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Photochemical hydrogen evolution from alkaline solutions of xanthene dyes

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Abstract

The effect of the composition of five xanthene dyes (photoabsorber and photosensitizer) on the hydrogen photoproduction from aqueous solutions was investigated. It is suggested that triethanolamine (TEOA) can quench the excited singlet state of fluorescein in aqueous solution (1×10^{-4} mol l^{-1}, pH 12.5). As a result, a reduced form of fluorescein is produced, which can further reduce H^+ to H_2 in the presence of K_2PtCl_6 (5×10^{-5} mol l^{-1}). The quantum yield of H_2 photoproduction (Φ_{H_2}) is 0.024. For tetraiodofluorescein (erythrosin) in aqueous solution (1×10^{-4} mol l^{-1}), pH 12.5; K_2PtCl_6, 5×10^{-5} mol l^{-1}), Φ_{H_2} is as high as 0.30 owing to the inner molecular heavy atom effect. The quantum yields of fluorescence and intersystem crossing, Φ_F and Φ_{ISC}, were measured and compared with Φ_{H_2} for all the investigated dyes. The results show an important ability of xanthene dyes to enhance hydrogen photoproduction from alkaline aqueous solutions.

Keywords: Xanthene dyes; Hydrogen photoproduction

1. Introduction

Photochemical systems for the photoreduction of water are of considerable interest as models for the conversion of solar energy. In so-called sacrificial systems, hydrogen ions are reduced by electrons which are derived from an added donor rather than from the oxidation of hydroxyl ions [1–3]. Compared with metal complexes, organic dyes have been investigated only rarely as sensitizers for the photoreduction of water [4–6]; however, because of the common availability of organic dyes, it is of interest to explore the potential of representative examples as sensitizers.

The xanthene dyes studied in this work were chosen because they absorb over a wide range of the visible spectrum; these dyes are well known as sensitizers in photography, biological stains, redox indicators and, more recently, active media for use in dye lasers and sensitizers for the formation of singlet oxygen. Thus the photochemistry studied here may have wider implications.

In these systems, the dye (X) acts as a transducer and initiates the light-induced redox reactions which may be represented as [7]

$$X \xrightarrow{h\nu} [X]^*$$

$$[X]^* + D \longrightarrow [X]^- + D^+$$

$$[X]^- + H_2O \xrightarrow{\text{catalyst}} X + \tfrac{1}{2}H_2\uparrow + OH^-$$

The overall reaction is

$$D + H_2O \xrightarrow[\text{catalyst}]{h\nu} D^- + \tfrac{1}{2}H_2\uparrow + OH^-$$

In this paper, xanthene dyes (fluorescein, diiodofluorescein, dibromofluorescein, tetraiodofluorescein and tetrabromofluorescein) were used as photoabsorbers. Triethanolamine (TEOA) was applied as the electron donor and potassium chloroplatinate, K_2PtCl_6, was used as the catalyst. The photoreduction of xanthene dyes by ethylenediaminetetraacetic acid (EDTA) has been studied extensively [8,9]. This study suggests that TEOA can quench the excited singlet state of fluorescein (F) in aqueous solution (F, 1×10^{-4} M; TEOA, 0.2 M; pH 12.5) to produce a reduced form of F (F^-), which can further reduce H^+ to H_2 in the presence of a Pt catalyst (K_2PtCl_6, 5×10^{-5} M). The quantum yield of H_2 production (Φ_{H_2}) increases with an increase in intersystem crossing from the excited singlet state to the triplet state of the last four dyes due to the inner molecular heavy atom effect.

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2. Experimental details

2.1. Materials

The xanthene dyes (fluorescein (F), dibromofluorescein (DBF), diiodofluorescein (DIF), eosin or tetrabromofluorescein (TBF), erythrosin or tetraiodofluorescein (TIF)) were obtained commercially, and were purified by recrystallization from ethanol. Their formulae (stable form at pH 12.5) are given in Table 1 (see Section 3.1). The experimental uncertainty of the measurements is estimated to be 5%.

