

## Short Communication

**Cr(bpy)<sub>3</sub><sup>3+</sup>-sensitized (bpy ≡ 2,2'-bipyridyl) photoproduction of hydrogen from water**

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The photoreduction of water by homogeneous three-component systems consisting of a sensitizer, an electron donor and a mediator has been studied extensively in recent years [1, 2]. Sensitizers commonly used in this type of system are Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy ≡ 2,2'-bipyridyl) [3], metal porphyrins [4] and some organic dyes [5]. In this study Cr(bpy)<sub>3</sub><sup>3+</sup> was employed as the sensitizer. Although Cr(bpy)<sub>3</sub><sup>3+</sup> has been reported to reduce water directly in the presence of an electron donor on irradiation with visible light [6], its application to three-component systems does not seem to have attracted much interest. However, the photochemical and electrochemical properties of Cr(bpy)<sub>3</sub><sup>3+</sup> have been studied fairly well, and therefore by employing it as a sensitizer we may obtain valuable information on the mechanism of hydrogen production in three-component systems.

A quartz cell containing 3 ml of the sample solution was irradiated by using a 500 W ultrahigh mercury lamp filtered with 370 nm cut-off and IR filters. Argon was bubbled through the sample solution before irradiation. Some results for the production of hydrogen from solutions containing Cr(bpy)<sub>3</sub><sup>3+</sup>, Rh(bpy)<sub>3</sub><sup>3+</sup>, ethylenediaminetetraacetic acid (edta) and K<sub>2</sub>PtCl<sub>4</sub> are given in Table 1. Similar experiments with methyl viologen (MV<sup>2+</sup>) instead of Rh(bpy)<sub>3</sub><sup>3+</sup> were carried out and the results are listed in Table 2. The maximum hydrogen evolution was observed from pH 6 to pH 7 with Rh(bpy)<sub>3</sub><sup>3+</sup> and around pH 6 with MV<sup>2+</sup>. The amount of hydrogen evolved increases sharply with increases in the concentration of Cr(bpy)<sub>3</sub><sup>3+</sup>, Rh(bpy)<sub>3</sub><sup>3+</sup> or edta up to a certain concentration and then increases gradually above that concentration.

The evolution of hydrogen by three-component systems occurs by either an oxidative or a reductive quenching process. In the present system the oxidative quenching process involves the reduction of Rh(bpy)<sub>3</sub><sup>3+</sup> by photoexcited Cr(bpy)<sub>3</sub><sup>3+</sup>, and the reductive quenching process involves the reduction of photoexcited Cr(bpy)<sub>3</sub><sup>3+</sup> by edta and subsequent reduction of Rh(bpy)<sub>3</sub><sup>3+</sup> by Cr(bpy)<sub>3</sub><sup>2+</sup>. Reduced species of Rh(bpy)<sub>3</sub><sup>3+</sup> are directly responsible for hydrogen production. Kirch *et al.* [7] first considered

TABLE 1

Amount of hydrogen evolved from solutions containing  $\text{Cr}(\text{bpy})_3^{3+}$ ,  $\text{Rh}(\text{bpy})_3^{3+}$  and edta in the presence of  $1.67 \times 10^{-4}$  M  $\text{K}_2\text{PtCl}_4$  on irradiation for 30 min

$[\text{Cr}(\text{bpy})_3^{3+}]$ ( $\times 10^{-4}$ M)	$[\text{Rh}(\text{bpy})_3^{3+}]$ ( $\times 10^{-4}$ M)	[edta] ( $\times 10^{-2}$ M)	pH	Amount of $\text{H}_2$ (ml)
3.3	8.3	3.3	4.7	0.002
3.3	8.3	3.3	5.4	0.010
3.3	8.3	3.3	6.8	0.021
3.3	8.3	3.3	7.7	0.012
3.3	8.3	3.3	9.0	0.003
0.05	8.3	3.3	6.8	0.003
0.15	8.3	3.3	6.8	0.007
0.4	8.3	3.3	6.8	0.013
1	8.3	3.3	6.8	0.016
3.3	2	3.3	6.8	0.005
3.3	4.5	3.3	6.8	0.010
3.3	6.2	3.3	6.8	0.015
3.3	24.5	3.3	6.8	0.022
3.3	8.3	0.3	6.8	0.007
3.3	8.3	0.7	6.8	0.012
3.3	8.3	6.7	6.8	0.024

TABLE 2

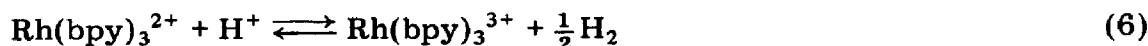
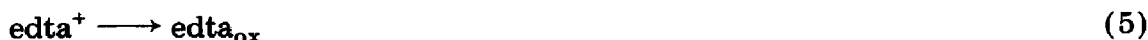
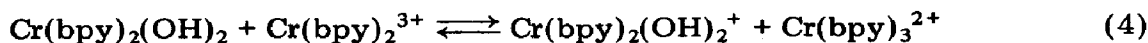
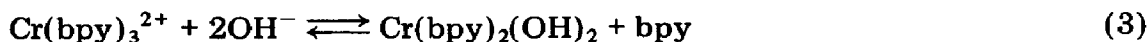
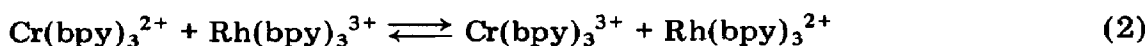
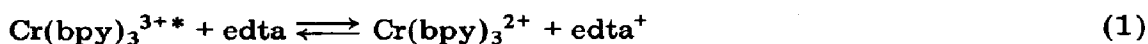
Amount of hydrogen evolved from solutions containing  $\text{Cr}(\text{bpy})_3^{3+}$ ,  $\text{MV}^{2+}$  and edta in the presence of  $1.67 \times 10^{-4}$  M  $\text{K}_2\text{PtCl}_4$  on irradiation for 30 min

