Rhenium-Mediated Photochemical Carbon Dioxide Reduction in Compressed Carbon Dioxide

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Rhenium-bipyridine complexes soluble in compressed CO_2 were prepared and employed in the first example of photochemical reduction of CO_2 mediated by metal complexes in compressed CO_2, without use of an organic liquid solvent.

Compressed (liquid or supercritical) CO_2 has been recently recognized as an innovative and ecologically benign reaction medium for chemical synthesis, especially metal-catalyzed processes.[1] Compared to conventional organic solvents, compressed CO_2 has many advantages such as nonflammability, nontoxicity, and ease of separation of products or catalysts from the reaction mixture. However, few reports have focused on photochemical reactions using metal complexes in compressed CO_2.[2] Furthermore, there have been no reports on photochemical CO_2 reduction mediated by metal complexes in compressed CO_2.[3] The reason for the few examples of photochemical reactions mediated by metal complexes in compressed CO_2 could be the poor solubility of ionic metal complexes. In the present work, we prepared rhenium-bipyridine complexes soluble in compressed CO_2 and succeeded in causing a photochemical CO_2 reduction.

Rhenium-bipyridine complexes have been known as photocatalysts for CO_2-to-CO reduction by visible-light irradiation in conventional organic solvents with amine.[4] Among them, phosphite-containing complexes such as [*fac*-$Re(bpy)(CO)_3P(OR)_3]^+$ X^- (bpy = 2,2'-bipyridine, R = C_2H_5 or *i*-C_3H_7, X = SbF_6 or PF_6) show high catalytic activities.[4c,d] However, when [*fac*-$Re(bpy)(CO)_3P(Oi\text{-}C_3H_7)_3]^+SbF_6^-$ (**$1^+SbF_6^-$**) was introduced into liquid CO_2, it was found to be insoluble, which is reflected by almost no absorption in the UV-VIS spectrum of saturated solution [Figure 1(a)].[5] We changed isopropyl groups of **$1^+SbF_6^-$** to hexyl groups because hexane has properties similar to CO_2, e.g. similar low polarity, comparable density and a weak solvating ability. Although the complex [*fac*-$Re(bpy)(CO)_3P(OC_6H_{13})_3]^+$ SbF_6^- (**$2^+SbF_6^-$**) showed a somewhat higher solubility,[6] the absorption at visible to near-ultraviolet region was still negligible [Figure 1(b)]. Recently, it has been reported that the fluorine substitution on organometallic catalysts enhances their solubility in compressed CO_2.[7] We therefore changed the counter anion SbF_6^- to tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($BArF^-$).[8] The complex **1^+BArF^-** gave rise to higher solubility, estimated to be 7.2×10^{-6} mol dm^{-3} [Figure 1(c)].[9] Finally, the substitution of both the phosphite ligand and the counter anion created a much CO_2-soluble complex **2^+BArF^-**,[10] having a maximum solubility of 2.5×10^{-5} mol dm^{-3} [Figure 1(d)]. The UV-VIS spectrum of **2^+BArF^-** clearly shows the triplet metal-to-ligand charge transfer (^{3}MLCT) absorption band around 340 nm, similar to other rhenium-bipyridine complexes in conventional organic solvents.[4b-d,11] It also shows corresponding emission at maximum wavelength of 520 nm with lifetime of 395 ns in liquid CO_2 (T = 26 °C, P = 7.6 MPa, ρ = 0.73 g cm^{-3}). The photochemical CO_2 reduction system using rhenium complexes requires an amine such as Et_3N to quench the ^{3}MLCT state.[4] The addition of Et_3N increased the maximum solubility of **2^+BArF^-** in liquid CO_2 to 4.4×10^{-5} mol dm^{-3} (T = 28 °C, P = 7.0 MPa, ρ = 0.70 g cm^{-3}, $[Et_3N]$ = 0.42 mol dm^{-3}, molar ratio of CO_2 / Et_3N = 36 / 1).