2.2. Fluorescence and phosphorescence spectra

The fluorescence excitation and emission spectra were measured on a Perkin–Elmer LS-5 luminescence spectrometer. The phosphorescence spectra were measured using a Hitachi MPF-4 luminescence spectrometer; ether:iso-pentane:alcohol(ethanol), 5:5:2 (EPA) was used as the solvent at 77 K. Fluorescence lifetime measurements were determined using a Horiba NAES-1100 time-correlated, single-photon-counting instrument.

2.3. Fluorescence quantum yield

The fluorescence quantum yield was measured on a Perkin–Elmer LS-5 spectrometer and calculated with a 3600 data station according to

$$\Phi = \frac{FA_0}{F_0 A}\,\Phi_0$$

where A is the absorbance, F is the fluorescence intensity and the subscript "0" stands for the reference dye. Φ_0(fluorescein) = 0.93 [10].

2.4. Intersystem crossing quantum yield

The intersystem crossing quantum yield was determined by the sensitized delayed fluorescence technique [11] and calculated using

$$\Phi_{ISC} = \frac{A}{A_0}\left(\frac{F_{D,0}}{F_D}\right)\Phi_{ISC,0}$$

where A is the absorbance, F_D is the delayed fluorescence intensity and the subscript "0" stands for the reference dye. $\Phi_{ISC,0}$(erythrosin) = 0.69 [12]. 9,10-Dimethylanthracene was chosen as the acceptor.

2.5. Hydrogen photoproduction

The visible-light-induced hydrogen production was carried out using the apparatus described in Ref. [13]. A hydrogen-producing catalyst, K_2PtCl_6, was added to the X–D aqueous solution for hydrogen evolution. It was necessary to deoxygenate the K_2PtCl_6-containing X–D solution for hydrogen photoproduction before illumination. The amount of hydrogen evolved was collected manometrically using a simple burette arrangement and the hydrogen obtained was identified by gas chromatography. A 500 W xenon lamp was used as the light source to mimic sunlight; its light energy density at the working area was about 80 mW cm^{-2}.

2.6. Quantum yield of H_2 photoproduction

ORIEL interference bandpass filters were used to obtain suitable monochromatic light for each xanthene dye. The light intensity (I_0) in the reaction cell was measured using $KFe(C_2O_4)_2$ chemical actinometer. The quantum yield of H_2 photoproduction for each dye, Φ_{H_2}, was calculated according to

$$\Phi_{H_2} = \frac{2 \times V_{H_2}}{22\,400 \times 3600 \times (1 - 10^{-D_\lambda}) I_0}$$

where V_{H_2} is the H_2 volume (ml) produced per hour, and in our experimental conditions $D_\lambda \approx 2$, i.e. $10^{-D_\lambda} \approx 0$.

3. Results and discussion

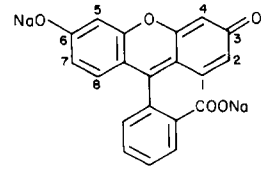
3.1. Quantum yields and lifetimes of xanthene dyes (Table 1)

As an example, Figs. 1(a) and 1(b) show the absorption spectrum and fluorescence emission spectrum of fluorescein in aqueous solution. From Fig. 1(a), the extinction coefficient ($\epsilon \approx 5 \times 10^4$ l mol^{-1} cm^{-1}) and the oscillator strength ($f = 0.378$) can be obtained; Fig. 1(b) yields the quantum yield of fluorescence ($\Phi_F = 0.93$). The fluorescence lifetime of fluorescein ($\tau_F = 7.6$ ns) and the lifetime of the singlet excited state [14]

Table 1
Quantum yields and lifetimes of xanthene dyes[a]

	F	DBF	TBF	DIF	TIF
Φ_F	0.93	0.48	0.34	0.14	0.07
τ_F (ns)	7.6	3.7	2.7	0.9	0.5
Φ_{ISC}	0.03	0.30	0.35	0.52	0.69

[a]Formulae (stable form at pH 12.5) are as follows: F, parent compound; DBF, 4,5: Br; TBF, 2,4,5,7: Br; DIF, 4,5: I; TIF, 2,4,5,7: I.



