High-pressure photocatalytic reduction of carbon dioxide using [fac-Re(bpy)(CO)$_3$$P$(O^{i}Pr)$_3$]$^+$ (bpy = 2,2′-bipyridine)

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Abstract

Photocatalytic CO_2-to-CO reduction using [fac-Re(bpy)(CO)$_3$$P$(O^{i}Pr)$_3$]$^+$ (bpy $= 2, 2'$-bipyridine) occurred with high efficiency in a high-pressure CO_2 gas/organic solvent system. At a CO_2 pressure of 1.36 MPa, the turnover number for CO formation was 3.8 times that in the conventional normal-pressure (0.10 MPa) system. Application of high-pressure CO_2 gas greatly increased the CO_2 concentration in the solvent phase. The high CO_2 concentration enhanced the reaction of one-electron-reduced catalytic species with CO_2, and effectively prevented the deactivation of the catalyst. © 2002 Elsevier Science B.V. All rights reserved.
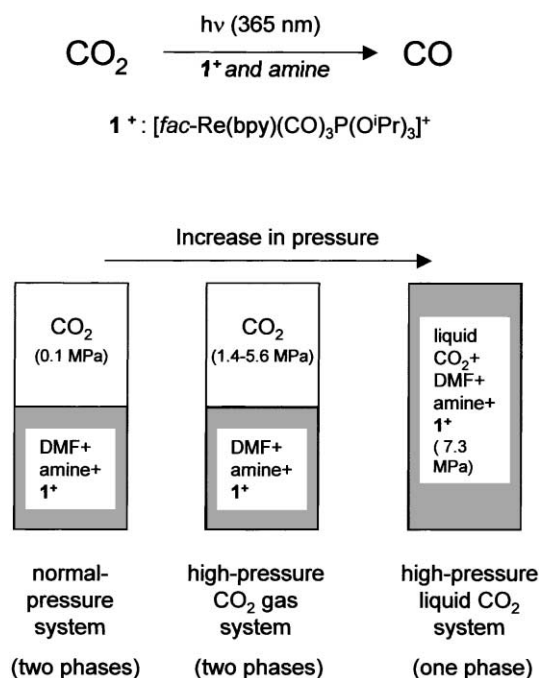
1. Introduction

Rhenium bipyridine complexes have received a great deal of attention with regard to their photophysical and photochemical properties [1,2]. In the presence of an amine electron donor, these complexes can act as photocatalysts in the visible-light photochemical reduction of CO_2-to-CO [3–13]. The catalytic systems exhibit high chemical specificity and can mediate two-electron-transfer without the assistance of a cocatalyst. The electron transfer from an amine to excited-state complexes is generally accepted as the initiation process of the photocatalysis [1–13]. Among the reported catalysts, phosphite-containing complexes show high quantum yields of CO formation; Hori et al., for example, reported a quantum

yield of 0.38 [5]. However, these catalysts are not very stable, and the turnover number for CO formation reaches a maximum of only 7–8.

Past reports have mainly focused on modifying the chemical structure to improve the catalytic performance. On the other hand, increasing the CO_2 pressure is another possible approach, because high-pressure may increase the rate of CO_2 reduction. The conventional two-phase 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 amine (Scheme 1). The solvent phase is irradiated, and the resulting CO is concentrated into the CO_2 gas phase. Previously, we demonstrated that CO_2 reduction can be achieved in high-pressure CO_2 by using a CO_2-soluble rhenium complex without an organic solvent; in this one-phase system, the reactor is full of liquid CO_2 [13]. However, the one-phase high-pressure system had no advantage for

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Scheme 1.

the production of CO over the conventional two-phase system; the presence of the gas phase seems important for efficient CO formation. Herein we describe the photocatalytic CO_2-to-CO reduction in a high-pressure two-phase system (high-pressure CO_2 gas/liquid solvent) using [fac-Re(bpy)(CO)$_3$$P$(O^{i}Pr)$_3$] ($\mathbf{1}^+$). The results are compared with those of the conventional two-phase normal-pressure system and the high-pressure one-phase system.

