt	0.86	-1.02	0.091

Dye:$FlBr_4$ ($5x10^{-4}$ M), Reducing agent:TEOA (10^{-2} M), Na_2SO_4 (0.2 M), pH = 12.6

Because the hydrogen production potential with pH = 12.6 is about -0.99 V vs SCE, hydrogen production is possible in any case. These results indicate that the semi-reduced dye can give an electron to either a semiconductor or Pt in the hydrogen production system using a Pt/(semiconductor) reduction catalyst, and moreover the potential of Pt loaded on the semiconductor, whose Fermi level is more positive than the hydrogen production potential, becomes negative enough for hydrogen production under irradiation. These agree with the results obtained in the previous section where the hydrogen production efficiency is almost independent on the kind of a supporting material of Pt.

The solid curve in Figure 3 shows the time dependence of the photocurrent. The current rises and decays very slowly when the light is turned on or off, taking several minutes to become constant. This behavior agrees with that of a typical photogalvanic cell with an irreversible reducing agent,[8] and is explained as follows. The long-lived semi-reduced dye formed in the bulk solution diffuses to the surface of the electrode (semiconductor or Pt), initiating the electron transfer and the current rises. On the other hand, we showed in §1 that the hydrogen production from the system composed of rose bengal, Pt/TiO_2 and EDTA in the aqueous solution at pH=5 is based on the dye-sensitization effect of the semiconductor.

