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Kinetic study on CO$_2$ photoreduction by Re complexes

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Abstract. The photoreduction of CO$_2$ using Re(btp)(CO)$_3$Cl (btp: bathophenanthroline) was investigated in a CO$_2$-saturated DMF-triethanolamine solution. CO formation was observed during irradiation with 365-nm light. Meanwhile, UV-vis spectral changes suggested that Re(btp)(CO)$_3$Cl was degraded and its amount decreased during irradiation. The degradation of Re(btp)(CO)$_3$Cl could cause CO formation, and the observed CO amount was the sum of CO produced by CO$_2$ reduction and Re(btp)(CO)$_3$Cl degradation. Thus, in the present paper, we discuss how the net amount of CO produced by CO$_2$ reduction could be determined via a kinetic study during UV irradiation which considers the CO production originating from the Re(btp)(CO)$_3$Cl degradation process.

1. Introduction
The use of CO$_2$ in chemical [1-4] and biological [5-7] CO$_2$-fixation reactions has been generating great interests because increasing atmospheric CO$_2$ concentration is considered to be responsible for global warming. Recently, much attention has been focused on photochemical CO$_2$ reduction because it can both reduce CO$_2$ and produce chemicals such as CO, CH$_3$OH and CH$_4$ as fuels [8]. Rhenium (Re) complexes are well known to have the potential to act as photocatalysts that photochemically reduce CO$_2$ to CO and/or COOH in the presence of electron donors such as triethanolamine (TEOA) [8-18]. Among the Re complexes, Re(bpy)(CO)$_3$Cl (bpy = 2,2'-bipyridine) has been reported to selectively reduce CO$_2$ to CO under UV irradiation. Many researchers have focused on increasing the reaction efficiency of CO$_2$ photoreduction and investigating its reaction mechanism by substituting Cl with a certain ligand [12,14,15]. We found that the amount of CO produced by CO$_2$ reduction greatly increased when the bpy moiety was substituted with bathophenanthroline (btp). However, since Re complexes originally have CO as a ligand, elimination of the CO ligand should be considered. Thus, an analytical method for determining the net amount of CO produced by CO$_2$ reduction, which takes Re complexes degradation into consideration, is required.

In this study, we investigate the degradation of Re(btp)(CO)$_3$Cl by undertaking a kinetic study on the change in UV-vis absorption of a Re(btp)(CO)$_3$Cl solution during UV irradiation, and establish an analytical method to determine the net amount of CO produced by CO$_2$ reduction during UV irradiation, using Re(btp)(CO)$_3$Cl as a CO$_2$-reducing photocatalyst.
2. Experimental

2.1. General procedures
UV-vis absorption spectra were measured using a Shimadzu UV-2200 spectrophotometer. IR spectra were recorded using a Perkin Elmer System 2000 FT-IR spectrometer. Elemental analysis was performed using a VARIO EL III analyzer. APCI mass spectra were measured using a Waters LCT Premier XE instrument in the negative-ion mode. The CO produced by CO$_2$ photoreduction was analyzed using a Shimadzu GCMS-QP2010 Plus instrument equipped with an Rt-Molsieve 5A column ($L = 30$ m, $\phi = 0.32$ mm, $d = 30$ µm).

2.2. Photochemical CO$_2$ reduction
Photochemical CO$_2$ reduction was performed using a previously reported method [15]. Figure 1 shows the experimental set-up for photochemical CO$_2$ reduction. The reaction took place in a quartz cell (vol. = 5 mL) containing 2.0 mL of a Re(btp)(CO)$_3$Cl DMF-triethanolamine (TEOA) (5:1, v/v) solution (conc. = 0.05 mM) which was stirred at room temperature. The solution was bubbled with CO$_2$ for 2 min at a flow rate of 200 mL/min, and sealed with a silicon-Teflon septum. A mercury lamp ($\lambda = 365$ nm, $I = 614$ µW/cm$^2$) was used as a light source for the photochemical reaction. The reaction products were analyzed by GC-MS. During irradiation, the amount of residual Re(btp)(CO)$_3$Cl was determined by measuring the absorption maximum at 290 nm.

