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Photochemical Catalytic Reduction of Carbon Dioxide by Visible Light Using $Ru^{II}(bipy)_3$ and $Re(CO)_3(bipy)Cl$ as Photocatalysts

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There are few studies concerning homogeneous photochemical reduction of carbon dioxide and usually the systems have been rather inefficient [1–7]. The best results developed so far have been reported by Lehn *et al.*, who used $Ru^{II}(bipy)_3$ as a photosensitizer and Co(II)-ions or complexes as catalysts to produce synthesis gas [8, 9]. They also reported the use of the $Ru^{II}(bipy)_3$ photosensitizer as a photocatalyst producing formate, [12] and $Re(CO)_3(bipy)Cl$ as a sensitizer and a catalyst producing carbon monoxide [9–11] which was the most effective system. We report here an improvement to this last system using $Ru^{II}(bipy)_3$ as a cocatalyst.

It has been claimed that use of several photosensitizers enhances the spectral domain of the visible-light-induced reactions and the yields of the products [13]. It has also been noted that $Ru^{II}(bipy)_3$ as a photosensitizer and $Re(CO)_3(bipy)Cl$ as a sensitizer-catalyst have the same kind of electrochemical and photochemical properties [10, 11]. We examined these two photocatalysts during carbon dioxide reduction by holding the concentration of one component constant while changing the other in TEOA:DMF solution (1:5) with a constant carbon dioxide amount*.

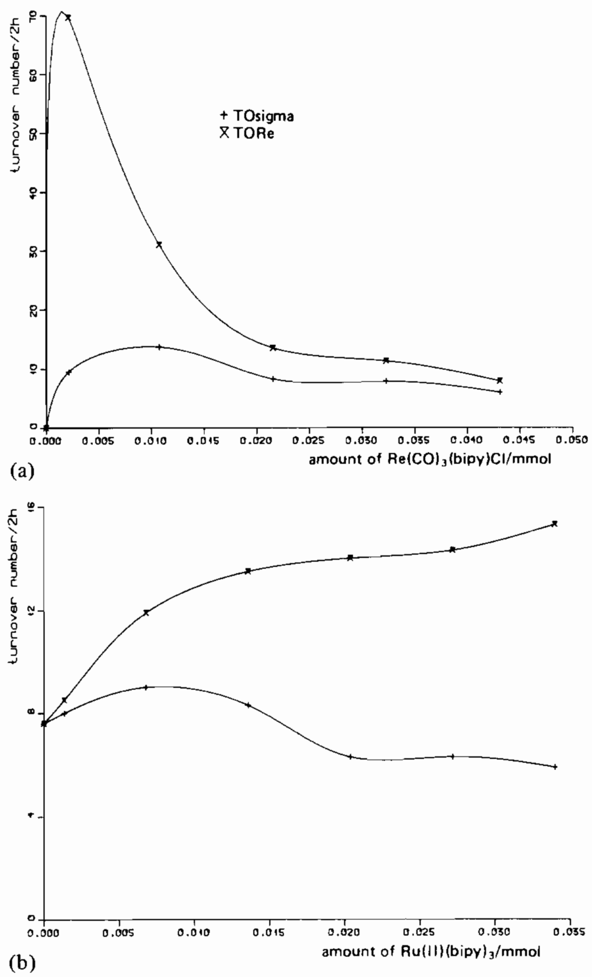

Fig. 1. Reduction of CO_2 by visible light in the $Ru^{II}(bipy)_3$/$Re^{I}(CO)_3(bipy)$/TEOA/NEt_4Cl system. Catalytic turnover numbers as a function of: (a) the amount of $Re^{I}(CO)_3(bipy)$ when the $Ru^{II}(bipy)_3$ concentration held constant (0.0136 mmol), and (b) as a function of the amount of $Ru^{II}(bipy)_3$ when the $Re^{I}(CO)_3(bipy)$ concentration held constant (0.02155 mmol). (The catalytic turnover numbers TOsigma and TORe, obtained by dividing mol of CO produced in 2 h by mol of the Ru and Re complexes and by mol of the Re complex, respectively).

