

Polypyridine Transition Metal Complexes as Light Emission Sensitizers in the Electrochemical Reduction of the Persulfate Ion

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Electrochemical reduction of polypyridine-type complexes of Cr(III), Ru(II), and Os(II) in the presence of $S_2O_8^{2-}$ ions is accompanied by light emission. The electrochemiluminescence (ecl) spectrum is identical to the photoluminescence spectrum of the complex which undergoes reduction. The net reaction in the electrochemical cell is the reduction of $S_2O_8^{2-}$ to SO_4^{2-} with the polypyridine complex acting as both an electron transfer mediator and as a light emission sensitizer. The experiments were carried out in aqueous solutions for the Cr(III) complexes and in dimethylformamide or acetonitrile for the Ru(II) and Os(II) complexes. The dependence of the ecl emission on $S_2O_8^{2-}$ concentration was examined. In preliminary experiments no light emission was obtained with Rh(III) and Ir(III) polypyridine complexes. The interconversion between chemical (and/or electrical) energy and light mediated by suitable sensitizers is briefly discussed.

Introduction

Light may be involved in many chemical processes. The best known cases are those in which light is used as a *reactant* (photochemical reactions, eqn. 1):



These reactions may allow the conversion of light into chemical or electrical energy [1] and may also be involved in other processes of practical or theoretical interest [2]. Less known are the cases in which light is generated as a *product* of a chemical reaction (chemiluminescent processes, eqn. 2):



Such processes allow the conversion of chemical or electrical energy into light and they are also very

interesting from the theoretical and practical points of view [3].

Electron transfer processes leading to luminescence emission are well known for organic molecules [3]. In the field of transition metal complexes, however, only a relatively small number of such processes have been reported. Much of the work in this area has been done by Bard and his co-workers [4]. In particular, they have carefully investigated the electrogenerated chemiluminescence (ecl) of $Ru(bpy)_3^{2+}$ ($bpy = 2,2'$ -bipyridine) solutions for both theoretical and practical purposes, showing that this complex exhibits excellent properties as an electron transfer reactant in chemiluminescence processes.

We have recently reported some chemiluminescent reactions involving Cr(III) and Ru(II) polypyridine complexes [5]. In this work we describe the chemiluminescent reactions which occur during the electrochemical reduction of polypyridine transition metal complexes in the presence of persulfate ions. The net result of such a process is actually the reduction of persulfate and the generation of light, with the polypyridine complexes playing the role of *light emission sensitizers*. To the extent that the same complexes are also widely used as *light absorption sensitizers* in artificial solar energy conversion systems [1, 6], the analogies between sensitized photochemical reactions and sensitized chemiluminescence processes are briefly underlined.

Experimental

Cr(III), Ru(II), Rh(III), Os(II), and Ir(III) complexes of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives were available from previous photochemical and photophysical investigations [7] and had been prepared according to published procedures. Triply distilled water and Merck

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spectroscopic grade acetonitrile (AN) and dimethylformamide (DMF) were used as solvents. Potassium persulfate (Merck), tetraethylammonium perchlorate: TEAP (Fluka), and NaClO_4 (Merck) were used as received. All the experiments were carried out at room temperature ($\sim 20^\circ\text{C}$) on solutions deaerated by nitrogen bubbling. The absorption spectra were measured by means of a Perkin-Elmer 323 spectrophotometer. Uncorrected photoluminescence and electroluminescence (ecl) spectra were recorded by using a Perkin-Elmer MPF 3 spectrofluorimeter equipped with an R 928 photomultiplier. Electrochemical experiments were performed with an Amel Electrochemolab system. Ecl experiments were carried out in a specially designed cell which can be placed in the cell compartment of the spectrofluorimeter. The working electrode was either a Pt sphere or a flat Pt electrode (geometric area, 0.40 cm^2). A silver wire quasi reference electrode and a Pt counter electrode were contained in separate tubes connected to the test solution *via* fritted glass disks. Before each ecl experiment, a cyclic voltammogram of the solution was recorded in order to establish the exact position of the reduction peaks *vs.* the quasi reference electrode. Nitrogen bubbling was used to stir the solution when it was necessary. The photochemical ex-

periments were carried out with a medium pressure Hg lamp equipped with a 434 nm interference filter. The intensity of the incident light on the reaction cell (3 ml capacity) was $6.5 \times 10^{-7}\text{ Nh}\nu/\text{min}$.