2. Experimental

2.1. Materials

All reagents and solvents were of high purity and were obtained from Kanto Chemical, Wako Pure Chemical Industries and Aldrich. Triethanolamine (TEOA) and dimethylformamide (DMF) were distilled under reduced pressure. Triethylamine (TEA) was distilled over KOH. The rhenium complex $\mathbf{1}^+$SbF$_6$$^-$ was prepared according to a literature procedure [14].

2.2. Photochemical reaction

A high-pressure mercury lamp (500 W) with a band-pass filter (365 nm) was used to produce 365 nm monochromatic light. A stainless steel high-pressure reactor (17.4 ml volume) equipped with four sapphire windows, a PTFE stirring bar, a bore hole for a thermocouple, and needle valves was charged with a DMF–amine solution (9.0 ml) (amine: TEOA or TEA, 0.80 M) containing $\mathbf{1}^+$ (2.47 mM). Carbon dioxide was bubbled through the solution for 20 min. With the aid of a compressor, the reactor was filled through the needle valve with a sufficient amount of CO_2 to attain the desired pressure. The sample solution was then irradiated for 0.5–24 h with stirring. In all runs, the stirring speed was kept constant and the temperature was $26 \pm 1\,^\circ$C. After irradiation, the pressure was released and the gas was collected in a sampling bag and subjected to measurements. Reactions under normal pressure were carried out with the same reactor.

2.3. Measurements

The saturated CO_2 concentrations in the DMF–amine mixtures under high-pressure were determined from the amount 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 literature titration method using Ba(OH)$_2$ [15,16]; in our procedure, we used a pH meter instead of an acid–base indicator. The amount of CO was measured with a gas chromatograph equipped with a methanizer (Ni catalyst, 400 $^\circ$C), a molecular sieve column (5A, 3 m), and a flame ionization detector. An active carbon column (2 m) and a thermal conductivity detector were also used for higher CO concentrations. UV–VIS spectral changes during the photoreaction were measured with a multichannel spectrophotometer connected to the reactor by optical fibers. The amount of $\mathbf{1}^+$ after 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$_2$PO$_4$–NaOH buffer (0.05 M, pH 5.9). Positive-ion electrospray mass spectra of the reaction solutions were measured by a previously reported procedure [17]. UV–VIS and IR spectra of the one-electron-reduced species of $\mathbf{1}^+$ prepared by flow
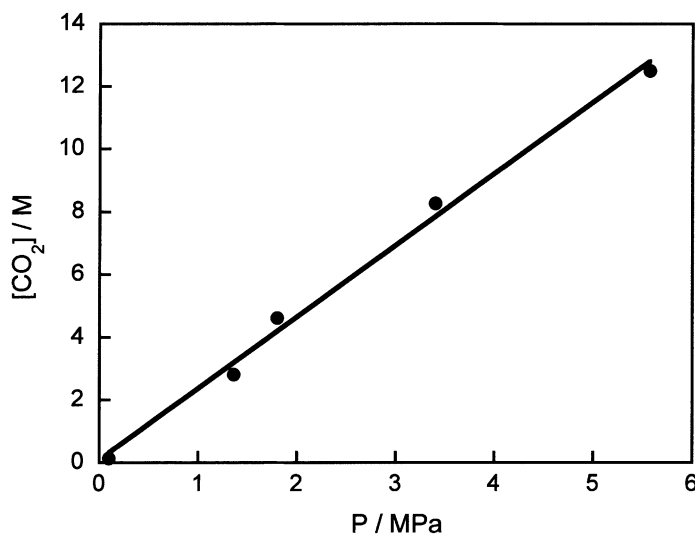
Fig. 1. Variation of saturated CO_2 concentration with CO_2 pressure. The liquid phase was a DMF solution containing TEOA (0.80 M). Temperature was kept at $26 \pm 1\,^\circ C$.

3. Results and discussion

electrolysis under normal pressure were measured by a reported method [9].