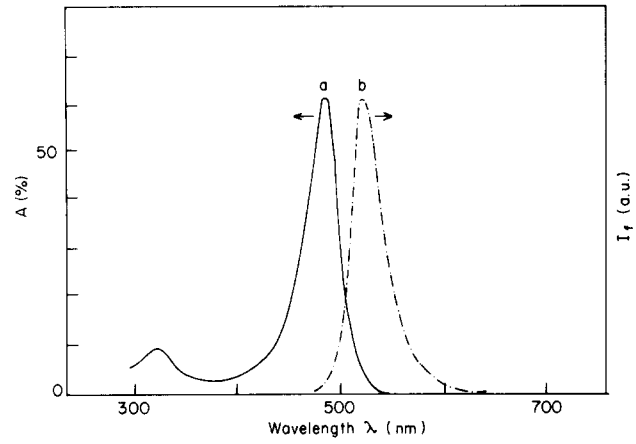


Fig. 1. Absorption (a) and fluorescence emission (b) spectra of fluorescein in aqueous solution (1×10^{-4} mol l^{-1}, pH 12.5); A, absorbance; I_f, fluorescence intensity (arbitrary units).

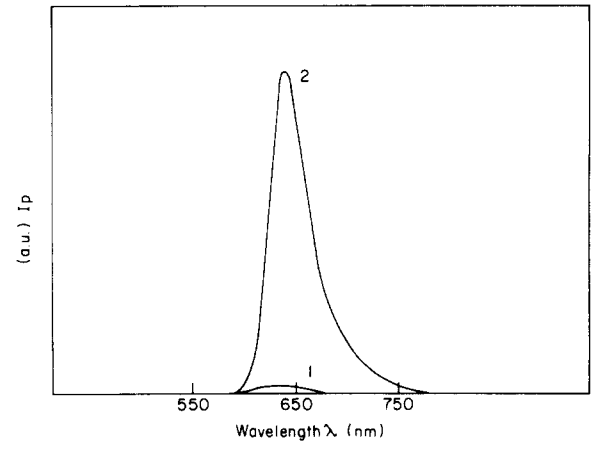


Fig. 2. Phosphorescence emission spectra of fluorescein (1) and erythrosin (2) in EPA (at 77 K); I_p, phosphorescence intensity (arbitrary units).

Table 2
Dynamic constants of fluorescein in alkaline aqueous solution

τ_S (ns)	k_S (s^{-1})	k_F (s^{-1})	k_{ISC} (s^{-1})	k_{IC} (s^{-1})	${}^Sk_q$ (M^{-1} s^{-1})
6.9	1.43×10^8	1.32×10^8	4.1×10^6	6.9×10^6	2.04×10^9

($\tau_S=\tau_F\times\Phi_F=6.9$ ns) can be calculated from the fluorescence lifetime measurements. The quantum yield of intersystem crossing was measured by the method described in Section 2.4 and is given in Table 1.

3.2. Dynamic constants of fluorescein in alkaline aqueous solution

The following photochemical processes should be considered

$$F \xrightarrow{h\nu} {}^SF^* \quad (1)$$

$${}^SF^* \xrightarrow{k_F} F + \text{fluorescence} \quad (2)$$

$${}^SF^* \xrightarrow{k_{IC}} F + \text{heat} \quad (3)$$

$${}^SF^* \xrightarrow{k_{ISC}} {}^TF^* \quad (4)$$

in which F represents fluorescein. We already know Φ_F, τ_F and τ_S. From Ref. [14], $k_F=1/\tau_F$, $k_S=1/\tau_S=k_F+k_{IC}+k_{ISC}$ and $k_{ISC}=\Phi_{ISC}\times k_S$; therefore, these data can be calculated as listed in Table 2. ${}^Sk_q$ is calculated in Section 3.4.

3.3. Phosphorescence emission and lifetime of fluorescein and erythrosin

As two extremes, the phosphorescence emission and lifetimes of fluorescein and erythrosin are compared (Fig. 2) in order to illustrate the inner molecular heavy atom effect on intersystem crossing (Table 1) and the phosphorescence emission of erythrosin.

