

Electrochemical and Photochemical Investigations of Two Novel Electron Relays for Hydrogen Generation from Water

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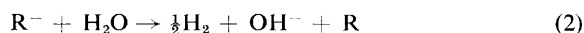
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Bis(carboxycyclopentadienyl)cobalt $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^+$ (**1**) and the cobalt(III) sepulchrate $\text{Co}(\text{sep})^{3+}$ (**2**) produce hydrogen from water after single electron reduction in an electrochemical process, and act as electron relays in photochemical hydrogen generating systems.

The generation of hydrogen from water using visible light is a challenging task for solar energy related research and is at present under extensive investigation.¹ Electron relay compounds (R) are of primary importance in these systems. They participate as electron acceptors in the initial photochemical reaction which involves either an electronically excited sensitizer (S^*) or the conduction band electron (e_{CB}^-) of a semiconductor² produced *via* band gap irradiation [reaction (1)].

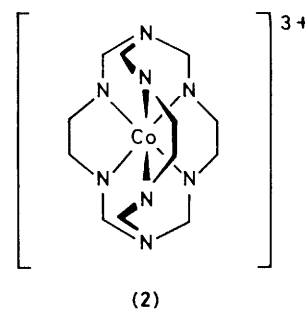
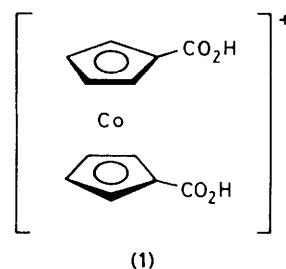


The reduced form of the relay (R^-) is then used to generate hydrogen from water [reaction (2)]. A number of relays have



been identified that produce hydrogen in the presence or absence of redox catalysts.³ However, most of these suffer from destructive side reactions, high colour, and/or unsuitable redox potential. We now report electrochemical and photochemical investigations of two novel electron relays, bis(carboxycyclopentadienyl)cobalt [$\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^+$] (**1**) and the cobalt(III) sepulchrate [$\text{Co}(\text{sep})^{3+}$] (**2**) which show promise as electron mediator compounds for hydrogen generation from water.

$\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^+$ and $\text{Co}(\text{sep})^{3+}$ were synthesized and purified according to procedures reported elsewhere.^{4,5} Electrochemical experiments were performed with a stirred Hg pool working electrode, a saturated calomel reference electrode



(S.C.E.), and a Ti wire counter electrode separated from the working electrode compartment by a glass frit. A solution (15 ml) containing 0.66 mM relay compound in a phosphate or phthalate buffer was placed into the working compartment, degassed with nitrogen, and closed off from the atmosphere. A solution of colloidal platinum (2 ml; 0.08 mg/ml) was added to some experiments prior to degassing. This catalyst, pre-

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Table 1. Summary of electrolysis data.

Relay	Electrolyte, pH	E_{Relay} , V, S.C.E.	E_{Electro} , V, S.C.E.	Electrolysis in the absence of platinum				Electrolysis in the presence of platinum			
				Electrolysis time/min	Charge/C	Amount of H_2 produced/ μl	H_2 yield ^a /%	Electrolysis time/min	Charge/C	Amount of H_2 / μl	H_2 yield ^a /%
$\text{Co}(\text{sep})^{3+}$	KCl, phthalate buffer, pH 4	-0.54 ^b	-0.7	24	1.2	75	55	29	7.9	920	≥ 95
$\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^+$	KCl, phosphate buffer, pH 6.5	-0.87 ^c	-0.9	30	2.6	125	42	31	5.4	700	≥ 95
Methyl viologen	KCl, phosphate buffer, pH 6.5	-0.69	-0.75	19	1.9	2.5	≤ 2	31	4.6	240	45
No relay	KCl, phthalate buffer, pH 4		-0.7					27	0.8	75	80
No relay	KCl, phosphate buffer, pH 6.5		-0.9					28	0.7	55	70

^a Ratio of charge required for the formation of a measured amount of hydrogen (*via* proton reduction) to charge passed during electrolysis. ^b E° for $\text{Co}(\text{sep})^{3+/2+}$ does not change with pH. ^c Relay potential is pH-dependent (ref. 4c).