Figure 2 shows the UV-VIS spectral changes of the liquid CO_2 containing **2^+BArF^-** and Et_3N under 365 nm irradiation.[12] After irradiation started, absorption maxima around 400 and

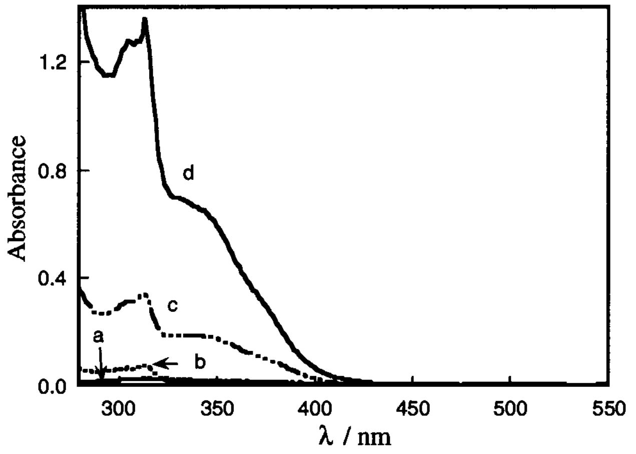

Figure 1. UV-VIS spectra of (a) **$1^+SbF_6^-$**, (b) **$2^+SbF_6^-$**, (c) **1^+BArF^-**, and (d) **2^+BArF^-** in liquid CO_2 (T = 26 °C, P = 7.9 MPa, ρ = 0.75 g cm^{-3}).

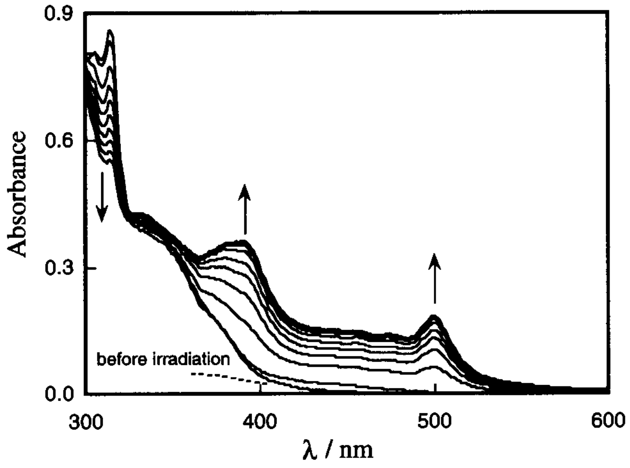

Figure 2. UV-VIS spectral changes of the liquid CO_2 (T = 28 °C, P = 7.0 MPa, ρ = 0.70 g cm^{-3}) containing **2^+BArF^-** (1.4×10^{-5} mol dm^{-3}) and Et_3N (0.42 mol dm^{-3}) under 365 nm irradiation. Light intensity was 2.44×10^{-9} einstein s^{-1} (1 einstein = 6.022×10^{23} photons). Time interval was 120 s.

500 nm appeared. This feature is very similar to that observed in the organic solvent-amine mixtures of other rhenium-bipyridine complexes under irradiation,[4c,d] and the new absorption bands that grow during irradiation are attributed to the one-electron reduced complex [*fac*-Re(bpy•$^-$)(CO)$_3$P(OC$_6$H$_{13}$)$_3$]. The one-electron reduced rhenium complexes are recognized as key precursors for the photochemical CO$_2$ reduction in conventional organic solvent.[4,11] Therefore this accumulation suggests the ability of **2**$^+$**BArF**$^-$to cause photochemical CO$_2$ reduction in liquid CO$_2$.