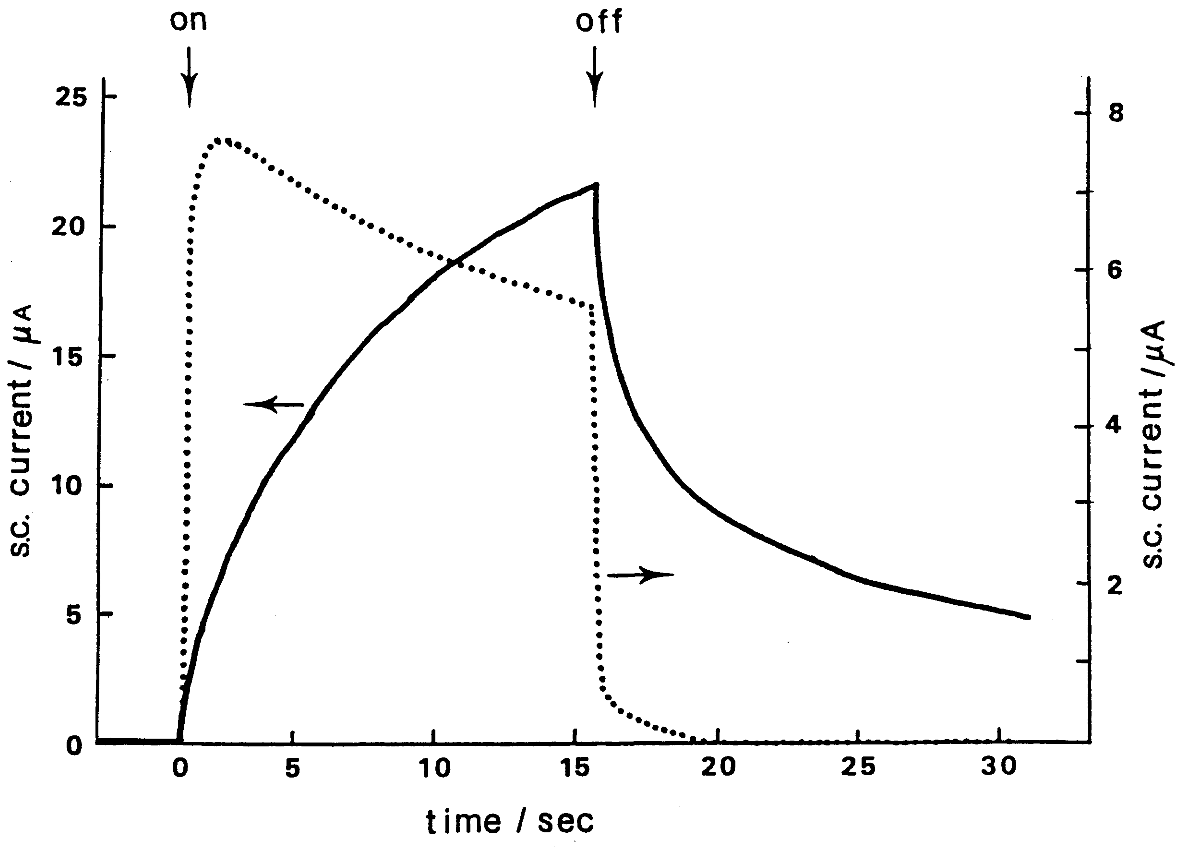

Figure 3. Change of photocurrent vs time.
light electrode potential : 0.4 V vs SCE,
solid curve : <ZnO|eosin Y,TEOA|Pt> ,
pH=12.6, 518 nm irradiation,
dotted curve : <ZnO|rose bengal,EDTA|Pt>,
pH=6.0, 620 nm irradiation.

Actually the time response of the current produced in the cell composed of ZnO, Pt, rose bengal and EDTA as the light electrode, a dark electrode, a sensitizer and a reducing agent (pH=5) is very fast (<ms) and is shown in Figure 3 (dotted curve). The response time of dye-sensitized semiconductor

cells is known to be very fast, because the electron transfer occurs from the adsorbed excited dye to a semiconductor electrode.[5]

On the other hand rose bengal can be also classified in one of the fluorescein derivatives. In fact it serves as the sensitizer of photogalvanic type hydrogen-producting system in the high pH region, althogh the rate decreases soon by the irradiation. In the neutral or acidic solution, however, the semi-reduced dye is not produced efficiently and its lifetime is not so long. Thus the photogalvanic process can not occur efficiently. However, this dye adsorbs on the surface of semiconductor well, [4] so that the electron transfer process from the excited dye to semiconductor occurs more efficiently than the formation of the semi-reduced dye at low pH region. Consequently the system composed of rose bengal behaves as the dye-sensitized semiconductor system in the neutral and acidic solution, and as the photogalvanic system in the alkaline solution.

We also investigated the dependence of V_{op} and I_{sc} on the kinds of the fluorescein derivatives. The results are shown in Table III. V_{op} is not very sensitive to the kind of dye, which means that each semi-reduced radical has the almost same oxidation potential. $\Phi_{I_{sc}}$ also increased with heavy-atom substitution except FlI_4. FlI_4 is easily decomposed as described previously, so that the apparent quantum yield might

TABLE III: Open Voltage and Quantum Yield of Short Circuit Current Using Various Fluorescein Derivatives as Sensitizers.

Dye	Open Voltage (V)	V vs SCE	Q.Y. of I_{sc}
Fl	1.01	-1.17	0.014
$\mathrm{FlCl_2}$	1.01	-1.15	0.055
$\mathrm{FlBr_2}$	1.05	-1.17	0.13
$\mathrm{FlBr_4}$	0.99	-1.16	0.21
$\mathrm{FlI_4}$	1.01	-1.16	0.099

Light Electrode:$\mathrm{SnO_2}$,Dye:5×10^{-4} M, Reducing agent:TEOA (10^{-2} M), $\mathrm{Na_2SO_4}$:0.2 M, pH = 12.6

be small. There is also an interesting aspect that $\Phi_{I_{SC}}$ is larger than Φ_{H_2} in these systems.

(3) Reaction Mechanism

From the above discussions, the reaction mechanism of the present system would be described as follows.

$$\left.\begin{array}{lr} \mathrm{Dye} \xrightarrow{h\nu} {}^{1}\mathrm{Dye}^{*} & (2) \\ {}^{1}\mathrm{Dye}^{*} \longrightarrow {}^{3}\mathrm{Dye} & (3) \end{array}\right\} \quad \text{(Bulk)}$$

$$\left.\begin{array}{lr} {}^{3}\text{Dye} \xrightarrow{\text{Red}} \text{Dye}^{-\cdot} + \text{Red}^{+\cdot} & (4) \\ \text{Red}^{+\cdot} \xrightarrow{\qquad} \text{Decomposition} & (5) \end{array}\right\} \quad \text{(Bulk)}$$

$$\text{Dye}^{-\cdot} \xrightarrow[\text{or Pt}]{\text{TiO2}} \text{Dye} + e^{-} \qquad (6) \qquad \text{(Interface)}$$