![Figure 1: Experimental set-up for photochemical CO$_2$ reduction.](image)

2.3. Materials
All solvents were of high purity and were used as received from Kanto Chemical Co. Rhenium pentacarbonyl chloride (Re(CO)$_5$Cl), 2,2′-bipyridine (bpy), and bathophenanthroline (btp) were purchased from Aldrich Chemical Co., Kanto Chemical Co., and Tokyo Chemical Industry Co., respectively. All reagents were used without further purification.

2.4. Synthesis
Re(btp)(CO)$_3$Cl was synthesized as follows using a previously reported method [19] with some modifications. A solution of btp (249 mg, 0.75 mmol) in 100 mL of toluene was added to a solution of Re(CO)$_5$Cl (271 mg, 0.75 mmol) in 150 mL of toluene at 110 °C. The mixture was kept at 110 °C and stirred vigorously for 4 h until the solution became a brown-orange color. The solvent was then evaporated in vacuum, and the brown-orange compound was isolated by column chromatography (H = 400 mm, $\phi = 25$ mm) on silica using ethyl acetate as an eluent. After the solvent had been removed, the solid product was recrystallized from acetone-hexane. Yield: 65.0 mg (13.3%) Anal. Calcd for C$_{27}$H$_{16}$ClN$_2$O$_3$Re: C, 50.8; H, 2.5; N, 4.4; O, 7.5. Found: C, 51.1; H, 3.1; N, 3.9; O, 9.1. FT-IR (v$_{CO}$/cm$^{-1}$): 2022, 1920, 1897 in CH$_2$Cl$_2$. UV-Vis ($\varepsilon_{\text{max}}$/nm (ε/M·cm$^{-1}$) : 284 (18880) in MeOH. APCI-MS (m/z): 638.0 (M) in MeOH.
3. Results and discussion

3.1. CO formation in the reaction cell

CO was formed when Re(btp)(CO)$_3$Cl in the CO$_2$-saturated DMF-TEOA solution was irradiated with 365-nm light, as shown in figure 2. CO formation increased linearly for about 60 min, and then the CO amount reached the saturation point at about 120 min. Since the observed CO might include CO from the degradation of Re(btp)(CO)$_3$Cl, the CO production will be discussed in detail in the following section by employing a kinetic study.

![Figure 2. CO formation observed in a reaction cell during 365-nm light irradiation.](image)

3.2. Determination of the degradation rate constant ($k_d$) of Re(btp)(CO)$_3$Cl

We measured the in-situ UV-vis absorption spectra of Re(btp)(CO)$_3$Cl in the CO$_2$-saturated DMF-TEOA solution during the photochemical reaction by irradiation with 365-nm-light. "o" in figure 3 show the absorbance at 290 nm, which was attributed to the $\pi$-$\pi^*$ transition peak of the btp moiety of Re(btp)(CO)$_3$Cl. The absorbance intensity at 290 nm decreased during light irradiation, and further irradiation did not cause spectral changes. After removal of the light source, Re(btp)(CO)$_3$Cl retained its absorption intensity for more than 24 h. This results suggested that light irradiation induced Re(btp)(CO)$_3$Cl degradation. The amount of CO observed might include CO produced from Re(btp)(CO)$_3$Cl degradation. Therefore, we calculated the net amount of CO produced from CO$_2$ reduction by considering the CO production from Re(btp)(CO)$_3$Cl degradation using kinetic analysis. We assumed that this degradation involved CO-ligand elimination. We present the following reaction equation (1) for the degradation of Re(btp)(CO)$_3$Cl, with the assumption that the degradation proceeded by a first order reaction, and that the degradation of 1 mol of Re complexes produced 3 mol of CO, which was originally included as a ligand of Re(btp)(CO)$_3$Cl:

$$\text{Re(btp)(CO)}_3\text{Cl} \xrightarrow{k_d} \text{Re'} + 3\text{CO}, \quad (1)$$

where $k_d$ is the degradation rate constant, and Re’ represents a specific compound formed via the degradation. According to equation (1), the rate equation can be described by:

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Integration between the respective limits of \([\text{Re(btp)(CO)}_3\text{Cl}]_{t=0}, [\text{Re(btp)(CO)}_3\text{Cl}]_{t=\tau-1}\), and \([0, t]\) gives:

\[
[\text{Re(btp)(CO)}_3\text{Cl}] = [\text{Re(btp)(CO)}_3\text{Cl}]_{t=0} \times \exp(-k_d t),
\]

where \([\text{Re(btp)(CO)}_3\text{Cl}]_{t=0}\) and \([\text{Re(btp)(CO)}_3\text{Cl}]_{t=\tau-1}\) represent the \(\text{Re(btp)(CO)}_3\text{Cl}\) concentrations at an arbitrary time and at \(t = 0\), respectively. In the same way, the concentration of \(\text{Re}'\) is represented by:

\[
[\text{Re'}] = [\text{Re'}]_{t=\infty} \times \{1 - \exp(-k_d t)\},
\]

where \([\text{Re'}]_{t=\infty}\) and \([\text{Re'}]_{t=0}\) represent the \(\text{Re}'\) concentrations at an arbitrary time and at \(t = \infty\), respectively.

Therefore, using the Lambert-Beer law to convert concentration to absorbance, the experimental value of the absorption intensity at 290 nm (Abs.) can be represented by the sum of the decrease in the \(\text{Re(bpy)(CO)}_3\text{Cl}\) absorbance and the increase in the \(\text{Re}'\) absorbance by converting concentration to absorbance using the Lambert-Beer law as the following:

\[
\text{Abs.}_t = \varepsilon_1 \times [\text{Re(bpy)(CO)}_3\text{Cl}]_{t=0} \times \exp(-k_d t) + \varepsilon_2 \times [\text{Re'}]_{t=\infty} \times \{1 - \exp(-k_d t)\},
\]

where \(t\) represents the light irradiation time (the time for attaching a light source is defined as \(t = 0\)), Abs.\(_t\) is the observed absorbance at 290 nm at \(t\), and \(\varepsilon_1\) and \(\varepsilon_2\) are the molar adsorption coefficients at 290 nm for \(\text{Re(bpy)(CO)}_3\text{Cl}\) and \(\text{Re}'\), respectively (\(\varepsilon_1 = 36000 \text{M}^{-1}\text{cm}^{-1}\) and \(\varepsilon_2 = 16400 \text{M}^{-1}\text{cm}^{-1}\)). In figure 3, the experimental values of the absorbance at 290 nm, represented by “\(o\)”, could be well fitted to a bi-exponential function (equation (5)), as shown by the curve. The degradation rate constant \((k_d)\) is obtained as:

\[
k_d = 7.12 \times 10^{-4} \text{ s}^{-1}.
\]

The theoretical absorbance values at 290 nm for \(\text{Re(btp)(CO)}_3\text{Cl}\) and \(\text{Re}'\), which were calculated using equation (5), are also plotted in figure 3. It is clear that the amount of \(\text{Re(btp)(CO)}_3\text{Cl}\) decreased with increasing amount of \(\text{Re}'\), followed by complete degradation of \(\text{Re(btp)(CO)}_3\text{Cl}\).

The total observed CO formation (1.10 \(\mu\)mol) was sufficiently greater than the original amount of CO as ligands of \(\text{Re(btp)(CO)}_3\text{Cl}\) (0.30 \(\mu\)mol). Thus, it is considered that the CO formation originated from both the \(\text{Re(btp)(CO)}_3\text{Cl}\) degradation and CO\(_2\) reduction. The inset of figure 4 summarizes the two different routes of CO formation. Under 365-nm light irradiation, \(\text{Re(btp)(CO)}_3\text{Cl}\) could act as a photocatalyst to reduce CO\(_2\) to CO. On the other hand, light irradiation could also induce the degradation of \(\text{Re(btp)(CO)}_3\text{Cl}\) and adsorption of CO ligands.