If increasing the CO_2 pressure barely affected the solubility of CO_2 in the DMF–amine phase, we would not expect any dramatic increase in catalytic CO formation. We therefore initially measured the solubility of CO_2 in the DMF–amine solutions at various pressures. Fig. 1 shows the pressure dependence of the saturated CO_2 concentration in the DMF–TEOA phase. As expected, the solubility increased with increasing pressure. The CO_2 concentration at 0.10 MPa (normal pressure) was 0.13 M (No. 1 in Table 1).

Table 1
Solubility and catalysis data[a]

No.	Solvents	CO_2 pressure (MPa)	$[CO_2]$[b] (M)	CO formation rate (μmol h^{-1})	Saturated CO amount (μmol)	Turnover No.
1	DMF–TEOA[c]	0.10	0.13	6.6	90.5[d]	4.1
2	DMF–TEOA[c]	1.36	2.81	20.2	348.3[d]	15.6
3	DMF–TEOA[c]	1.80	4.62	21.3	336.7[d]	15.2
4	DMF–TEOA[c]	3.40	8.27	23.1	306.9[d]	13.8
5	DMF–TEOA[c]	5.57	12.5	24.1	261.7[d]	11.8
6	DMF–TEA[c]	0.10	0.19	6.2	21.8[d]	1.0
7	DMF–TEA[c]	3.90	10.2	15.9	76.1[d]	3.4
8	DMF–TEA[e]	7.30	15.8	4.0	9.0[f]	0.4

[a] Temperature was $26 \pm 1\,^\circ C$.

[b] Carbon dioxide concentration in the liquid solvent phase.

[c] The reaction system consisted of a CO_2 gas phase (8.4 ml) and a liquid solvent phase (DMF–amine (0.80 M), 9 ml).

[d] Irradiation time was 24 h.

[e] The reaction system consisted of a mixture of DMF–amine (3 ml) and liquid CO_2. There was no gas phase visually. The amount of TEA was the same as that of Nos. 6 and 7. The one-phase reaction was carried out using only TEA because TEA, unlike TEOA, is soluble in liquid CO_2.
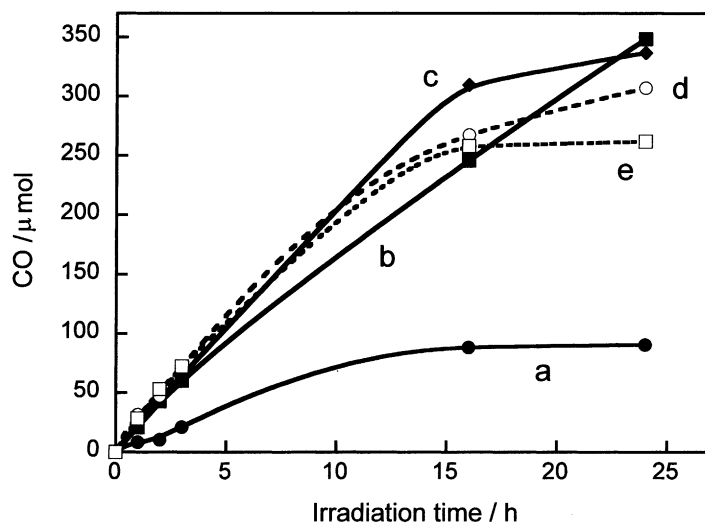
[f] Irradiation time was 16 h.

Fig. 2. Variation of CO formation with irradiation time. A CO_2-saturated DMF solution containing TEOA (0.80 M) and 1^+ (2.47 mM) was irradiated under CO_2 pressures of (a) 0.10 MPa; (b) 1.36 MPa; (c) 1.80 MPa; (d) 3.40 MPa and (e) 5.57 MPa. Irradiation wavelength was 365 nm.

When the pressure was 1.36 MPa, a typical pressure for the photochemical reactions, the concentration was 21 times that under normal pressure. The amine in the DMF–amine phase also affected the CO_2 concentration. Both under normal pressure (Nos. 1 and 6) and under high-pressure (Nos. 4 and 7), CO_2 was more soluble in DMF–TEA than in DMF–TEOA.