Here Red and e^{-} represent a reducing agent and an electron respectively. The processes, (2) - (5), occur in the bulk of the solution. The semi-reduced dye, which has a very long lifetime, diffuses to the surface of a reduction catalyst or an electrode to which the semi-reduced dye transfers an electron being oxidized into the original dye. The transferred electron generates electricity in a photo-electrochemical cell and is also used for the reductions of water in the hydrogen-producting system.

As was indicated in the previous section, the radical can transfer an electron to either TiO_2 or Pt electrodes and the efficiencies are almost the same. Thus the electron transfer might also occur to both the TiO_2 surface and particulate Pt loaded on the TiO_2 surface in the hydrogen production system using Pt/TiO_2 photocatalyst as the reduction catalyst. However, when TiO_2 alone was used, little hydrogen is produced. This indicates that TiO_2 is used as the electron carrier to the Pt site, as was suggested by M. Grätzel et al. in the $Ru(bipy)_3^{2+}$ - methylviologen(MV^{2+}) - $Pt/TiO_2/RuO_2$

system,[10] and TiO_2 itself is not a good catalyst for hydrogen production.

The initial efficiencies of hydrogen production and photocurrent with FlI_4 and TEOA are rather high compared to the other systems reported previously.[4] However, photofading of dyes also occurs even in this system and the reaction rate decreases gradually during the prolong irradiation as described in §1. Imamura et al. reported that halogenated fluorescein dyes are photochemically dehalogenated by visible light and ring system remains.[2-(b),11] They investigated the mechanism of this process by using γ-ray irradiation and a flash photolysis technique.[2-(d),12,13] According to their results, the semi-reduced dyes produced absorb the light around 400 nm and dehalogenation proceeds successively, resulting in the fluorescein formation. Even in the presence of a reduction catalyst, the same reactions seem to proceed, although its rate is much slower than that in the absence of a reduction catalyst. Curves (a) and (b) in Figure 4 represent the absorption spectra of the FlI_4 solution before and after prolonged irradiation, respectively. The peak position of (b) corresponds to that of the absorption spectrum of Fl.[11] Curve (c) shows the absorption intensity of Fl whose molar amount was same as that of FlI_4 used on (a). From the absorption intensities of (b) and (c), it is known that about 70 % of the FlI_4 was converted to Fl under these conditions (see the

