Hydrogen Photoproduction by Visible Light Irradiation of an Organorhenium Catalyst Incorporated into Aqueous Suspensions of Hectorite

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When incorporated into aqueous suspension of hectorite clay mineral in the presence of triethanolamine, $[Re(bpy)(py)(CO)_3]^+$ (bpy = 2,2′-bipyridine; py = pyridine) is an efficient catalyst for the visible light ($\lambda > 395$ nm) photoproduction of hydrogen.

The quest for efficient processes for the chemical conversion and storage of solar energy has led mainly to the development of photochemical systems able to produce hydrogen.[1] So far, the most studied system has involved the simultaneous presence of a photosensitizer, such as tris-bipyridylruthenium $[Ru(bpy)_3{}^{2+}]$, and of an electron-relay, such as methylviologen (MV^{2+}). Sacrificial photogeneration of hydrogen was performed when $Ru(bpy)_3{}^{2+}$ and MV^{2+} were irradiated in the presence of an electron donor and of a suitable catalyst, colloidal platinum for example.[1] Photochemical systems have also been designed for the reduction of carbon dioxide.[2] It has been shown that a rhenium complex, *fac*-$[Re(bpy)(CO)_3X]$ (X = Cl or Br) can act both as photosensitizer and catalyst for the photoreduction of CO_2 into CO in triethanolamine (TEOA)–dimethylformamide (DMF) solutions.[3,4] The presence of water in DMF led to some H_2 production with a concurrent decrease of the CO production.

Smectite clay minerals can assist the photoproduction of hydrogen by intercalation of the photoactive cationic species[5] and recently, anionic photocatalysts have been intercalated into synthetic hydrotalcite.[6]

We report here that a cationic rhenium complex, $[Re(bpy)(py)(CO)_3]^+$ (bpy = 2,2′-bipyridine, py = pyridine), incorporated into aqueous suspensions of hectorite, is an active catalyst for the photoproduction of hydrogen, in the presence of TEOA.

When an aqueous solution of $[Re(bpy)(py)(CO)_3]^+$-$(CF_3SO_3)^-$[†] (7.6×10^{-4} M) was irradiated by visible light, in the presence of TEOA, a small amount of hydrogen was detected in the first minutes following the beginning of the

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[†] $[Re(bpy)(py)(CO)_3]^+(CF_3SO_3)^-$ was synthesized by the procedure of Wrighton *et al.*[7] Elemental analyses (C, H, and N) (Guelph Chem. Labs) were satisfactory. I.r. and ^1H n.m.r. spectra were in perfect agreement with the structure. The position of the Re LCT band was ~345 nm (ε 4000 $dm^3\,cm^{-1}\,mol^{-1}$, sh). The $PF_6{}^-$ salt of the same cation has been previously described by Caspar and Meyer.[8]

Table 1. Photoproduction of hydrogen catalysed by $[Re(bpy)(py)(CO)_3]^+$ in aqueous suspensions of hectorite.[a]

Experiment	$[Re(bpy)(py)(CO)_3]^+$ /mM	Hectorite (Ht) or montmorillonite(Mt)[b] /mg	Irradiation time/h	H_2 produced[c]/ml	Turnover number[d]
1	0.764	–	0.17	0.33	
			3.4	0.31	
			6.0	0.31	0.3
2	0.764	75 (Mt)	0.73	0.28	
			1.3	0.28	
			16.5	0.47	0.5
3	0.764	75 (Ht)	0.5	0.26	
			1.9	0.95	
			3.6	1.81	
			21.1	7.22	13
4	0.764	150 (Ht)	0.75	0.47	
			2.4	3.27	
			4.2	4.98	
			21.5	11.5	21
5	0.764	225 (Ht)	1.0	0.27	
			2.0	1.20	
			3.9	2.69	
			20.6	6.74	12
6	0.127	20 (Ht)	1.0	0.48	
			2.3	1.17	
			4.1	1.79	
			21.0	2.98	32

[a] The illumination source was a 450 W Xenon lamp with ≤395 nm cut-off filter. The solutions were prepared as follows: $[Re(bpy)(py)(CO)_3(CF_3SO_3)]$ was added to an aqueous suspension of the clay mineral (55 ml) and stirred for 1 h. After incorporation of the organometallic cationic compound in the clay, TEOA (5 ml) was added to the mixture which was then submitted to irradiation by visible light. A different order of addition (TEOA before Re^I) led to a decrease of hydrogen production. No hydrogen was produced in the absence of TEOA or of the Re^I compound, or in the dark. All the additions were carried out under argon atmosphere with rapid stirring. [b] Hectorite was from San Bernardino, California, and montmorillonite was a Wyoming Bentonite from Clay Spur, Wyoming. The two clays were decarbonated and bleached and the <2 μm fraction was separated by conventional techniques (gravitation). [c] Determined by gas chromatography (Gow Mac 550 P) on a 5 Å molecular sieves column. [d] Calculated as the ratio between the quantities of H^+ photoreduced and Re^I.

irradiation. The production of hydrogen then levelled off before a turnover of 1 was obtained (Table 1, experiment 1). In the presence of montmorillonite, the same behaviour was observed with the formation of hydrogen only at the earlier stages of the irradiation (experiment 2). Only very small amounts of hydrogen (~0.1 ml) were detected when $[Re(bpy)(py)(CO)_3]^+(CF_3SO_3)^-$ (10 mg) was loaded on silica gel (150 mg) and irradiated for 20 h. The results were dramatically different when hectorite was the swelling clay in which the cationic rhenium catalyst was incorporated‡ (experiments 3—6). The initial amounts of hydrogen produced were comparable with the cases of the homogeneous solution and of the montmorillonite suspension. In the case of hectorite, however, the production was sustained for at least 20 h, and turnover numbers of 20 to 30 were obtained. There was an optimum ratio Re^I : hectorite corresponding to 50—60% of the cationic exchange capacity.

At this stage, one can only speculate on the mechanism leading to the production of hydrogen. The first event of the process is the irradiation into the MLCT band [π^*(bpy) ← Re^I]. The excited state potential of $^*Re^I/Re^0$ for a similar compound, $[(CH_3CN)Re(CO)_3(Phen)]^+$ (phen = 1,10-phenanthroline), is approximately +1.5 V *vs.* standard calomel electrode (S.C.E.).[9] Assuming a value in the same order of magnitude for $^*[Re(bpy)(py)(CO)_3]^+$, reductive quenching by TEOA can then occur. The Re^0 derivative is then reoxidized with a concurrent reduction of H^+ (in high concentration at the proximity of the clay surface). This is in agreement with the reduction potential of $[Re(bpy)(py)(CO)_3]^+PF_6^-$ in acetonitrile, −1.18 V *vs.* S.C.E.[8]

We thank the Natural Sciences and Engineering Research Council of Canada (N.S.E.R.C.C.) and the Development Fund of the Sciences Faculty of the University of Ottawa for financial support.

Received, 20th July 1987; Com. 1045

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‡ The maximum quantity of $[Re(bpy)(py)(CO)_3]^+$ adsorbed by hectorite (<2 μm fraction of the Ca^{2+} homoionic form) was 0.61 ± 0.05 mequiv. g^{-1}. This value is close to the calculated cationic exchange capacity (0.67 mequiv. g^{-1}).[5b,c]