Under CO_2 pressure, irradiation of a DMF–TEOA or DMF–TEA solution containing 1^+ caused photocatalytic CO_2-to-CO reduction. Fig. 2 shows the
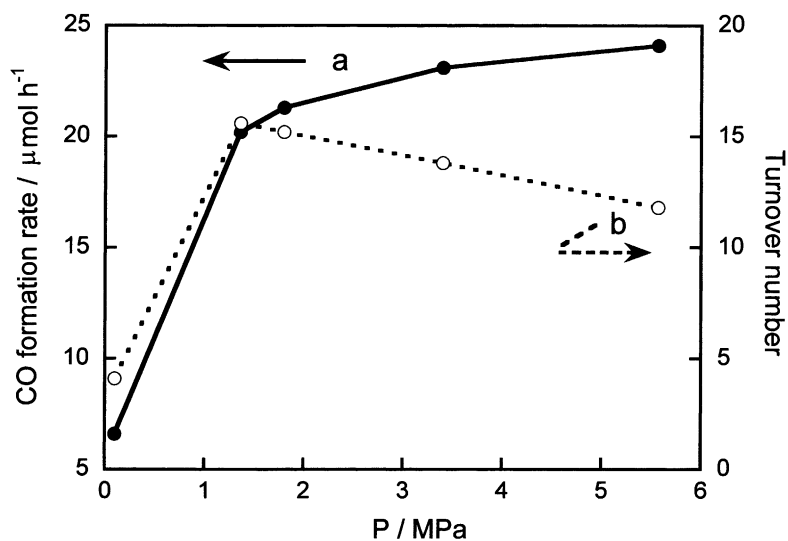

Fig. 3. (a) CO formation rate and (b) turnover number for the catalytic formation of CO as a function of pressure for a DMF solution containing TEOA (0.80 M) and 1^+ (2.47 mM).
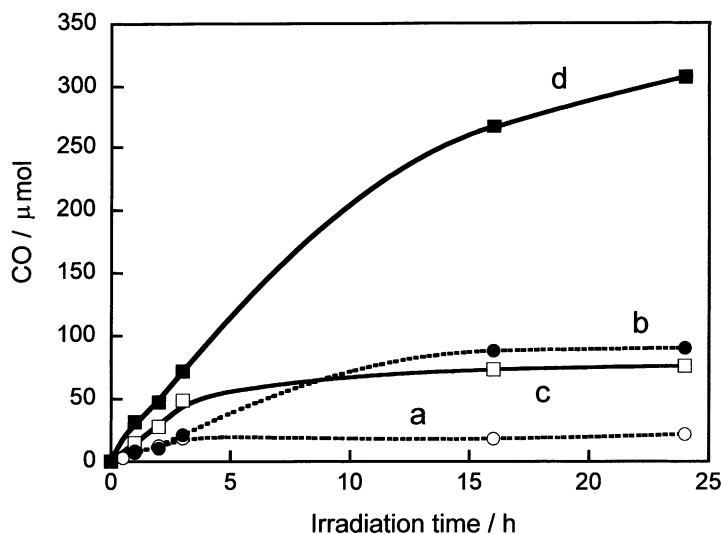
Fig. 4. Influence of amine on CO formation. A CO_2-saturated DMF solution containing TEOA or TEA (0.80 M) and $\mathbf{1}^+$ (2.47 mM) was irradiated under CO_2 pressure: (a) TEA, 0.10 MPa; (b) TEA, 3.90 MPa; (c) TEOA, 0.10 MPa and (d) TEOA, 3.40 MPa.

dependence of CO formation on irradiation time under various CO_2 pressures, where TEOA was used as the amine. The CO formation rate (Table 1), evaluated in the irradiation period where CO was produced linearly with respect to time, greatly increased with increasing pressure from 0.10 to 1.36 MPa (Fig. 3a). Further increasing the pressure from 1.36 to 5.57 MPa resulted in a gradual increase in the CO formation rate. The maximum CO formation rate at 5.57 MPa was 3.7 times that under normal pressure. The turnover number (the saturated CO amount/$\mathbf{1}^+$ used) showed a somewhat

different tendency with increasing pressure. It reached a maximum value of 15.6 at 1.36 MPa and then gradually decreased (Fig. 3b). This maximum value was 3.8 times that under normal pressure.