Results

Current-potential curves obtained with a Pt electrode for DMF solutions containing (a) $\text{Ru}(\text{bpy})_3^{2+}$ $1.0 \times 10^{-3}\text{ M}$, (b) $\text{S}_2\text{O}_8^{2-}$ $5.0 \times 10^{-4}\text{ M}$, and (c) $\text{Ru}(\text{bpy})_3^{2+}$ $1.0 \times 10^{-3}\text{ M}$ and $\text{S}_2\text{O}_8^{2-}$ $5.0 \times 10^{-4}\text{ M}$ are shown in Fig. 1. Saturated solution of $\text{K}_2\text{S}_2\text{O}_8$ in DMF showed a poorly defined irreversible reduction peak at about 0.47 V vs. SCE , which moved to more negative potentials with decreasing $\text{K}_2\text{S}_2\text{O}_8$ concentration. Figure 2 shows the curves obtained for aqueous solutions (pH 6) of (a) $\text{Cr}(\text{bpy})_3^{3+}$ $1.0 \times 10^{-3}\text{ M}$, (b) $\text{S}_2\text{O}_8^{2-}$ $5.0 \times 10^{-4}\text{ M}$, and (c) $\text{Cr}(\text{bpy})_3^{3+}$ $1.0 \times 10^{-3}\text{ M}$ and $\text{S}_2\text{O}_8^{2-}$ $5.0 \times 10^{-4}\text{ M}$; the behavior of a solution containing the supporting electrolyte alone on the Pt electrode is also shown

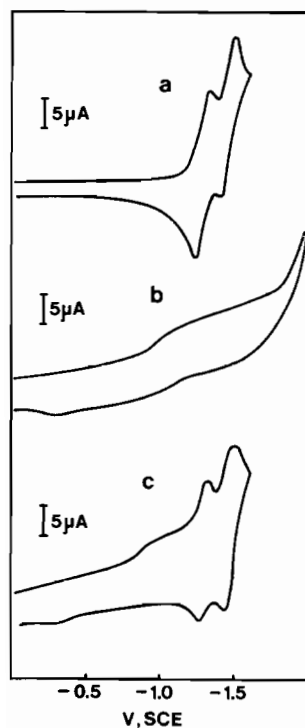


Fig. 1. Current-potential curves at Pt electrode (sweep rate 250 mV/s) for DMF solutions containing: (a) $1.0 \times 10^{-3}\text{ M}$ $\text{Ru}(\text{bpy})_3^{2+}$; (b) $5.0 \times 10^{-4}\text{ M}$ $\text{S}_2\text{O}_8^{2-}$; (c) $1.0 \times 10^{-3}\text{ M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and $5.0 \times 10^{-4}\text{ M}$ $\text{S}_2\text{O}_8^{2-}$. In all cases 0.1 M TEAP was also present as supporting electrolyte.

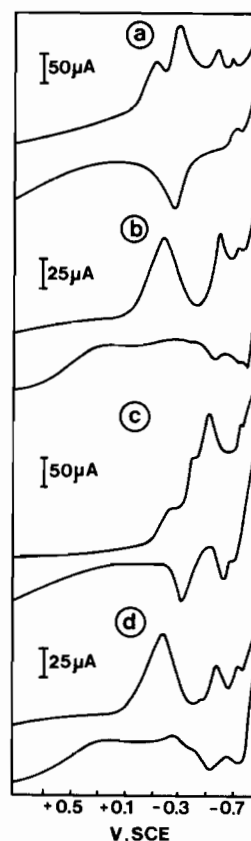


Fig. 2. Current-potential curves at Pt electrode (sweep rate 600 mV/s) for aqueous solutions containing: (a) $1.0 \times 10^{-3}\text{ M}$ $\text{Cr}(\text{bpy})_3^{3+}$; (b) $5.0 \times 10^{-4}\text{ M}$ $\text{S}_2\text{O}_8^{2-}$; (c) $1.0 \times 10^{-3}\text{ M}$ $\text{Cr}(\text{bpy})_3^{3+}$ and $5.0 \times 10^{-4}\text{ M}$ $\text{S}_2\text{O}_8^{2-}$; (d) 0.1 M NaClO_4 , which was the supporting electrolyte.