If the amount of $Ru^{II}(bipy)_3$ is held constant and the concentration of $Re(CO)_3(bipy)Cl$ is varied, we found that the activity of the Re catalyst was highest at a low concentration of $Re(CO)_3(bipy)Cl$ and the maximum total activity was achieved with the 1:1 mole ratio (Fig. 1a). Compared to the system developed by Lehn *et al.* [9], this system produced 50% more carbon monoxide in a short-term photolysis. By holding the $Re(CO)_3(bipy)Cl$ concentration constant and changing the amount of $Ru^{II}(bipy)_3$ in solution, the activity of the Re catalyst was observed to increase quickly as a function of the $Ru^{II}(bipy)_3$ concentration. A maximum in the total activity was detected with an $Ru^{II}(bipy)_3$ concentra-

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*$Ru(bipy)_3Cl_2 \cdot 5H_2O$ and $Re(CO)_3(bipy)Cl$ were synthesised according to the literature methods [15, 16]. Carbon dioxide was high purity grade (99.95%). Triethanolamine, NEt_4Cl and dimethylformamide were pro-analysis grade. All these materials were stored in air and used without further purification.

Irradiation experiments were performed on a 30 ml solution contained in a round bottom flask equipped with a Teflon stopcock (115 ml capacity) and stirred magnetically at 500–1000 rpm. The reactor was evacuated before the experiment using a pump-freeze-thaw cycle. The coolant was liquid nitrogen and the evacuation was performed for about 2 min. After evacuation a measured amount of carbon dioxide was added into the reactor.

The light source was a 250 W slide-projector equipped with a 400 nm cut-off filter and a focusing lens. After irradiation the gaseous products (H_2, CO_2 and CO) were analysed by a gas chromatograph.

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tion of 0.01 mmol. If the concentration of $Ru^{II}(bipy)_3$ was further increased, the activity of the Re catalyst remained almost unchanged and the total activity was diminished (Fig. 1b).

Two experiments were done using direct diffuse sunlight as a light source. The amount of carbon monoxide produced was higher than that produced with a 250 W halogen lamp equipped with UV-filter. These higher yields are caused by a larger spectral domain and a more intense radiation compared to the halogen lamp. After 18 h irradiation of $Ru^{II}(bipy)_3$ in the presence of the NEt_4Cl electrolyte, hardly any carbon monoxide was generated. UV–Vis spectroscopy indicated that $Ru^{II}(bipy)_3$ had been reduced to $Ru^{I}(bipy)_3$.

Some NMR experiments were performed to determine the decomposition products of triethanolamine and possible formate production from carbon dioxide. Using long term photolysis and an NMR-tube as a reaction vessel, it was found that TEOA decomposes to diethanolamine and glycolaldehyde. In quantitative ^{13}C NMR measurements, the concentrations of glycolaldehyde and diethanolamine were found to be at a maximum 7% of the amount of TEOA, using normal catalyst amounts and low solvent volume (1/10 of the normal reaction volume). No formate was found in the present measurements. Its detection would probably have demanded the use of ^{13}C enriched carbon dioxide.

The results above suggest the following reaction mechanism involving the known generation of reduced photocatalysts [10, 11]:

$$\mathrm{Ru^{II}(bipy)_3} + h\nu \rightleftharpoons {}^*\mathrm{Ru^{II}(bipy)_3} \tag{1}$$

$$^*\mathrm{Ru^{II}(bipy)_3} + \mathrm{TEOA} \rightleftharpoons \mathrm{Ru^{I}(bipy)_3} + \mathrm{TEOA^+} \tag{2}$$

$$\mathrm{TEOA^+} \rightleftharpoons \text{decomposition products} \tag{3}$$

$$\mathrm{Re^{I}(CO)_3(bipy)Cl} + h\nu \rightleftharpoons {}^*\mathrm{Re^{I}(CO)_3(bipy)Cl} \tag{4}$$

$$^*\mathrm{Re^{I}(CO)_3(bipy)Cl} + \mathrm{TEOA} \rightleftharpoons \mathrm{Re^{0}(CO)_3(bipy)Cl} + \mathrm{TEOA^+} \tag{5}$$

TABLE I. Carbon Dioxide Reduction with $Ru^{II}(bipy)_3$ and $Re(CO)_3(bipy)$ in a TEOA:DMF Solution using NEt_4Cl as an Electrolyte. Amounts of Catalysts and Results