An increase in CO formation with increasing pressure was also observed when TEA was used instead of TEOA (Fig. 4). However, the catalysis was less stable, and eventually both CO formation rate and turnover number were lower in the DMF–TEA system than in the DMF–TEOA system (compare Nos. 1, 6 and 4, 7 in Table 1). Even though
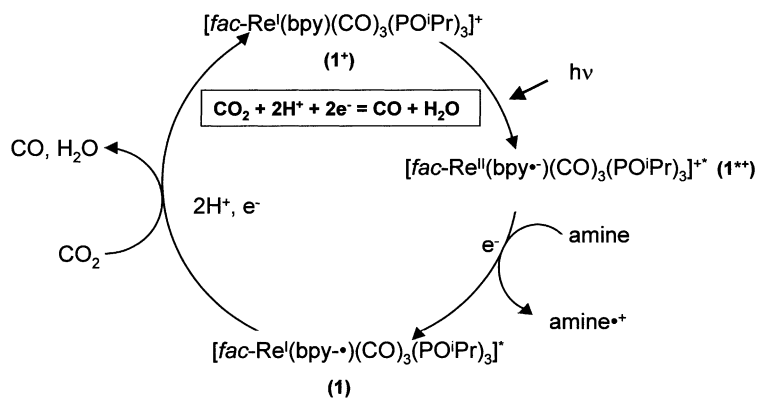
Scheme 2.

CO_2 is more soluble in DMF–TEA than in DMF–TEOA (vide supra), and TEA is a better electron donor than TEOA (pK_a(TEA) = 10.72, pK_a(TEOA) = 7.76) [18], CO_2-to-CO reduction is more efficient in the DMF–TEOA system than in the DMF–TEA system. A similar tendency was observed for fac-Re(bpy)(CO)$_3$Cl under normal pressure [10].

The catalytic CO_2-to-CO reduction requires not only two electrons but also two protons (Scheme 2). The most likely proton donor is the amine. Like the irradiation of other rhenium bipyridine complexes, irradiation of 1^+ in the presence of the amine causes an electron transfer from the amine to the excited complex 1^{*+} to produce the one-electron-reduced complex 1 and an amine radical. In the case of TEA, the radical species is $N^{\bullet+}(CH_2CH_3)_3$ (Eq. (1)). This radical can transfer a proton to give another radical and the conjugate acid $TEAH^+$ [19] (Eq. (2)).

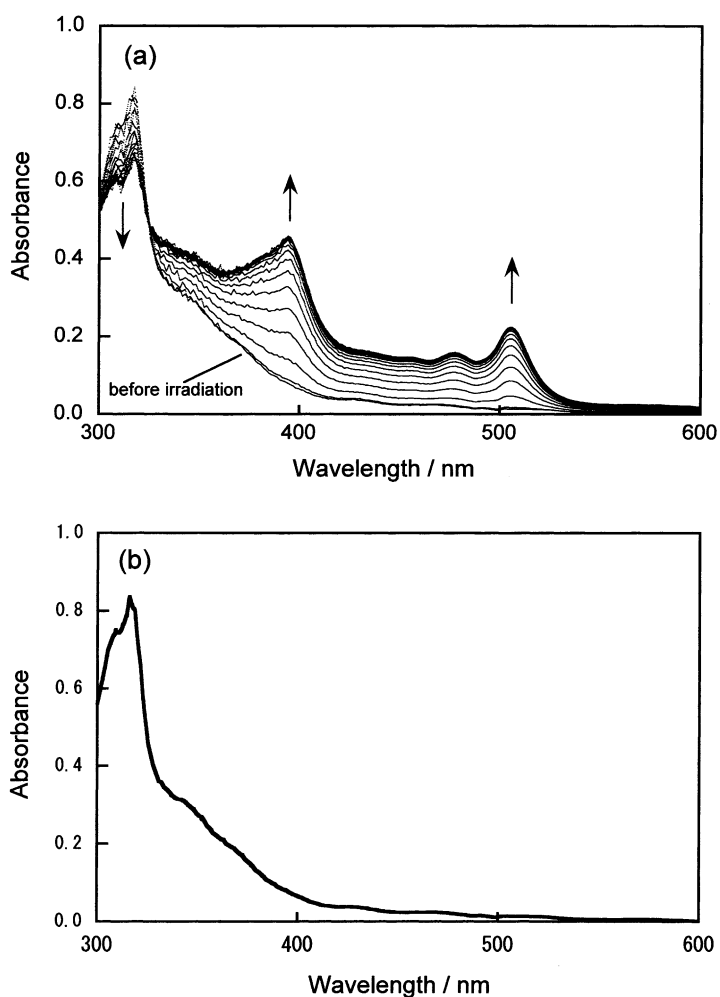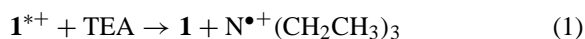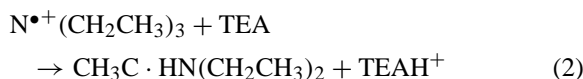$$1^{*+} + TEA \rightarrow 1 + N^{\bullet+}(CH_2CH_3)_3 \qquad (1)$$