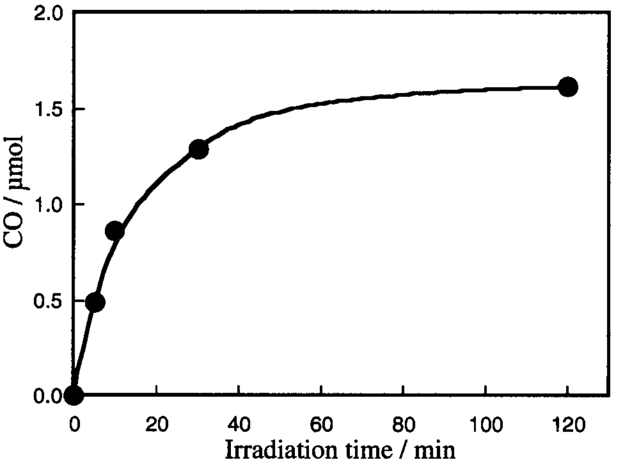

Figure 3. Irradiation-time dependence of CO formation using **2**$^+$**BArF**$^-$(4.4 × 10^{-5} mol dm^{-3}) and Et$_3$N (0.42 mol dm^{-3}) in liquid CO$_2$ (T = 28 °C, P = 7.0 MPa, ρ = 0.70 g cm^{-3}). Irradiation wavelength was 365 nm and the light intensity was 6.85 × 10^{-8} einstein s^{-1}.

Figure 3 shows the dependence of CO formation on irradiation time using **2**$^+$**BArF**$^-$ and Et$_3$N in liquid CO$_2$.[13] As expected, CO was formed and the final amount was 1.61 × 10^{-6} mol (turnover number = 2.2). In the control experiment with argon-saturated DMF, no CO was formed. This indicates that the origin of CO is CO$_2$, rather than the decomposition of **2**$^+$**BArF**$^-$. On the other hand, when insoluble **1**$^+$**SbF**$_6$$^-$ was used under the same reaction conditions, no CO was formed even after a 19-h irradiation. Therefore, it is obvious that the complex must be soluble in liquid CO$_2$ to cause the CO formation.

In summary, we have demonstrated that the CO$_2$-soluble rhenium complex **2**$^+$**BArF**$^-$ causes photochemical CO$_2$ reduction in compressed CO$_2$.

References and Notes

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5 UV-VIS spectra were collected in a high-pressure cell equipped with sapphire windows (cell volume = 17 cm^3, optical path length = 4 cm). This cell was the same as that used for the photochemical experiments. Using a pump, the cell was filled with a weighed amount of CO$_2$ (11.4 – 12.3 g) to adjust the desired pressure and density.

6 The preparation method of **2**$^+$**SbF**$_6$$^-$ was similar to that of **1**$^+$**SbF**$_6$$^-$ [H. Hori, K. Koike, M. Ishizuka, K. Takeuchi, T. Ibusuki, and O. Ishitani, *J. Organomet. Chem.*, **530**, 169 (1997)], except that P(OC$_6$H$_{13}$)$_3$ was used as a reactant and CH$_2$Cl$_2$ / pentane were used as recrystallization solvents.

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8 The anion substitution was carried out by mixing the MeOH solution of SbF$_6^-$ salt and saturated MeOH solution of NaBArF·2H$_2$O, followed by crystallization with water.

9 The saturation concentrations were estimated from the Lambert-Beer equation by using the extinction coefficients measured at low complex concentrations, wherein the complex is completely soluble in liquid CO$_2$. The extinction coefficients in liquid CO$_2$ were similar to those in CH$_2$Cl$_2$, as shown in the Note 10.

10 Analytical data of **2**$^+$**BArF**$^-$: Found: C, 46.50; H, 3.47; N, 1.41%. Calcd for C$_{63}$H$_{59}$O$_6$N$_2$PBF$_{24}$Re C, 46.59; H, 3.66; N, 1.72%. UV-VIS: λ_{max} (liquid CO$_2$ at T = 26 °C, P = 7.9 MPa, ρ = 0.75 g cm^{-3}) / nm (ε / dm^{3}mol^{-1}cm^{-1}) 305 (12700), 314 (13900), 340 (6700); λ_{max} (CH$_2$Cl$_2$) / nm (ε / dm^{3}mol^{-1}cm^{-1}) 307 (11700), 316 (13500), 347 (4600).

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12 A high pressure Hg lamp (500 W) with a band pass filter (365 nm) was used to produce the monochromatic light.

13 Amount of CO was measured by a gas chromatograph with a methanizer (Ni catalyst, 400 °C) and a flame ionization detector.