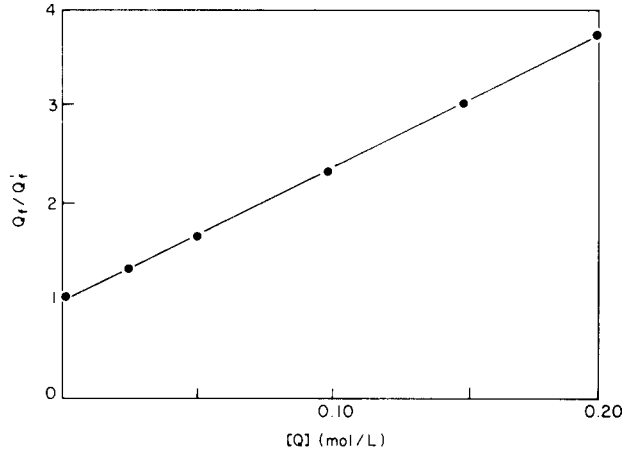


Fig. 3. Fluorescence quenching of fluorescein in aqueous solution (1×10^{-4} mol l^{-1}, pH 12.5) by TEOA; Φ_F, Φ_F', fluorescence quantum yields in the absence and presence of TEOA; [Q], concentrations of TEOA in solution.

There is a strong phosphorescence emission from erythrosin solution; its lifetime can be estimated from the long phosphorescence decay curve using a good oscilloscope. In our experimental conditions, the phosphorescence lifetime of erythrosin (5.0 ms) is about six orders of magnitude longer than the fluorescence lifetime of fluorescein (6.9 ns).

3.4. Quenching of the excited states of fluorescein and erythrosin by TEOA (Q)

The quenching can be expressed as (X stands for xanthene dyes)

$${}^SX^* + Q \xrightarrow{{}^Sk_q} X^- + Q^+ \quad (5)$$

$${}^TX^* + Q \xrightarrow{{}^Tk_q} X^- + Q^+ \quad (6)$$

Fig. 3 shows the fluorescence quenching of an aqueous solution of fluorescein, which is in accordance with the Stern–Volmer rule

$$\Phi_F/\Phi_F' = 1 + {}^S k_q \tau_S [Q]$$

where Φ_F and Φ_F' are the fluorescence quantum yields in the absence and presence of TEOA (concentration [Q]) in aqueous solution respectively. ${}^S k_q$ is the bimolecular quenching rate constant and τ is the fluorescence lifetime (τ_S). From the straight line in Fig. 3, ${}^S k_q \tau_S = 14.1\ (\text{mol l}^{-1})^{-1}$ and ${}^S k_q = 2.04 \times 10^9\ (\text{mol l}^{-1})^{-1}\ \text{s}^{-1}$ can be calculated.

For erythrosin, fluorescence quenching of an aqueous solution by TEOA cannot be detected. In addition, we have not observed the phosphorescence quenching of erythrosin by TEOA at 77 K, which is consistent with the results reported in Ref. [15]. We have detected the phosphorescence quenching of erythrosin by TEOA using room temperature phosphorescence (RTP) technology, which will be reported in due course.

3.5. Mechanism of photoproduction of H_2 in an alkaline aqueous solution of fluorescein

It is well known that electron transfer from TEOA to the dye triplet excited state yields the very stable reduced state of the dye [15,16] which possesses a high reducing power [6,7]. According to the literature [6,9], the possible mechanism for the photoproduction of H_2 in an alkaline aqueous solution of fluorescein (F) is

$$F \xrightarrow{h\nu} {}^S F^* \tag{7}$$

$${}^S F^* \xrightarrow{k_{ISC}} {}^T F^* \tag{8}$$

$${}^T F^* + D \xrightarrow{{}^T k_q} F^- + D^+ \tag{9}$$

$$F^- + H_2O \xrightarrow[(Pt)]{k_r} F + \tfrac{1}{2}H_2\uparrow + OH^- \tag{10}$$