Fig. 5. UV–VIS spectral changes of a DMF–TEOA solution (TEOA, 0.8 M) containing $1^+SbF_6^-$ (22 μM) during irradiation (365 nm) under CO_2 pressures of (a) 0.10 MPa and (b) 1.50 MPa. The spectra were recorded for 170 s after irradiation started. Time interval was 10 s. Path length was 4.0 cm.

$$N^{\bullet+}(CH_2CH_3)_3 + TEA$$

$$\rightarrow CH_3C \cdot HN(CH_2CH_3)_2 + TEAH^+ \qquad (2)$$

The conjugate acid may act as the proton source in the catalytic system. TEOA can act as both the electron donor and the proton donor, whereas the stronger base, TEA, can act only as an electron donor. This may explain why CO_2-to-CO reduction is less efficient in the DMF–TEA system than in the DMF–TEOA system.

To examine why the CO formation rate increased with increasing CO_2 pressure, we measured the UV–VIS spectral changes during the photochemical reactions. Fig. 5 shows the UV–VIS spectral changes of a DMF–TEOA solution containing $\mathbf{1}^+$ during irradiation under normal and high CO_2 pressures. When the CO_2 pressure was 0.10 MPa, absorption maxima around 394 and 505 nm appeared after irradiation started (Fig. 5a). These absorption maxima can be assigned to the one-electron-reduced species $\mathbf{1}$ on the basis of spectral similarity with the product from the flow electrolysis of $\mathbf{1}^+$ (Fig. 6). IR spectral analysis of the product from the flow electrolysis of $\mathbf{1}^+$ showed that the three $\nu(CO)$ bands of the one-electron-reduced species $\mathbf{1}$ were shifted to lower frequencies (Fig. 7). This shift reflects the fact that $\mathbf{1}$ has an electron on the bipyridine ligand, similar to other rhenium bipyridine complexes [6,9–11,14].

When the pressure was 1.50 MPa, the UV–VIS spectra before and after irradiation were nearly identical, and a negligible amount of $\mathbf{1}$ accumulated
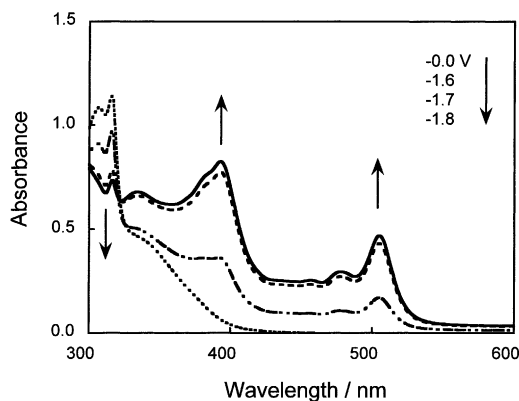

Fig. 7. IR spectral changes of a MeCN solution containing $\mathbf{1}^+$ (0.50 mM) and ^{n}Bu$_4$NClO$_4$ (0.1 M). The solution was reduced from 0 to -2.0 V vs. Ag/AgNO$_3$. Downward and upward arrows indicate loss of $\mathbf{1}^+$ and generation of the one-electron-reduced species $\mathbf{1}$, respectively. The $\nu(CO)$ (cm^{-1}) frequencies of $\mathbf{1}^+$ are 2045, 1958, and 1925, and those of $\mathbf{1}$ are 2020, 1925, and 1893.