(curve d). More concentrated solutions of $S_2O_8^{2-}$ in water showed a distinct irreversible reduction peak at about -0.53 V. Saturated AN solutions of $K_2S_2O_8$ ($<5 \times 10^{-5}$ M) showed an irreversible reduction peak at about -0.52 V.

The solutions of the complexes used were stable in the dark. Addition of $K_2S_2O_8$ did not cause any reaction. Luminescence experiments showed that $S_2O_8^{2-}$ does not quench the emitting excited state of the complexes under the experimental conditions used. Prolonged irradiation (~ 10 h) of 10^{-3} M Ru(bpy) $_3^{2+}$ in DMF solutions saturated with $K_2S_2O_8$ did not cause any variation in the absorption and emission spectra.

For the Ru(II), Os(II), Rh(III) and Ir(III) complexes the experiments were carried out in DMF or AN because their first reduction peak lies at too negative potentials to be studied in water. The Cr(III) complexes were studied in water because they are known to give a relatively strong luminescence in this solvent.

For the experiments in DMF, when a potential corresponding to the irreversible $S_2O_8^{2-}$ reduction peak was applied to the working electrode of the ecl cell no emission was observed in all cases. However, when a more negative potential (corresponding to the first reduction wave of the complex) was applied, luminescence emission was observed for all the Ru(II) and Os(II) complexes (see, for example, Fig. 3). By contrast, no emission was observed with Rh(phen) $_3^{3+}$ and Ir(phen) $_2Cl_2^+$. For the Ru(II) complexes the orange luminescence was quite bright and clearly visible to the non-dark-adapted eye. Also in the cases of the Cr(III)– $S_2O_8^{2-}$ – H_2O systems luminescence

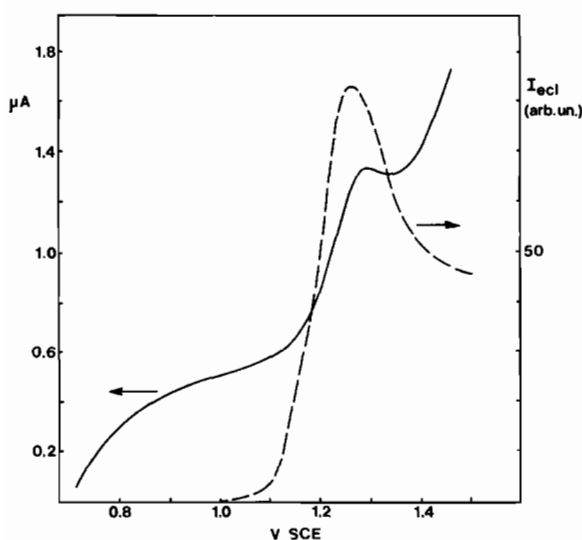


Fig. 3. Current–potential (full line) and ecl emission intensity–potential (dotted line) for a DMF solution containing 1.0×10^{-3} M Ru(bpy) $_3^{2+}$, 5.0×10^{-4} M $S_2O_8^{2-}$, and 0.1 M TEAP supporting electrolyte.

was only obtained when a potential sufficiently negative to reduce the complex was applied. The observed ecl spectrum was in all cases identical in shape and λ_{max} to the photoluminescence spectrum recorded before applying the potential. For the Ru(II) complexes, the emission intensity decreased slowly with time, probably due to some passivation phenomenon at the working electrode. When the electrode was cleaned by immersion in hot nitric acid, the intensity resumed the initial value. For the Cr(III) complexes the emission intensity decreased more rapidly and could not be restored by cleaning the electrode. The relative ecl intensities were estimated by comparing the heights of the ecl emission band maxima under identical experimental conditions. Corrections for the different sensitivities of the photomultiplier at different wavelengths were made using the sensitivity curve supplied by the manufacturer. Successive experiments carried out on identical solutions showed that the reproducibility of the light intensity measurements was within 10%, the error being mainly due to slight differences in the position of the working electrode in the ecl cell.