Experiment	$Ru(bipy)_3Cl_2{\bullet}5H_2O$ (mmol)	$Re(CO)_3(bipy)Cl$ (mmol)	CO (ml)	TOsigma	Photolysis time (h)	CO_2 obs. (mmol)	H_2 (ml)
1	0.00136	0.02155	4.50	8	2	1.0	
2	0.0068	0.02155	6.29	9	2	0.9	
3	0.0136	0.02155	7.12	8	2	0.9	
4	0.0204	0.02155	7.39	6	2	0.9	
5	0.0272	0.02155	7.54	6	2	0.9	
6	0.0340	0.02155	8.08	6	2	0.9	
7	0.0136	0.00215	3.67	10	2	1.0	
8	0.0136	0.01075	8.16	14	2	0.9	
9	0.0136	0.0323	8.93	8	2	0.9	
10	0.0136	0.0431	8.35	6	2	0.9	
11	–	0.02155	4.03	7	2	0.9	
12	0.0136	0.02155	2.18	3	2	1.0[a]	
12			3.49	4	4	0.9	0.20
13	0.0136	0.02155	0.17	0.2	2	0.8[b]	
13			0.40	0.5	4	0.7	
14	0.0136	0.02155	–	–	2	0.8[c]	
14			–	–	15.5	0.11	
15	0.0136	0.01075	–	0.3	2	–	0.17
15			–	0.4	5	–	0.24
15b*			0.27	1.0	13	1.0	0.35
15b			0.27	1.0	22	1.0	0.36
16	0.0136	0.01075	5.55	9	2	0.9	0.06
16			7.56	17	18	0.7	2.63
17	0.0136	0.02155	8.35	10	1.9	0.7[d]	0.04
18	0.0136	0.02155	13.66	18	3	0.7[d]	1.37
19	0.0136	–	0.04	4	2	1.0	1.41
19			0.07	6	18	1.0	1.89

The amount of the electrolyte NEt_4Cl was 100 mg/0.796 mmol. *Without electrolyte. Loaded CO_2 amount 2.785 mmol. [a] 5 ml H_2O/25 ml TEOA:DMF 1:5. [b] 10 ml H_2O/20 ml TEOA:DMF 1:5. [c] 30 ml TEOA:DMF 1:5. [d] Direct diffuse sunlight, no UV-filter. TOsigma = mol products/mol catalysts (sensitizers). Experiment 15: no CO_2; 15b: CO_2 added.

It has been shown that the $Re^0(CO)_3(bipy)Cl$ catalyst reduces carbon dioxide to monoxide [10, 11]. According to these observations, the better efficiency in our system is most probably due to the reaction:

$$Ru^I(bipy)_3 + Re^I(CO)_3(bipy)Cl \rightleftharpoons Re^0(CO)_3(bipy)Cl + Ru^{II}(bipy)_3 \quad (6)$$

In principle $Ru^{II}(bipy)_3$ could be reduced to $Ru^I(bipy)_3$ by the $Re^0(CO)_3(bipy)Cl$ photocatalyst, but according to our results this reaction does not occur, as it would lead to a diminished reduction of carbon dioxide. This has been confirmed by UV–Vis spectroscopy. After photolysis, only the absorption maxima of $Ru^{II}(bipy)_3$ were found.

The present photochemical carbon dioxide reduction system is unstable. The generation of carbon monoxide ceases after 5–7 h photolysis and the system begins to produce hydrogen. The amount of hydrogen is rather low. After 18 h photolysis the maximum amount of hydrogen was 2.63 ml. It has been postulated that the reason for the deactivation of the Re catalyst is that a formate complex is generated [11, 14]. This may be the main reason for the instability of the present system.

When water was added to this system a dramatic drop in the rate of generation of carbon monoxide was noted. When the amount of water reached 33 vol% the reaction ceased. The explanations for this behaviour may be the poor solubility of $Re(CO)_3(bipy)Cl$ in water and the change in solvent properties.

This system also demands the presence of an electrolyte to stabilize the chloride anion of $Re(CO)_3(bipy)Cl$. NEt_4Cl was used for this purpose. The reaction rate is diminished if no electrolyte is present in the solution. A similar phenomenon has been noted earlier [9].

The described system achieves efficient carbon dioxide reduction in short-time photolysis. It is the most effective system known currently, but its stability is poor for long-time usage.

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