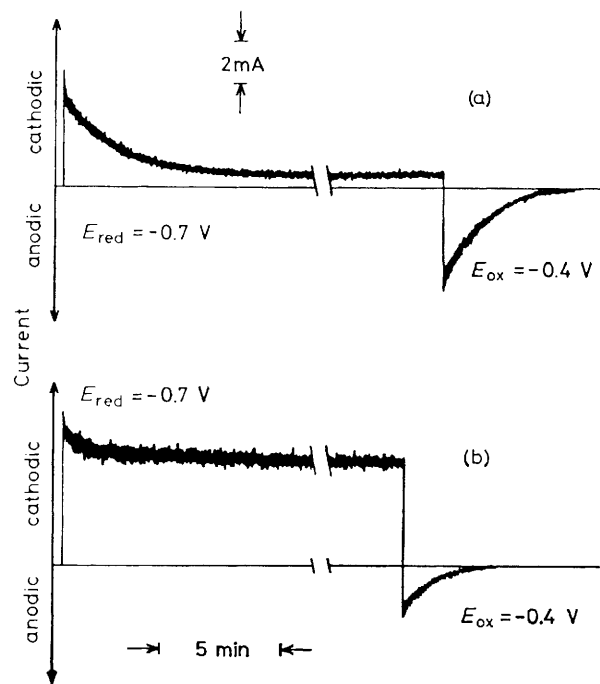
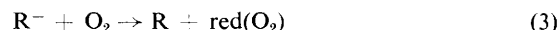


Figure 1. The course of controlled potential electrolysis of $\text{Co}(\text{sep})^{3+}$ in (a) the absence and (b) the presence of colloidal Pt. Conditions are as indicated in Table 1.

pared by a citrate reduction method,⁶ consisted of 30 Å particles.

Figure 1(a) shows a typical current vs. time curve for the reduction of $\text{Co}(\text{sep})^{3+}$ in the absence of Pt catalyst. The reduction current never dropped to zero, indicating a catalytic regeneration of the oxidized form of the relay. Also, the charge consumed during reduction exceeded one equivalent, while the reverse charge necessary for complete reoxidation was significantly less than one equivalent. There are two processes

which could account for this behaviour, reaction of reduced relay with oxygen present in the cell as impurity [reaction (3)]



or reduction of water to hydrogen according to reaction (2). Gas chromatographic analysis of the gas above the solution showed that the latter reaction dominates. This is shown in Table 1 where the charge passed through the circuit is compared with the volume of hydrogen evolved. About 55% of the reduction current can be accounted for by hydrogen in the gas phase. The current vs. time profile of the electrolysis is altered by the addition of colloidal Pt [Figure 1(b)]. Significantly increased currents are observed during reduction but only minor amounts of reduced relay can be subsequently reoxidized. Gas chromatographic analysis during electrolysis showed that the charge passed is used virtually quantitatively for the production of hydrogen (Table 1).

Similarly encouraging results are obtained when $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^+$ is used as an electron relay. These results are summarized in Table 1. The observed yield of hydrogen accounts for 42% and over 95% of the charge passed through the circuit, in the absence and presence of catalyst, respectively. These results are in marked contrast to the data obtained with methyl viologen as an electron relay (Table 1); no hydrogen is produced in the Pt free solution and the H_2 yield is only 45% when catalyst is present. Apparently the reoxidation of reduced methyl viologen by oxygen impurities plays a major role in this system.†

The potential of these novel electron relays to mediate light induced generation of hydrogen from water was tested in a well studied photochemical system consisting of 0.2 mM $\text{Ru}(\text{bpy})_2^{2+}$ (bpy = bipyridine) as sensitizer, 0.01 M ethylenediaminetetra-acetic acid (EDTA) as sacrificial electron donor, and 5 mM relay. In some samples, colloidal Pt was present in

† The rate for the reaction of $\text{Co}(\text{sep})^{2+}$ with O_2 is only $44 \text{ l mol}^{-1} \text{ s}^{-1}$ at room temperature (ref. 6b) compared with $8 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for reduced methyl viologen.

the same concentration as in the electrochemical experiments described above. After degassing with argon, samples were irradiated in a merry-go-round type sample holder at 28 °C with a 250 W tungsten-halogen lamp fitted with a 435 nm cut-off filter. The generation of hydrogen was monitored by gas chromatography at intervals throughout photolysis. For purposes of comparison, analogous samples containing 5 mM methyl viologen as the relay were photolysed simultaneously. The pH was 4.6 for all the samples.

In the presence of Pt catalyst, both new relays were successful in mediating the generation of hydrogen in this system. Hydrogen was produced at a constant rate and no spectral changes or other evidence of decomposition of the relay could be detected in either case, even after prolonged irradiation. Irradiation of solutions containing these relays alone in the absence of sensitizer showed that both $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$ and $\text{Co}(\text{sep})^{3+}$ as well as their reduced forms are extremely stable and do not undergo any photodegradation. [Absorption spectral data for the oxidized and reduced forms of the relays: $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$ in H_2O ,¹ $\epsilon_{405, \text{nm}} = 310$, $\epsilon_{222} = 1400$, $\epsilon_{274} = 21\,000$; 0.1 M NaOH solution of $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2)_2^{2-}$ made by electrochemical reduction, $\epsilon_{485} \geq 1300$, $\epsilon_{382} \geq 420$, $\epsilon_{330} \geq 3300$; $\text{Co}(\text{sep})^{3+}$ in H_2O ,⁵ $\epsilon_{472} = 109$, $\epsilon_{396} = 9.9$, $\epsilon_{340} = 116$; reduced $\text{Co}(\text{sep})^{2+}$ in H_2O ,⁵ $\epsilon \text{ ca. } 8$ at 465 nm and $\epsilon \text{ ca. } 5$ at 915 nm.] In the presence of sensitizer and Pt catalyst the relative rates of hydrogen production were 11, 4, and 1 for methyl viologen, $\text{Co}(\text{sep})^{3+}$, and $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$, respectively. § In all cases, no hydrogen could be detected after several hours of irradiation of samples without Pt catalyst. Presumably, the rate of reaction (2) is slow under photolysis conditions for these relays.