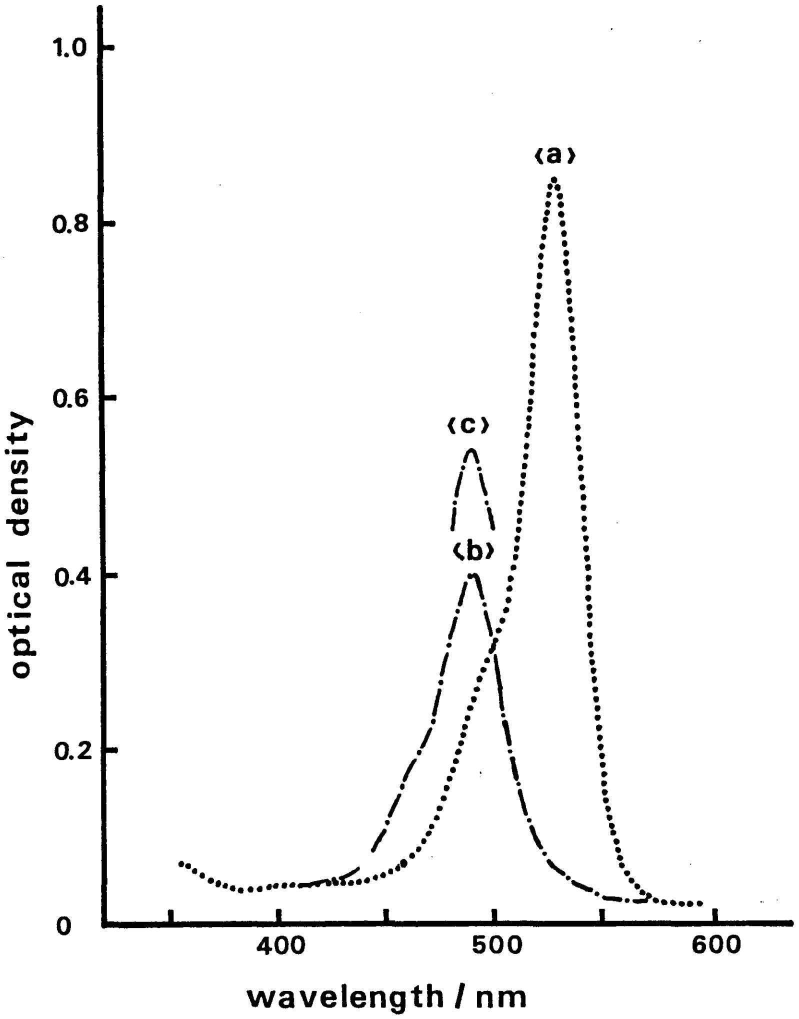

Figure 4. Absorption spectra of erythrosin(FlI_4) in the presence of TEOA.

(a) Before irradiation, (b) after irradation for 30 hours in the presence of Pt/SiO_2, (c) absorption intensity of fluorescein(Fl) whose molar amount is same as that of FlI_4 on curve (a).

Light source : 500-W Xe lamp(λ>470 nm), FlI_4 : 9.5x10^{-6}M, TEOA : 10^{-3}M, pH = 12.5, path length of the cell : 1 mm.

caption of Figure 4). For the rest of FlI_4 (30 %), ring system might have been decomposed. Halide ions (0.5 M) were added the solution in an attempt to prevent the dehalogenation, but no effect was observed.

In Figure 5 is shown the schematical picture of the hydrogen production process. This is a so-called two-component system, i.e., electron relay free system,[14] and the dye serves as both a sensitizer and an electron relay.[6-8] This process is similar to that of photogalvanic cells,[5] so that we may call this a photogalvanic-type hydrogen-producting system.

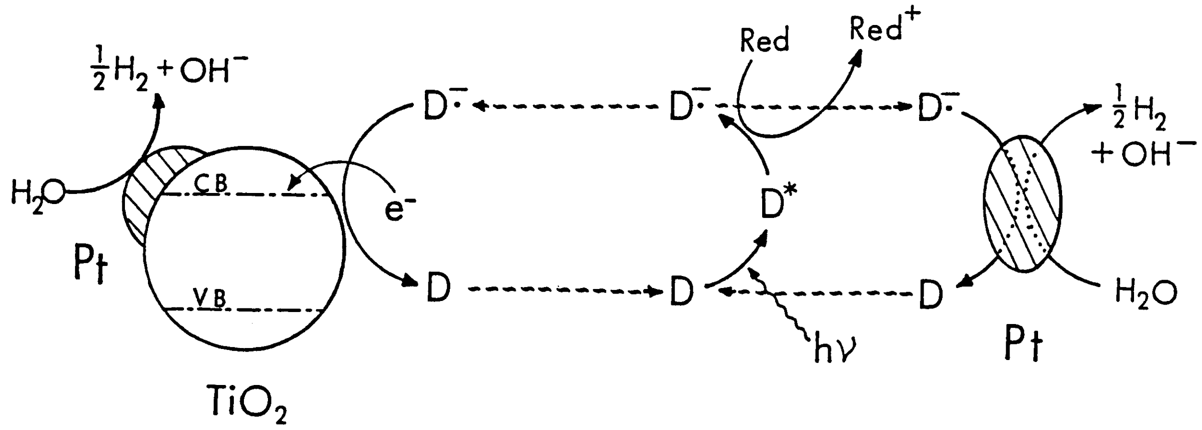

Figure 5. Schematic illustration of the hydrogen-producting process for halogenated fluorescein derivatives in the presence of a reduction catalyst and a reducing agent.

