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Remarkable Solvent Effects on the Photocatalytic Behavior of [fac-Re(bpy)$(CO)_3$Br] (bpy = 2,2'-bipyridine). Selective Hydrogen Evolution in Ether Solvents in the Presence of Triethylamine

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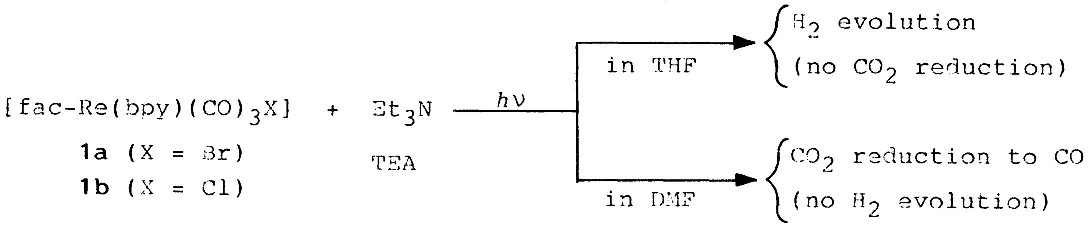
Irradiation of [fac-Re(bpy)$(CO)_3$Br] and triethylamine in tetrahydrofuran at > 400 nm results in the catalytic H_2 evolution without the CO_2 reduction to CO, while the CO_2 reduction occurs with little H_2 evolution in N,N-dimethylformamide and acetonitrile.

Photoredox chemistry of transition-metal complexes has recently received much attention to achieve net two-electron photocatalyses in homogeneous solution, particularly the photoreduction of water[1-4] and carbon dioxide[1,2,5-7] by a one-electron reductant. The photocatalytic systems reported so far usually require both a redox photosensitizer such as $[Ru(bpy)_3]^{2+}$ acting as a 1e$^-$ shuttle and a cocatalyst such as a Co(II),[1,3] Ni(II),[2] Pd(I),[4] or Ru(II)[7] complex working as a 1e$^-$/2e$^-$ relay for the formation of H_2, CO, or HCO_2^-. Interestingly, however, the reduction of CO_2 to CO by aliphatic tertiary amines efficiently occurs without H_2 evolution upon irradiation of a Re(I) complex, [fac-Re(bpy)$(CO)_3$X] (**1a**, X = Br; **1b**, X = Cl), in N,N-dimethylformamide (DMF) in the absence of an extra 1e$^-$/2e$^-$ relay.[5,3] In this paper, we wish to report remarkable solvent effects on the photocatalytic behavior of **1a,b**, i.e., selective H_2 evolution without the CO_2 reduction in ether solvents, particularly in tetrahydrofuran (THF).



Irradiation of **1a,b** and triethylamine (TEA) in DMF[9] resulted in ethylation of the bpy ligand under Ar[10] or in the CO_2 reduction under CO_2 along with formation of CO_2-incorporated Re(I) complexes,[5,11] while H_2 was not formed. In THF, by contrast, H_2 was evolved under Ar and even under CO_2 with neither the CO_2 reduction nor formation of the CO_2-incorporated complexes. The H_2 evolution again occurred in such ether solvents as 1,2-dimethoxyethane, 2-methyltetrahydrofuran, tetrahydropyran, and 1,4-dioxane in lower yields but not at all in such non-ether solvents as DMF, acetonitrile, acetone, methanol, and dichloromethane. Moreover, a photobleaching of **1a,b** in THF was 6 - 9 times slower than that in the non-ether solvents. Details of the H_2 evolution were therefore investigated with **1a** in THF; the photocatalytic activities of **1a,b** were confirmed to be very similar to each other.

The H_2 evolution is initially linear with irradiation time and then levels off due to a photobleaching of **1a**, as shown in Fig. 1. At level-off points, however, molar ratios of H_2 formed to **1a** used (turn-over numbers abbreviated as TON) are 7 for a dry THF solution and 10 in the presence of 1.0 mol dm^{-3} water, demonstrating that the H_2 evolution is photocatalytic. Table 1 summarizes effects of some additives on the initial rate and TON of the H_2 evolution and on the **1a** photobleaching. Tetrabutylammonium bromide remarkably diminishes the photocatalytic activity of **1a** and enhances the **1a** photobleaching, while the addition of 1.0 mol dm^{-3} water brings about a substantial increase of TON with only a slight decrease of the initial rate. Upon raising the reaction temperature to 47 °C, moreover, the **1a** photobleaching becomes still slower with an increase of the initial rate of the H_2 evolution and, as a result, TON reaches 15. With triethanolamine used in place of TEA, the H_2 evolution is very inefficient even though **1a** is comparably photobleached, an interesting observation in relation with the CO_2 photoreduction which favors triethanolamine more than TEA.[5,8]