The reason for the poor performance of $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$ as a relay, despite its larger driving force, was revealed by flash photolysis. Using a frequency doubled Nd laser apparatus,⁷ the quenching of the $\text{Ru}(\text{bpy})_3^{2+}$ excited state in argon degassed aqueous solution (ionic strength 0.1 M, NaCl) by each relay was studied. For $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$, k_q was found to be $1.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and was approximately constant over the pH range 1–10. Recovery of ground state bleaching at 475 nm followed the same first order kinetics as decay of emission at 600 nm, indicating that energy transfer quenching or rapid back reaction in the cage accounted for almost all quenching reactions. In the case of $\text{Co}(\text{sep})^{3+}$, analogous experiments gave an overall quenching rate constant of $2.6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, but in this case, bleaching at 480 nm showed both a short and a long time recovery. The short-time component corresponded to unquenched $\text{Ru}(\text{bpy})_3^{2+}$ excited states, as verified by emission decay at 600 nm, while the long-time recovery (100 μs time scale) was due to the back reaction of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Co}(\text{sep})^{2+}$ generated by electron transfer quenching and subsequent cage escape. The net amount of electron transfer was calculated[¶] to be 90% of the total quenching reactions.

§ Absolute rates for hydrogen production were 29 $\mu\text{l/h}$, 11 $\mu\text{l/h}$, and 2.6 $\mu\text{l/h}$ for methyl viologen, $\text{Co}(\text{sep})^{3+}$, and $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$, respectively, for samples with 5 ml liquid and 5 ml gas volume. These rates are affected by the reduced light level obtained by the use of a merry-go-round type sample holder, but may be compared to those reported for different experimental conditions (reference 1 and references therein) by using the methyl viologen result as a standard.

¶ Extinction coefficients at 480 nm used in the calculation were 6100, 2000, and 180, for $\text{Ru}(\text{bpy})_3^{2+}$, $[\text{Ru}(\text{bipy})_3^{2+}]^*$, and $\text{Ru}(\text{bpy})_3^{3+}$, respectively. The value for the excited state species was taken from U. Lachshish, P. Infelta, and M. Grätzel, *Chem. Phys. Lett.*, 1979, **62**, 317. Absorption of $\text{Co}(\text{sep})^{2+}$ was negligible.

In contrast, methyl viologen quenches $\text{Ru}(\text{bpy})_3^{2+}$ with a rate constant of $6.5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ under similar conditions (ionic strength 0.1M, acetate buffer) and only 25% net electron transfer due to fast cage recombination.⁸ Presumably, the higher fraction of cage escape in the case of $\text{Co}(\text{sep})^{3+}$ is due to the higher positive charge of the reduced form. These data predict that $\text{Co}(\text{sep})^{3+}$ would be a better relay than methyl viologen when used in conjunction with $\text{Ru}(\text{bpy})_3^{2+}$, and we attribute its poorer performance partly to its orange colour which results in a significant inner filter effect [in contrast, yellow $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$ does not absorb significantly above 435 nm under experimental conditions]. In addition, the driving force available for carrying out reaction (2) under experimental pH conditions is ca. 160 mV for methyl viologen and only ca. 25 mV for $\text{Co}(\text{sep})^{3+}$, which may significantly affect the relative rates.

The investigation of these two new electron relays in other light-driven hydrogen-generating systems is currently in progress. Preliminary results obtained from band gap irradiation of CdS powder in aqueous dispersions⁹ (pH 4.7, EDTA as sacrificial donor) show that $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$ is able to effect a several-fold increase in hydrogen production, without the addition of Pt catalyst. In this system, reaction (2) is apparently competitive with other oxidations of the reduced relay. Also, the negative charge of the deprotonated relay at this pH may positively affect the rate of reaction (1), as strong adsorption of relay to the negatively charged CdS surface is not a problem. $\text{Co}(\text{sep})^{3+}$ is ineffective as a relay for the CdS system at pH 4.7 in the absence of Pt.

In conclusion, the electrochemical and photochemical experiments underline the suitability of $\text{Co}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2^-$ and $\text{Co}(\text{sep})^{3+}$ as one electron transfer mediators and hydrogen generating relays. They both have reversible redox couples with fast electron transfer rates and extremely high chemical stability in the two oxidation states of interest.

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