in which ${}^S F^*$ and ${}^T F^*$ represent the excited singlet and triplet states respectively, F^- is the reduced state and D is the electron donor. In our experimental conditions (F, 1×10^{-4} mol l^{-1}; pH 12.5; using TEOA as D at about 0.1 M), Φ_F is as high as 0.93 and Φ_{ISC} is as low as 0.03. The fluorescence quenching follows the Stern–Volmer equation (Fig. 3). Since the energy of the excited state of TEOA is much higher than that of F, energy transfer between them is not possible. We have calculated the free energy of electron transfer between ${}^S F^*$ and TEOA

$${}^S F^* + \text{TEOA} \xrightarrow{{}^S k_q} F^- + \text{TEOA}^+ \tag{11}$$

by the Weller experimental equation [17]

$$\Delta G = 23.06\left(E_{D/D^+} - E_{A^-/A} - \frac{e^2}{\epsilon a}\right) - \Delta E_{0,0} \tag{12}$$

in which $E_{D/D^+}(\text{TEOA}) = 0.64$ V, $E_{A^-/A}(F) = -1.36$ V and $e^2/\epsilon a = 0.06$ V, so that $\Delta G = -12.12$ kcal mol^{-1} (much less than zero). This means that it is possible for reaction (11) to take place. From reaction (10), the hydrogen volume produced becomes

$$V_{H_2} = k_r[F^-] = \Phi_{H_2} I \tag{13}$$

where I is the light intensity. If F^- can be produced from both ${}^S F^*$ and ${}^T F^*$, at the steady state

$$\Phi_{H_2} = {}^S\Phi_{H_2} + {}^T\Phi_{H_2} \tag{14}$$

$${}^S\Phi_{H_2} = \frac{{}^S k_q[D]}{k_S + {}^S k_q[D]} \times \rho \tag{15}$$

$${}^T\Phi_{H_2} = \frac{k_{ISC}}{k_S + {}^S k_q[D]} \times \frac{{}^T k_q[D]}{k_T + {}^T k_q[D]} \times \sigma \tag{16}$$

in which ${}^S\Phi_{H_2}$ and ${}^T\Phi_{H_2}$ represent the contributions of the excited singlet and triplet states to Φ_{H_2} respectively, $k_S = 1/\tau_S = 1.43 \times 10^8\ \text{s}^{-1}$ is the rate constant of ${}^1F^*$ disappearance, $k_T = k_p + {}^T k_{IC}$ is the rate constant of ${}^T F^*$ disappearance and ρ and σ are the related constants of electron transfer between ${}^S F^*$, ${}^T F^*$ and TEOA respectively catalysing the production of H_2.

Because $k_S(1.43 \times 10^8\ \text{s}^{-1}) \gg k_{ISC}(4.13 \times 10^6)$ and $[D] \approx 0.1$ M, for fluorescein ${}^T\Phi_{H_2} \approx 0$, i.e.

$$\Phi_{H_2} \approx {}^S\Phi_{H_2} = \frac{{}^S k_q[D]}{k_S + {}^S k_q[D]} \times \rho \tag{15'}$$

We have measured $\Phi_{H_2} = 0.024$ at $[D] = 0.2$ M; ${}^S k_q = 2.04 \times 10^9$ and $k_S = 1.43 \times 10^8$, so that $\rho = 0.033$. We can convert Eq. (15′) into the following form

$$\frac{1}{\Phi_{H_2}} = \frac{1}{\rho} + \frac{k_S}{\rho \times {}^S k_q} \times \frac{1}{[D]} = 31 + 2.2 \times \frac{1}{[D]} \tag{15''}$$

Comparing the calculated $1/\Phi_{H_2}$ vs. 1/[D] curve based on Eq. (15″) with the experimental results, it can be seen that they agree well within experimental error (Fig. 4). Thus the mechanism of H_2 photoproduction from fluorescein aqueous solution can be proposed to involve electron transfer between ${}^S F^*$ and TEOA to form F^-, followed by the catalytic reduction of H^+ by