(Fig. 5b). The one-electron-reduced rhenium complexes can react with CO_2 in the dark and this step is one of the rate-limiting steps in the photocatalyzed reduction of CO_2 [6]. The differences in the UV–VIS spectra suggest that the rate of reaction of $\mathbf{1}$ with CO_2 under high-pressure is much faster than that at normal pressure.

Another favorable effect associated with higher CO_2 pressure was greater stability of $\mathbf{1}^+$. When a CO_2-saturated DMF solution containing TEOA and $\mathbf{1}^+$ was irradiated for 16 h under a normal pressure of CO_2 (see Fig. 2a), the HPLC chromatogram of the reaction solution showed no peak corresponding to $\mathbf{1}^+$, and further irradiation caused no increase in the CO amount. Fig. 8 a shows the electrospray mass spectrum of this reaction solution. The spectrum shows a large peak at m/z 815 but no peak corresponding to $\mathbf{1}^+$ (m/z 635). When the reaction was carried out under a pressure of 1.36 MPa for 16 h (Fig. 2b), 11.2% of the initial amount of catalyst $\mathbf{1}^+$ remained; further irradiation continued to produce CO. The electrospray mass spectrum of this high-pressure sample showed peaks at m/z 635 ($\mathbf{1}^+$) and m/z 815 (Fig. 8b). The m/z 815 peak can be assigned to the complex having two phosphite ligands, i.e. [Re(bpy)(CO)$_2${$P(O^iPr)_3$}$_2$]$^+$ ($\mathbf{2}^+$). This suggests that, in addition to the catalytic CO formation process, photoinduced ligand substitution

Fig. 6. UV–VIS spectral changes of a MeCN solution containing $\mathbf{1}^+$ (0.56 mM) and ^{n}Bu$_4$NPF$_6$ (0.1 M) under an argon atmosphere by the flow electrolysis technique. Path length was 0.15 cm. The solution was reduced at 0 to -1.8 V vs. I$_2$/I$^-$.
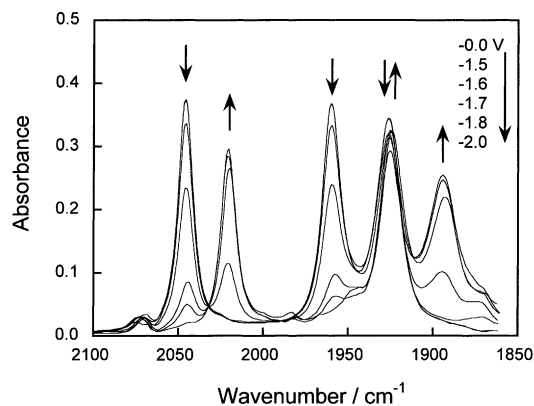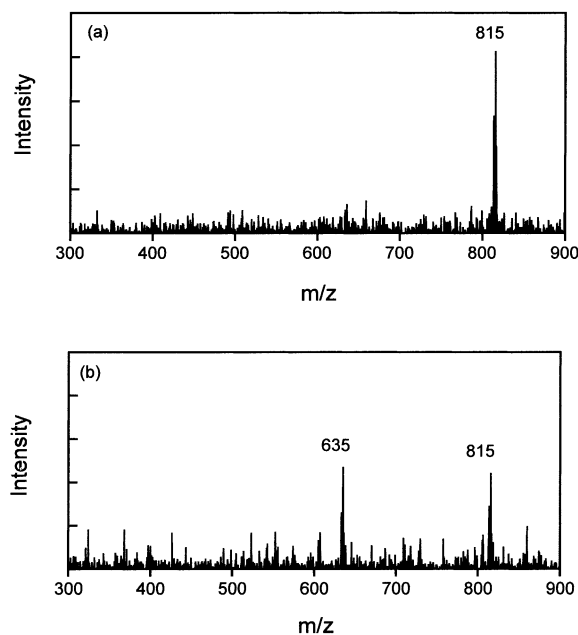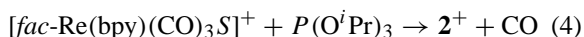
Fig. 8. Electrospray mass spectra of the reaction mixtures. A CO_2-saturated DMF solution containing TEOA (0.80 M) and $\mathbf{1^+}$ (2.47 mM) was irradiated (365 nm) for 16 h under (a) 0.10 MPa and (b) 1.36 MPa of CO_2.

