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Efficient rhenium-catalyzed photochemical carbon dioxide reduction under high pressure

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Abstract

The photocatalytic reduction of CO_2-to-CO was carried out under high pressure with [*fac*-Re(bpy)$(CO)_3$Cl] (bpy = 2,2′-bipyridine) as the catalyst. The use of high-pressure CO_2 gas was much more effective than the addition of excess Cl^- ions for increasing the stability of the catalyst and achieving efficient CO formation. The turnover number for CO formation at 2.45 MPa of CO_2 reached a maximum of 41.8, which was 5.1 times the turnover number for the conventional normal-pressure system.

Keywords: High pressure; Carbon dioxide; Rhenium; Photocatalyst

1. Introduction

Rhenium(I) diimine complexes have received a great deal of attention because of their photochemical properties [1]. They can photocatalyze for the selective reduction of CO_2-to-CO by visible-light irradiation in the presence of an amine-electron donor, without the assistance of a cocatalyst [2–11]. Among them, [*fac*-Re(bpy)$(CO)_3$Cl] (bpy = 2,2′-bipyridine) (**1**) shows the highest turnover number for CO formation [2]. However, while photocatalyzing the reduction of CO_2, the catalyst **1** simultaneously causes a formate complex [*fac*-Re(bpy)$(CO)_3$OC(O)H], which has little CO formation ability [2]. Therefore, a large excess of Cl^- ions must be added to the reaction solution to suppress the formate complex formation [2]. The addition of excess Cl^- ions does effectively prolong the catalytic reaction, but in general the use of large amounts of species that are not directly involved in the photocatalytic cycle seems undesirable in view of 'atom economy' [12].

The conventional photochemical reaction system consists of a normal-pressure (0.10 MPa) CO_2 gas phase over a CO_2-saturated solvent phase containing the catalyst and the amine. Increasing the CO_2 pressure is an interesting approach to increase the efficiency of catalysis because the high pressure, which increases the CO_2 concentration in the solvent phase, may increase the reactivity of the catalyst toward CO_2 [11].

Herein we describe photocatalytic CO_2-to-CO reduction using **1** in a system with high-pressure CO_2 gas and a liquid solvent (Et_3N/DMF). This high-pressure system was much more efficient for catalytic CO formation than the conventional normal-pressure system either with or without excess Cl^- ions.

2. Experimental section

2.1. Materials

All reagents and solvents were of high purity and were obtained from Kanto Chemical and Aldrich. Triethylamine was distilled over KOH. Dimethylformamide (DMF) was distilled under reduced pressure.

2.2. Photochemical reaction under high pressure

A high-pressure mercury lamp (500 W) with a band-pass filter was used to produce 365-nm monochromatic light. A high-pressure reactor (29.4-ml volume) equipped

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with sapphire windows was charged with an Et_3N/DMF solution (9 ml, Et_3N 0.80 M) containing **1** (1.1 mg, 2.38 μmol). Then the reactor was connected to a CO_2 cylinder through the needle valve and charged to the desired CO_2 pressure. The sample solution was then irradiated for 0–25 h with stirring. In all runs, the temperature was maintained at 27 °C. After irradiation, the pressure was released, and the gas was collected in a sampling bag and subjected to measurements.

2.3. Measurements

The saturated CO_2 concentrations in the Et_3N/DMF mixtures (Et_3N 0.80 M) under high pressure were determined from the weight of charged CO_2, the pressure, and the volumes of the gas and liquid phases. The CO_2 concentrations under normal pressure were obtained by a titration method [13]. The amount of CO was measured with a gas chromatograph equipped with a methanizer, a molecular-sieve column, and a flame ionization detector. The amount of **1** during irradiation was measured with a reversed-phase HPLC system consisting of a UV detector, an ODS column, and a mobile phase consisting of a mixture (60:40, v/v) of methanol and KH_2PO_4–NaOH buffer (0.05 M).

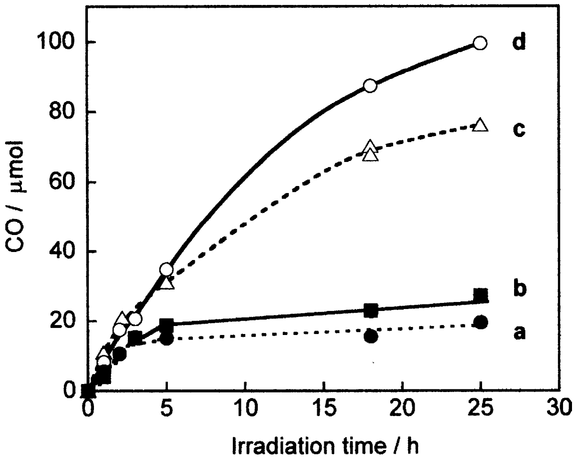


Fig. 1. Irradiation-time dependence of CO formation catalyzed by **1** under various CO_2 pressures: (a) 0.10 MPa; (b) 0.10 MPa with excess Cl^- ions; (c) 1.21 MPa; (d) 2.45 MPa. Irradiation wavelength was 365 nm.