$[\text{Cr}(\text{bpy})_3^{3+}]$ ( $\times 10^{-4}$ M)	$[\text{MV}^{2+}]$ ( $\times 10^{-4}$ M)	[edta] ( $\times 10^{-2}$ M)	pH	Amount of $\text{H}_2$ (ml)
3.3	8.3	3.3	3.5	0.009
3.3	8.3	3.3	4.3	0.015
3.3	8.3	3.3	5.9	0.018
3.3	8.3	3.3	6.9	0.017
3.3	8.3	3.3	7.7	0.012
3.3	1.5	3.3	5.9	0.007
3.3	5	3.3	5.9	0.010
3.3	10	3.3	5.9	0.017
3.3	20	3.3	5.9	0.017

$\text{Rh}(\text{bpy})_3^+$  as such a species. However, Chan *et al.* [8] later showed that  $\text{Rh}(\text{bpy})_3^{2+}$  rather than  $\text{Rh}(\text{bpy})_3^+$  reduces water. The standard redox potentials reported for  $\text{Rh}(\text{bpy})_3^{2+}|\text{Rh}(\text{bpy})_3^{3+}$  and  $\text{Cr}(\text{bpy})_3^{3+}|\text{Cr}(\text{bpy})_3^{4+}$  are  $-0.7$  V [8] and  $-0.1$  V [9] respectively, whereas the standard redox potential for  $\text{Cr}(\text{bpy})_3^{2+}|\text{Cr}(\text{bpy})_3^{3+}$  is  $-0.25$  V [9]. A simple comparison of these values suggests that the reduction of  $\text{Rh}(\text{bpy})_3^{3+}$  by  $\text{Cr}(\text{bpy})_3^{2+}$  is more probable than the direct reduction of  $\text{Rh}(\text{bpy})_3^{3+}$  by photoexcited  $\text{Cr}(\text{bpy})_3^{3+}$ .

To ensure the reduction of  $\text{Rh}(\text{bpy})_3^{3+}$  by  $\text{Cr}(\text{bpy})_3^{2+}$ ,  $\text{Cr}(\text{bpy})_3(\text{ClO}_4)_2$  was added to deaerated water buffered at pH 6.8. The solution became wine red and the colour remained unchanged. A small amount of evolved hydrogen was detected. When  $\text{Rh}(\text{bpy})_3^{3+}$  was added to the above solution, the colour of the solution changed quickly and more hydrogen was evolved. However, this reaction did not occur at pH 2.1. The absorption spectrum after the evolution of hydrogen showed the formation of  $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$ . A reductive quenching process was thus indicated for the present hydrogen evolution system. A hydrolysed species is also formed in the present three-component system. The production of  $\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2^{3+}$  from  $\text{Cr}(\text{bpy})_3^{2+}$  and  $\text{Cr}(\text{bpy})_3^{3+}$  has been reported in the literature [10, 11]. Analogously in the present system  $\text{Cr}(\text{bpy})_3^{3+}$  is considered to be converted to  $\text{Cr}(\text{bpy})_2(\text{OH})_2^+$  after reduction to  $\text{Cr}(\text{bpy})_3^{2+}$  as well as by direct photoaquation [12]. This hydrolysed species is inactive in sensitizing hydrogen evolution.

The evolution of hydrogen from a  $\text{Cr}(\text{bpy})_3^{2+}$  solution in the presence of colloidal platinum was little affected by the addition of  $\text{Rh}(\text{bpy})_3^{3+}$ , unlike in the absence of colloidal platinum. However, the effect of the  $\text{Rh}(\text{bpy})_3^{3+}$  concentration on the hydrogen evolution in the three-component system is significant (Table 1). We assume that the role of  $\text{Rh}(\text{bpy})_3^{3+}$  is its quick reaction with  $\text{Cr}(\text{bpy})_3^{2+}$  to suppress the back reaction between  $\text{Cr}(\text{bpy})_3^{2+}$  and  $\text{edta}^+$ . Indeed the evolution of hydrogen from  $\text{Cr}(\text{bpy})_3^{2+}$  in the presence of colloidal platinum is relatively slow, whereas the reduction of  $\text{Rh}(\text{bpy})_3^{3+}$  by  $\text{Cr}(\text{bpy})_3^{2+}$  is a quick reaction. The overall reactions discussed above are summarized as follows:



When  $\text{MV}^{2+}$  is used as the mediator instead of  $\text{Rh}(\text{bpy})_3^{3+}$ , a reductive quenching process is also more probable than an oxidative quenching process, since the standard redox potential for  $\text{MV}^+|\text{MV}^{2+}$  ( $-0.44$  V) is closer to that for  $\text{Cr}(\text{bpy})_3^{2+}|\text{Cr}(\text{bpy})_3^{3+}$  ( $-0.25$  V) than that for  $\text{Cr}(\text{bpy})_3^{3+*}|\text{Cr}(\text{bpy})_3^{4+}$  ( $-0.1$  V). When  $\text{Cr}(\text{bpy})_3(\text{ClO}_4)_2$  was added to a deaerated  $\text{MV}^{2+}$  solution, the solution became blue, showing the formation of  $\text{MV}^+$ , and evolution of hydrogen was observed in the presence of colloidal platinum. The reductive quenching process was thus confirmed for the system with  $\text{MV}^{2+}$  as the mediator.

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