The relative photoluminescence intensities were obtained by comparing the heights of the maxima of the photoluminescence spectra under identical instrumental conditions for solutions having the same optical density at the same irradiation wavelength. Relative photoluminescence quantum yields were estimated from comparison of the area of the emission bands. In both cases appropriate corrections were made to account for the different sensitivity of the phototube at different wavelengths.

A summary of the experiments performed is presented in Table I, which also gives the spectroscopic and electrochemical data that are relevant for the discussion of the results obtained.

For the Ru(bpy) $_3^{2+}$ – $S_2O_8^{2-}$ –DMF system, the ecl intensity was found to depend on the $S_2O_8^{2-}$ concentration with a maximum at $[S_2O_8^{2-}] = 5.0 \times 10^{-4}$. A similar behavior was observed for the Cr(bpy) $_3^{3+}$ – $S_2O_8^{2-}$ – H_2O system, except that the maximum ecl intensity was obtained for $[S_2O_8^{2-}] = 1.0 \times 10^{-4}$. In both cases for low $S_2O_8^{2-}$ concentrations stirring the solution led to an increase in the ecl emission. Preliminary experiments carried out on DMF solutions containing 1.0×10^{-3} M Ru(bpy) $_3^{2+}$ and 5.0×10^{-4} M $S_2O_8^{2-}$ showed that the ecl intensity increased on stepping the potential to values corresponding to the second reduction wave of the complex. A similar behavior was observed for aqueous solutions containing 1.0×10^{-2} M Cr(bpy) $_3^{3+}$ and 1.0×10^{-3} M $S_2O_8^{2-}$.

In order to test the stability of Ru(bpy) $_3^{2+}$ under ecl conditions, experiments were made on AN solutions containing 1.0×10^{-4} M Ru(bpy) $_3^{2+}$, 1.0×10^{-2} M $K_2S_2O_8$ (most of which was initially not dissolved because solubility of potassium persulfate

TABLE I. Electrochemical, Photoluminescence and Electrochemiluminescence^a Data.

Complex, M	E ⁰ (M ⁺ /M) ^b (V)	E ⁰ (M/M ⁻) ^b (V)	E(*M) ^c (eV)	λ _{max} ^d (nm)	I _{ecl} ^e	I _p ^f
Ru(bpy) ₃ ²⁺	+1.26	-1.28	2.12	610	100	100
Ru(4,4'-Me ₂ bpy) ₃ ²⁺	+1.10	-1.37	2.04	605	40	94
Ru(bpy) ₂ (CN) ₂	+0.85 ^g	-1.54 ^g	2.15	660	15	33
Ru(phen) ₃ ²⁺	+1.26	-1.36	2.18	610	25	98
Ru(5-Cl-phen) ₃ ²⁺	+1.36	-1.15	2.15	610	25	100
Ru(4,7-Me ₂ phen) ₃ ²⁺	+1.09	-1.47	2.12	610	20	78
Ru(5,6-Me ₂ phen) ₃ ²⁺	+1.20	-1.34	2.14	610	35	55
Ru(phen) ₂ (CN) ₂	+0.88 ^g	-1.55 ^g	2.19	660	25	50
Os(phen) ₃ ²⁺	+0.82	-1.21	1.78	740	40	32
Cr(bpy) ₃ ³⁺		-0.26	1.71	727	25	30
Cr(4,4'-Me ₂ bpy) ₃ ³⁺		-0.45 ^h	1.70 ^h	727	45	75
Cr(phen) ₃ ³⁺		-0.28 ^h	1.71	727	8	125
Cr(5-Cl-phen) ₃ ³⁺		-0.17 ^h	1.70	727	7	97

^aExperimental conditions for ecl experiments were as follows: [M] = 1.0 × 10⁻³, [S₂O₈²⁻] = 5.0 × 10⁻⁴, room temperature; the solvent was DMF for the Ru and Os complexes and water for the Cr complexes. ^bRef. 6a; aqueous solution vs. NHE, unless otherwise noted.