The components of this system are very similar to those of a dye-sensitized semiconductor system, but the reaction mechanisms are quite different from each other. The latter process can be explained as described Chapter I. That is,

$$\mathrm{Dye} \xrightarrow{\quad h\nu \quad} \mathrm{Dye}^{*} \tag{7}$$

$$\mathrm{Dye}^{*} \xrightarrow[\text{semiconductor}]{} \mathrm{Dye}^{+\cdot} + e^{-}_{cb} \tag{8}$$

$$\mathrm{Dye}^{+\cdot} \xrightarrow{\quad \mathrm{Red} \quad} \mathrm{Dye} + \mathrm{Red}^{+\cdot} \tag{9}$$

$$\mathrm{Red}^{+\cdot} \xrightarrow{\qquad} \text{decomposition} \tag{10}$$

Here e^{-}_{cb} represents an electron in the conduction band of the semiconductor. This electron is used for the reduction of water and the current as well. In this case the excited dye is quenched by the oxidative electron transfer to the semiconductor, so that only the dye adsorbed on the semiconductor surface and the dye that exists in the diffusion layer formed by the excited state dye can participate in the electron transfer. This process is illustrated in Figure 6. Consequently the apparent quantum yield of hydrogen production becomes low even if the electron transfer occurs efficiently between the semiconductor and the adsorbed dye.

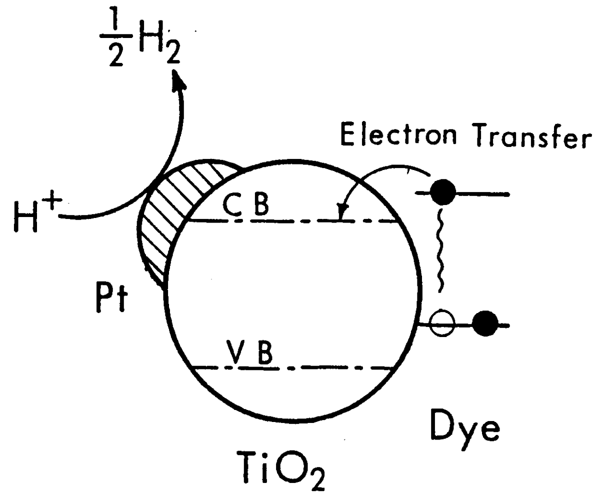

Figure 6. Schematic illustration of hydrogen productions process for dye-sensitized semiconductor system.

However, in the photogalvanic-type hydrogen-producting system, the excited dye is quenched by the reductive process forming a very stable radical, so that almost all the dye molecules in the bulk solution can participate in the electron transfer. This is the reason why the quantum yield is high in this system.

However as was indicated previously, most dyes might be able to behave both as the sensitizers of photogalvanic type systems (reductive quenching of the excited state dyes forming semi-reduced dyes) and the sensitizers of the dye-sensitized semiconductor systems (oxidative quenching of the excited state dyes accompanied by the electron transfer from dyes to a semiconductor). One of the main determination factors of the process is the pH of solution. For example, in the case of a fluorescein derivative the photogalvanic type process occurs more efficiently than the dye-sensitized semiconductor type process at the high pH region, although the latter occurs more efficiently than the former at low pH region.

[Conclusion]

The mechanism of hydrogen production with a fluorescein derivative and a reducing agent at the high pH region was confirmed by the spectroscopic and the electrochemical experiments. The excited dye is reduced via a triplet state forming a very stable semi-reduced radical. The radical diffuses to the surface of a reduction catalyst initiating the electron transfer, and hydrogen is produced from water. In this case the existence of a semiconductor is not so important.

Photogalvanic cells with a very high open voltage (∼1V) and a high quantum yield of a short cicuit current (1∼20%) can also be constructed with fluorescein derivatives.

The mechanisms based on two different processes, oxidative and reductive electron transfer processes, were shown and it was suggested that pH of the solution is one of the main determnation factors of the mechanism in the case of a fluorescein derivative as a sensitizer.

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