3. Results and discussion

The irradiation-time dependence of CO formation using **1** in Et_3N/DMF solutions under various pressures is shown in Fig. 1. When the reaction was carried out under normal pressure (Fig. 1a), steady CO formation stopped at ca. 3 h, and the amount of CO after 25 h of irradiation was 19.6 μmol, which corresponds to a turnover number of 8.2 (Table 1). Addition of a 23-fold excess of Et_4NCl (Cl^- source) to the reaction solution increased the duration of steady CO formation to ca. 5 h (Fig. 1b) and the turnover number at 25 h was 11.5. The saturated CO_2 concentration in the Et_3N/DMF solution under normal pressure was measured to be 0.19 M. Increasing the CO_2 pressure increased the CO_2 concentration in the Et_3N/DMF solution; that is, 1.21 MPa of CO_2 gas raised the CO_2 concentration in the liquid phase to 2.63 M (Table 1). The increased CO_2 concentration in the reaction solution had a favorable effect on the catalytic CO formation (compare Figs. 1a, c, and d). At higher-than-normal pressures, steady CO formation continued much longer than it did under normal pressure either with or without excess Cl^- ions. The CO formation rate, calculated from the data in the region where the CO amount increased linearly with respect to time, increased with increasing pressure (Table 1). The CO formation rate under 2.45 MPa of CO_2 was 6.80 μmol h^{-1}, which is 1.3 times the rate obtained under normal pressure. At 2.45 MPa of CO_2, the CO amount after 25 h of irradiation reached 99.5 μmol, which corresponds to a turnover number of 41.8. This value is 5.1 times that obtained under normal pressure without excess Cl^- ions and 3.6 times that obtained with excess Cl^- ions.

To determine why CO formation increased at higher CO_2 pressures, we used HPLC to measure the concentration of **1** during the photocatalytic reduction of CO_2.

Table 1
CO formation data catalyzed by **1** under several CO_2 pressures

Entry	$P(CO_2)$ (MPa)	$[CO_2]^a$ (M)	CO formation rate[b] (μmol h^{-1})	CO amount[c] (μmol)	Turnover number[d]
1	0.10	0.19	5.14	19.6	8.2
2[e]	0.10	0.19	5.11	27.3	11.5
3	1.21	2.63	5.95	76.2	32.0
4	2.45	5.44	6.80	99.5	41.8

[a] CO_2 concentration in the Et_3N (0.80 M)/DMF mixture.

[b] Calculated from the data in the time region where the CO amount increased linearly with respect to time; 0–3 h for entries 1 and 2 (a and b in Fig. 1) and 0–5 h for entries 3 and 4 (c and d in Fig. 1).

[c] CO amount after 25 h of irradiation.

[d] Turnover number = (mol of CO at 25 h)/(mol of catalyst **1** used).

[e] NEt_4Cl (6.07 mM) was added.

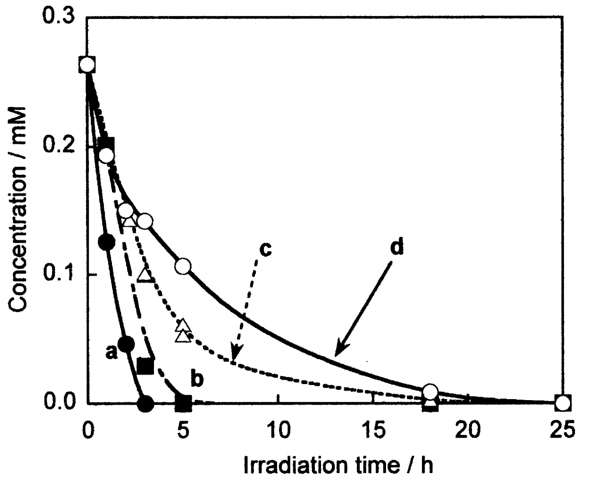
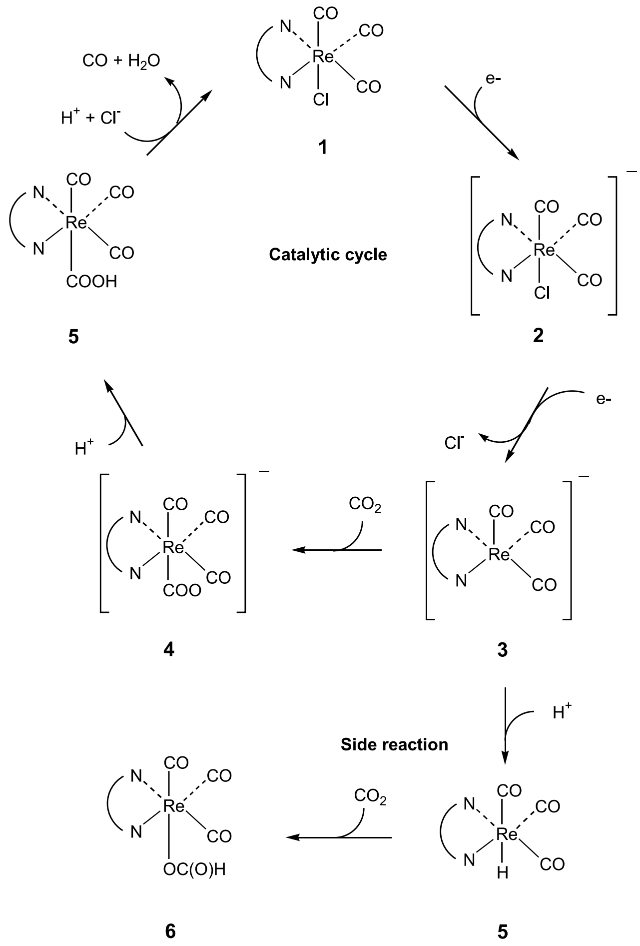