^cEnergy of the zero-zero transition of the emitting excited state, from ref. 6a unless otherwise noted.

^dMaxima of the ecl and photoluminescence emission spectra.

^eRelative intensity of ecl emission at λ_{max}, corrected for phototube response.

^fRelative intensity of photoluminescence emission at λ_{max} under standard conditions (see text), corrected for phototube response. ^gS. Roffia and M. Ciano, *J. Electroanal. Chem.*, 77, 349 (1977); DMF vs. SCE. ^hRef. 7e.

in AN is lower than 5 × 10⁻⁵ M), and 0.1 M TEAP. When the potential corresponding to the first reduction wave of the ruthenium complex was applied to the Pt flat electrode (current density of 0.75 × 10⁻³ A/cm²), a bright, constant ecl emission was observed for about 2 hours. For longer time periods a decrease in the emission intensity was observed which, however, could be prevented by cleaning the electrode. Working in this way, a practically constant emission intensity was observed for 8 hours, at which time the experiment was terminated. Spectrophotometric measurements showed that Ru(bpy)₃²⁺ concentration was practically unchanged. Under such conditions, cyclic voltammetric curves showed that most (~70%) of the cathodic reduction involved the Ru(bpy)₃²⁺ complex. Thus, during this experiment each Ru(bpy)₃²⁺ molecule had to be involved, on average, in more than 50 reduction-oxidation cycles.

Discussion

Electrochemiluminescence Mechanism

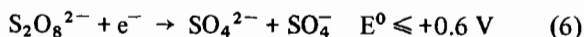
The polypyridine complexes used in this work are known to emit luminescence upon photo-excitation [6, 7]. The quantum yield of formation of the emitting excited state is unity for Ru(bpy)₃²⁺ [7f], Ru(phen)₃²⁺ [7f], Ru(bpy)₂(CN)₂ [7a], Cr(bpy)₃³⁺ [7a], Cr(phen)₃³⁺ [7g], and presumably also for the other complexes. The photoluminescence quantum yield is known to be 7.5 × 10⁻² for Ru(bpy)₃²⁺ in AN at 25 °C [4e] and 4.3 × 10⁻³ for Ir(phen)₂Cl₂⁺

in DMF at 15 °C [8]. The photoluminescence quantum yields of Os(phen)₃²⁺ and Cr(bpy)₃³⁺ were estimated to be about 3 and 15 times smaller than that of Ru(bpy)₃²⁺. No attempt was made to evaluate the quantum yield of Rh(phen)₃³⁺, which is known to be an extremely weak emitter [7c,d]. Table I shows the relative photoluminescence intensities of various complexes at the maximum of the emission band. Note that such values reflect not only the emission quantum yield but also the narrowness of the emission band. Thus the Cr(III) complexes have relatively high I_p values in spite of their low emission quantum yields. The energy of the emitting excited state and the redox potentials are also given in Table I. Each complex (hereafter indicated by M for the sake of simplicity) undergoes reversible one-electron reduction (eqn. 3) and oxidation (eqn. 4) reactions, exception being made for the Cr(III) complexes whose oxidation



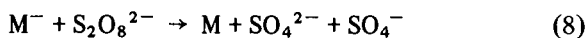
has yet to be observed [6].

The persulfate ion is a well-known two-electron oxidant whose reduction potentials in aqueous solution are [9]:



At a Pt electrode $S_2O_8^{2-}$ is irreversibly reduced (Figs. 1 and 2 and Results). Since the SO_4^- radical ion is a much stronger oxidant than $S_2O_8^{2-}$, the transfer of one electron to $S_2O_8^{2-}$ at the electrode is immediately followed by the transfer of a second electron with reduction of $S_2O_8^{2-}$ to two SO_4^{2-} ions (eqn. 5).