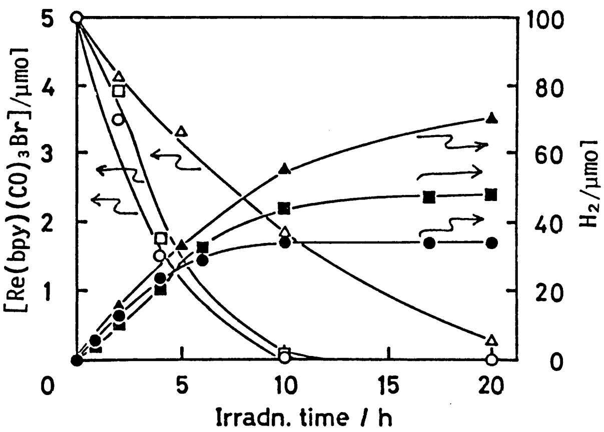


Fig. 1. Hydrogen evolution and photobleaching of **1a** in a dry THF solution at 15 °C (-●-;-○-) and in the presence of 1.0 mol dm^{-3} water at 15 °C (-■-;-□-) and at 47 °C (-▲-;-△-); irradiation of **1a** (1.0 mmol dm^{-3}) and TEA (1.0 mol dm^{-3}) in 5 cm^3 THF at > 400 nm. For details see reference 9.

Although mechanistic details of the photocatalytic H_2 evolution are still un-

Table 1. Effects of Additives on Photocatalytic H_2 Evolution[a)]

	TEA[b)]								TEOA[c)]
	Additives								
			H_2O (1.0 M†)						
	None	Bu_4NBr (10 mM†)	Temperature/°C 0	15	47	bpy (50 mM†)	CO[d)]	$P(OEt)_3$ (20 mM†)	
H_2 μmol h^{-1}	6.5	1.0	3.8	5.6	7.1	5.6	5.0	∿1	1.3
H_2 TON[e)]	7	<2	8	10	15	9	10	<1	2
-**1a**[f)]/μmol h^{-1}	0.70	>2.5[g)]	0.65	0.61	0.55	0.24	0.60	>2.5[g)]	0.75

a) Unless otherwise stated, the reaction temperature was 15 ± 1 °C; for details of experimental procedures see reference 9. b) Triethylamine. c) Triethanolamine. d) For CO-saturated solution. e) Turn-over numbers represented by molar ratios of H_2 formed to **1a** used. f) Photobleaching of **1a**. g) Almost complete photobleaching within 2 h. † 1 M = 1 mol dm^{-3}.

known, the primary process should be electron transfer from TEA to the luminescent state of **1a**.[5,8,10,12)] It was however found that the photoevolved dihydrogen is exclusively a mixture of D_2 and HD from D_2O in undeuterated THF but H_2 from H_2O in THF-d_8.[13)] The H_2 evolution is clearly the consequence of a two-electron event. The $1e^-/2e^-$ conversion might follow the liberation of a ligand from $\mathbf{1a}^{\bullet-}$, perhaps that of the Br^- ligand which is strongly suggested by the efficient exchange of this ligand with Cl^- induced by the photoelectron transfer of **1a**.[5)] The remarkable effects of Bu_4NBr and $P(OEt)_3$ appear to arise from the interception of [Re(bpy)-$(CO)_3$] and/or subsequent intermediates by Br^- or $P(OEt)_3$, which would shut off the pathway for H_2 evolution but which would open up channels for the degradation of **1a**. On the other hand, the liberation of either the bpy or the CO ligand is unlikely to be important, since the H_2 evolution is not significantly affected by either free bpy or CO added and since neither free bpy nor CO was detected in the photocatalytic reaction. The loss of the bpy ligand appears to be a channel for the **1a** degradation since free bpy added significantly prevented the **1a** photobleaching. Finally it should be noted that the present finding reveals the unique, versatile photocatalytic capabilities of **1a,b** in the reduction of water or CO_2 in homogeneous solution depending on solvent used, though the H_2 evolution photocatalyzed by $[fac\text{-}Re(bpy)(pyridine)(CO)_3]^+$ was reported to occur only in a heterogeneous suspension of hectorite clay mineral.[14)]

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9) A 5-cm^3 solution of **1a** (1.0 mmol dm^{-3}), TEA (1.0 mol dm^{-3}), and, if necessary, appropriate additives placed in a Pyrex tube (8 mm i.d.) was flushed with Ar, CO_2, or CO and then irradiated through 1.0 cm pathlength of 1.0 mol dm^{-3} $NaNO_2$ aqueous solution with an Eikosha tungsten-halogen lamp in a water bath maintained usually at 15 °C ± 1 °C. The progress of the photoreaction was followed by VPC, TLC, and HPLC.

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12) The luminescence of **1a** was quenched by TEA at 9×10^7 dm^3 mol^{-1} s^{-1} in DMF and at 5×10^7 dm^3 mol^{-1} s^{-1} in THF.

13) The HD formation in the presence of D_2O as well as the H_2 evolution even in dry THF can be easily attributed to the efficient liberation of a proton from the cation radical of TEA: W. F. Smithe, Jr., J. Am. Chem. Soc., 94, 186 (1972); P. J. DeLaive, T. K. Foreman, C. Giannotti, and D. G. Whitten, ibid., 102, 5627 (1980).

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