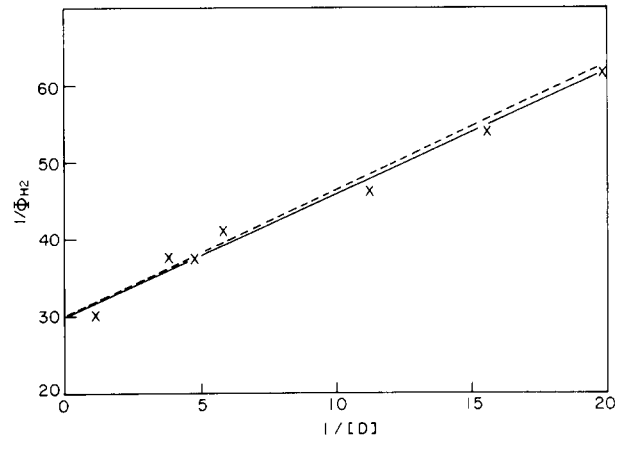


Fig. 4. Diagram of $1/\Phi_{H_2}$ vs. 1/[D] (F, 1×10^{-4} mol l^{-1}, pH 12.5); [D] is the concentration of TEOA: ——, experimental curve; – – –, calculated curve (take $\rho = 0.033$). Φ_{H_2}, quantum yield of H_2 photoproduction.

F^-. The analyses and calculations for the other four dyes are currently under study in our laboratory.

3.6. Quantum yields of H_2 photoproduction from aqueous solutions of xanthene dyes

Fig. 5 illustrates the relationship between the H_2 volume produced and the irradiation time at the wavelength corresponding to the absorption peak of fluorescein and erythrosin in aqueous solution. Table 3 shows the relationship between the quantum yields of fluorescence (Φ_F), intersystem crossing (Φ_{ISC}) and H_2 photoproduction (Φ_{H_2}) of the five xanthene dyes. Owing to the inner molecular heavy atom (Br and I, especially I), the quantum yields of intersystem crossing (Φ_{ISC}) for DBF, DIF, TBF and TIF are much larger than that for F. The excited singlet states, $^SX^*$, of these four dyes can easily convert to the excited triplet states, $^TX^*$, through intersystem crossing. The lifetime of $^TX^*$ is much longer than that of $^SX^*$; therefore, the probability that $^TX^*$ will form X^- is much larger than that for $^SX^*$, leading to high quantum yields of H_2 photoproduction (Φ_{H_2}).

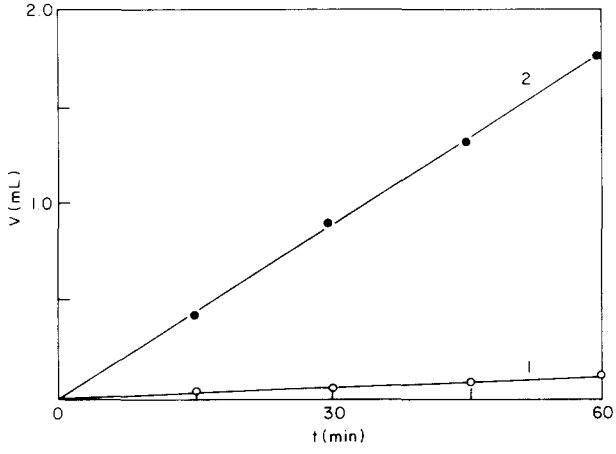


Fig. 5. Relationship between the volume of H_2 evolved (V) and the irradiation time t (I_0 is the light intensity at the reaction cell (1.27×10^{-7} einstein s^{-1})): (1) fluorescein, λ (irradiation wavelength) = 480 nm; (2) erythrosin: λ = 500 nm.

Table 3
Quantum yields of fluorescence (Φ_F), intersystem crossing (Φ_{ISC}) and H_2 photoproduction (Φ_{H_2})

	F	DBF	TBF	DIF	TIF
Φ_F	0.93	0.48	0.34	0.14	0.07
Φ_{ISC}	0.03	0.30	0.35	0.52	0.69
Φ_{H_2}	0.024	0.10	0.20	0.25	0.30

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