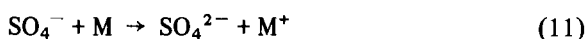
Electrochemiluminescence was only observed when the potential applied to the working electrode was negative enough to cause the reduction of the complex (Fig. 3). In most cases such a potential was also negative enough to allow the reduction of persulfate. However, persulfate ions directly reduced at the electrode are wasted because the SO_4^{2-} ions so obtained are unreactive. Thus, the initial step of the sequence leading to luminescence is certainly reaction 3, and the mechanism of the overall process is probably the following. The M^- complex obtained in the electrochemical reduction reacts with $S_2O_8^{2-}$ near the electrode (eqn. 8) [10]. The strongly oxidizing



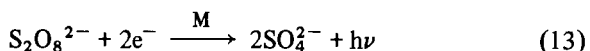
SO_4^- species so obtained can oxidize another reduced complex to produce an excited state (eqn. 9) which then emits (eqn. 10):



Alternatively, SO_4^- can oxidize an M complex yielding an M^+ species (eqn. 11) whose comproportionation with an M^- species can produce an excited state (eqn. 12) which then emits (eqn. 10):



Of course, other reactions can also occur, such as the decomposition of M^- , the quenching of $*M$ by M^- , or the oxidation of M^- by adventitious impurities. These reactions, while affecting the ecl efficiency, do not substantially change the nature of the net reaction which corresponds to the electrochemical reduction of $S_2O_8^{2-}$, with the complex undergoing a cyclic redox process and playing the role of electron transfer mediator and light emission sensitizer:



As mentioned above, the one-electron oxidation product (*i.e.*, the M^+ species) is unknown for the Cr(III) complexes. For such complexes we had shown previously [5a] that chemiluminescence can be obtained on mixing $S_2O_8^{2-}$ and M^- solutions. This suggests that in the ecl experiments the emitting excited state of the Cr(III) complexes is generated

by reaction (9), although reaction (12) cannot be excluded. For the Ru(II) and Os(II) complexes the M^+ species is well known and easily accessible through reaction (11) and the occurrence of reaction (12) is also well documented by Bard's ecl studies [4a,c]. Thus, both reaction mechanisms may be responsible for the observed luminescence. The relative ecl intensities (Table I) do not follow closely the relative photoluminescence intensities, showing that other factors related to the heterogeneous or homogeneous electron transfer processes play some role.

The lack of ecl emission in the experiments with $Rh(phen)_3^{3+}$ and $Ir(phen)_2Cl_2^+$ may be related to the weak photoluminescence emission of these complexes. The $Rh(phen)_3^{3+}$ photoluminescence can hardly be seen at room temperature [7c,d], whereas for the Ir complex the quantum yield of emission is relatively high but the emission band is very broad (because of the presence of two emitting states [8]), so that the height of the photoluminescence peak is very small. The lack of ecl emission for these two complexes, however, could also have more subtle origins. It should be noted that whereas for the Ru(II), Os(II), and Cr(III) complexes excitation and reduction involve the occupation of the same orbital [6, 11], the electronic situation for $Rh(phen)_3^{3+}$ and $Ir(phen)_2Cl_2^+$ is more complicated because of the presence of almost isoenergetic metal-centered and ligand-centered orbitals [7d, 8, 11].

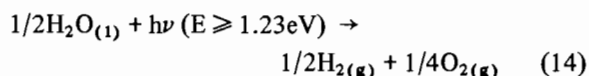
The mechanism discussed above can account for the dependence of the ecl intensity on $S_2O_8^{2-}$ concentration observed for $Ru(bpy)_3^{2+}$ and $Cr(bpy)_3^{3+}$. High $S_2O_8^{2-}$ concentrations decrease the ecl intensity, not only because of the competition between $S_2O_8^{2-}$ and M for electrodic reduction, but also because of the competition between $S_2O_8^{2-}$ and SO_4^- for M^- (eqns. 8 and 9). On the other hand, at low $S_2O_8^{2-}$ concentrations other reactions involving M^- (*i.e.*, ligand dissociation, oxidation by impurities, *etc.*) may prevail over reaction 8. As a consequence, fewer SO_4^- radicals are produced and reactions 9 and 11 become less probable. Clearly the relative rate of the various competing processes (and thus the optimum $S_2O_8^{2-}$ concentration for ecl emission) depend on the specific complex used.