reactions with solvent molecules (*S*; DMF or TEOA) occur (Eq. (3)); the unstable solvent complexes that are formed then react with free $P(O^iPr)_3$ to produce $\mathbf{2^+}$ (Eq. (4)). Photoinduced ligand substitution reactions with solvent molecules have been observed in some rhenium bipyridine complexes [7,8].

$$\mathbf{1^+} + S \rightarrow [fac\text{-}Re(bpy)(CO)_3 S]^+ + P(O^iPr)_3 \quad (3)$$

$$[fac\text{-}Re(bpy)(CO)_3 S]^+ + P(O^iPr)_3 \rightarrow \mathbf{2^+} + CO \quad (4)$$

At all CO_2 pressures, we detected $\mathbf{2^+}$, but not $\mathbf{1^+}$, in the electrospray mass spectra of the reaction mixtures after CO saturation was achieved. The complex $\mathbf{2^+}$ probably is not able to produce CO in the presence of TEOA, because $[Re(bpy)(CO)_2\{P(OEt)_3\}_2]^+$, an analogue of $\mathbf{2^+}$, was only partly quenched by TEOA [9]. Therefore the amount of CO does not increase after the formation of $\mathbf{2^+}$, resulting in deactivation of the rhenium catalyst.

Increasing the CO_2 pressure to 1.36 MPa effectively prevents this deactivation process. However, increasing the CO_2 pressure above 1.36 MPa causes a decrease in the turnover number. We assume that the solubility of CO in the DMF–TEOA phase under normal pressure is low because the solubilities of CO in DMF and TEOA are 2.5×10^{-3} and 4.8×10^{-4} M, respectively [10]. Therefore, most of the CO molecules produced during irradiation move to the gas phase under normal pressure. In the extremely high-pressure case, where the CO_2 pressure is raised until CO_2 becomes liquid and the reactor is almost full of liquid CO_2 (No. 8 in Table 1), the turnover number falls below the normal-pressure value (compare Nos. 6 and 8). This observation suggests that lack of gas phase forces the CO molecules to locate near the rhenium complexes and blocks the CO_2 molecules from coordinating to the rhenium active sites, resulting in a low turnover number for CO formation. Therefore, the presence of a gas phase is very important. A moderate pressure such as 1.36 MPa is desirable for efficient CO formation.

4. Conclusion

Photocatalytic CO_2-to-CO reduction using [*fac*-Re(bpy)(CO)$_3P(O^iPr)_3$]$^+$ ($\mathbf{1^+}$) (bpy = 2, 2′-bipyridine) was carried out in a high-pressure CO_2 gas/organic solvent system. At a CO_2 pressure of 1.36 MPa, using TEOA as an electron donor, the turnover number for CO formation reached a maximum value of 15.6, which is 3.8 times that in the conventional normal-pressure (0.10 MPa) system. Application of high-pressure CO_2 gas increased the CO_2 concentration in the solvent phase. Increasing the CO_2 concentration enhanced the reaction rate of one-electron-reduced catalyst species $\mathbf{1}$ with CO_2, and stabilized the catalyst $\mathbf{1^+}$. Further increasing the pressure from 1.36 MPa caused a decrease in the turnover number, although CO formation rate was still increased. As a whole, a moderate CO_2 pressure such as 1.36 MPa is desirable for efficient CO formation.

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