Fig. 2. Changes in the concentration of **1** during the photocatalytic reduction of CO_2 under various pressures: (a) 0.10 MPa; (b) 0.10 MPa with excess Cl^- ions; (c) 1.21 MPa; (d) 2.45 MPa.

Fig. 2 shows the changes in the concentration of **1** during the photocatalytic reduction of CO_2 under several pressures. In the reaction under normal pressure without excess Cl^- ions (Fig. 2a), **1** is rather unstable: 52.4% of **1** had decomposed after only 1 h of irradiation. After 3 h of irradiation, **1** disappeared from the chromatogram. Accordingly, steady CO formation stopped at ca. 3 h (Fig. 1a). The addition of excess Cl^- ions increased the stability of **1** somewhat: the catalyst was still detected at 3 h (11.0% based on **1** used), and it disappeared after 5 h (Fig. 2b). Accordingly, steady CO formation continued until 5 h in the presence of excess Cl^- ions (Fig. 1b). Increased CO_2 pressure effectively stabilized **1**. When the CO_2 pressure was increased to 1.21 MPa, which gave a CO_2 concentration of 2.63 M in the Et_3N/DMF phase, **1** was detected until 18 h (1.0%; Fig. 2c). When the CO_2 pressure was raised to 2.45 MPa, the CO_2 concentration in the solvent phase increased to 5.44 M, and the highest stability of **1** was achieved (Fig. 2d).



Scheme 1.

The reason why increasing CO_2 pressure increases the CO formation ability can be explained as follows. Scheme 1 shows a previously proposed photocatalytic cycle for the CO formation using **1** [14,15], together with the formation process of the formate complex **6** [15,16], which is the by-product having little CO formation ability [2]. After the formation of one-electron reduced species **2** by the photoelectron transfer, Cl^- loss occurs with the second-electron injection to form the coordinatively unsaturated intermediate **3**. Then, CO_2 can coordinate to the Re center in the intermediate **3** to form the CO_2 complex **4**. The CO_2 complex **4** is protonated to give the metalloacid **5**. Then, **5** is dehydroxylated, yielding $Re(bpy)(CO)_4^+$ which reacts with Cl^-, and liberates CO, to return the catalyst **1**. Increasing Cl^- ions in the solvent phase may enhance this last reaction and preserve the catalyst longer. On the other hand, the side reaction, i.e., the formate formation results from a competing reaction of the unsaturated intermediate **3** with H^+ instead of reaction with CO_2 [15]. The resulting hydride complex **5** inserts CO_2 to give the formate complex **6** [15,16]. At the competition process between CO_2 and H^+ for the intermediate **3**, an increase in CO_2 pressure, which led to an increase in the CO_2 concentration in the solvent phase, may produce **4** largely and effectively suppress the reaction of **3** with H^+. Thus, increasing CO_2 pressure increases the catalytic CO formation.

In conclusion, we applied high-pressure CO_2 gas to the photocatalytic CO_2-to-CO reduction using catalyst **1**. To increase the stability of **1** and raise the efficiency of CO formation, the use of high CO_2 pressure was much more effective than the addition of excess Cl^- ions. Despite the fact that we did not use additives intended to minimize the side reaction of the catalyst **1**, the turnover number for CO formation reached a maximum of 41.8, which was 5.1 times that obtained with the conventional normal-pressure system.

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