We would like to note that the electrochemical reduction of $S_2O_8^{2-}$ mediated by Ru(II), Os(II) and Cr(III) polypyridine complexes is quite similar to the electrochemical oxidation of $C_2O_4^{2-}$ mediated by $Ru(bpy)_3^{2+}$ recently reported by Rubistein and Bard [4f]. In both systems the polypyridine complex not only catalyzes a slow electrochemical reaction, but also converts chemical and electrical energy into light. The interest in these systems from a practical point of view has already been emphasized by Rubistein and Bard [4f]. The constant ecl emission obtained in this work from the $Ru(bpy)_3^{2+}-S_2O_8^{2-}$

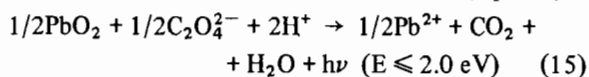
AN system for long time periods is another example of ecl processes susceptible to interesting applications.

Light Absorption and Light Emission Sensitizers

Several photochemical reactions do not occur because the reactants are unable to absorb light. For example, the splitting of water into hydrogen and oxygen by visible light (eqn. 14) is thermodynamically



possible but it does not occur because water does not absorb visible radiation. In the same way several reactions which are potentially chemiluminescent do not generate light because the reaction products are unable to emit. For example, the reaction between lead dioxide and oxalate in acid medium (eqn. 15) is



sufficiently exoergonic to generate visible light, but appears to lead only to the formation of heat.

Thermodynamically allowed photochemical or chemiluminescent reactions which do not occur because of light absorption or light emission problems can be induced by suitable sensitizers. The use of *light absorption sensitizers* in photochemical processes (Fig. 4a) has long been known and has recently received much attention for artificial solar energy conversion systems [1, 6]. Indeed, it has been shown

that reaction 14 can be sensitized by Ru-polypyridine complexes [1b]. The use of *light emission sensitizers* to obtain chemiluminescence (Fig. 4b) is much less known. An outstanding example of this kind of process has recently been reported by Rubistein and Bard [4f], who showed that the reduction of lead dioxide by oxalate (reaction 15) does produce light when the reaction is mediated by $\text{Ru}(\text{bpy})_3^{2+}$.

In the light absorption sensitization scheme (Fig. 4a) the redox species generated by the excited state electron transfer reaction may also be used to 'charge' electrodes. This allows the conversion of light into electrical energy (photogalvanic systems, [12]) or the use of light energy to generate electrical energy and, at the same time, to cause a net chemical reaction (some interesting examples of the latter process have been reported recently [13]). Similarly, in the light emission sensitization scheme (Fig. 4b) the redox species may be generated electrochemically. This allows the conversion of electrical energy into light (regenerative ecl systems [4a,f]), or the combined use of chemical and electrical energy to produce light. The systems described in this paper (eqn. 13) are examples of this last type of process.

Acknowledgements

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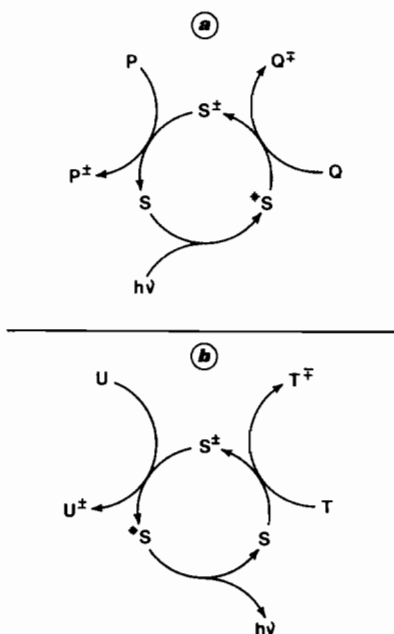


Fig. 4. Light absorption (a) and light emission (b) sensitization schemes. S is the sensitizer and Q, P, T, and U are chemical species or electrodes.

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