Regarding CO produced by \(\text{Re(btp)(CO)}_3\text{Cl}\) degradation, the following equation could be derived:

\[
[\text{CO}]_t = 3 \times [\text{CO}]_{t=\infty} \times \{1 - \exp(-k_d t)\}.
\]

In equation (7), the value of \(3 \times [\text{CO}]_{t=\infty}\) corresponds to the total concentration of CO produced by \(\text{Re(btp)(CO)}_3\text{Cl}\) degradation.
Figure 3. Absorbance at 290 nm for Re(btp)(CO)$_3$Cl in the DMF-TEOA solution during 365-nm light irradiation. (○: experimental value, Δ: absorbance of Re', □: absorbance of Re(btp)(CO)$_3$Cl, -: fitting function)

Figure 4. Amount of CO$_{red}$ and Re(btp)(CO)$_3$Cl vs. irradiation time plots (◊: amount of CO$_{red}$, ♦: amount of Re(btp)(CO)$_3$Cl, -: fitting function). The inset figure is a schematic illustration for CO formation through two different routes under 365-nm light irradiation.

3.3. Determination of the net amount of CO produced by CO$_2$ reduction
Taking the above discussion into consideration, if we assume that the CO$_2$ reduction equation is simply represented by equation (8), then the rate equation of CO formation can be described as equation (9):
where $k_{\text{red}}$ is the rate constant for CO$_2$-to-CO reduction, $\text{CO}_{\text{red}}$ is CO produced by CO$_2$ reduction, and $a$ is a constant when CO$_2$ concentration, $[\text{CO}_2]$, could be considered to be constant. Integration between the limits $\{[\text{CO}_{\text{red}}]_{t=0}, [\text{CO}_{\text{red}}]_{t}\}$ and $[0, t]$ gives the equation for the $\text{CO}_{\text{red}}$ concentration, $[\text{CO}_{\text{red}}]$, at any time, $t$: 

$$[\text{CO}_{\text{red}}]_{t} = [\text{CO}_{\text{red}}]_{t=\infty} \times \{1 - \exp(-k_{\text{red}}t)\},$$

where $[\text{CO}_{\text{red}}]_{t=\infty}$ corresponds to the total amount of CO$_{\text{red}}$ produced. We calculated the amount of CO produced by Re(btp)(CO)$_3$Cl degradation using equations (6) and (7), and determined the amount of CO$_{\text{red}}$ by subtracting the amount of CO produced by Re(btp)(CO)$_3$Cl degradation from the experimental values for CO generation in the reaction cell at an arbitrary irradiation time. The results are plotted as a function of irradiation time in figure 4. These plots fit well to a mono-exponential function based on equation (10), and the following rate constant ($k_{\text{red}}$) and the total amount of CO$_{\text{red}}$ produced ($\text{CO}_{\text{red},t=\infty}$) were obtained as the fit parameters:

$$k_{\text{red}} = 4.20 \times 10^{-4} \text{ s}^{-1},$$

$$\text{CO}_{\text{red},t=\infty} = 8.73 \times 10^{-1} \pm 3.93 \times 10^{-6} \mu\text{mol}.$$

The calculated amount of Re(btp)(CO)$_3$Cl using equation (3) is also plotted in figure 4, represented by “♦”. It is clear that CO formation reaches the saturation point with decreasing amount of Re(btp)(CO)$_3$Cl, depending on the irradiation time.

We determined the efficiency of the CO$_{\text{red}}$ production on Re(btp)(CO)$_3$Cl to be 8.73 mol/cathmol⋅2h, which was calculated by dividing $\text{CO}_{\text{red},t=\infty}$ by the initial amount of Re(btp)(CO)$_3$Cl in the reaction solution. We took the degradation process of Re(btp)(CO)$_3$Cl into consideration, and improved the calculation accuracy of CO$_{\text{red}}$. If the degradation process could be suppressed such as by optimization of the light intensity and irradiation wavelength, Re(btp)(CO)$_3$Cl has the potential to be applied to possible CO$_2$ utilization systems.

### 4. Conclusions

CO$_2$ photoreduction was examined using Re(btp)(CO)$_3$Cl as a photocatalyst. The observed CO was found to be produced by both Re(btp)(CO)$_3$Cl degradation and CO$_2$ reduction. Assuming that the degradation involved CO-ligand elimination, we determined the net amount of CO produced by CO$_2$ reduction in a kinetic study by subtracting the CO produced by Re(btp)(CO)$_3$Cl degradation from the CO observed in the reaction cell at an arbitrary irradiation time. We improved the calculation accuracy of CO amount produced by CO$_2$ photoreduction. The CO production capacity resulting from CO$_2$ reduction using Re(btp)(CO)$_3$Cl was found to be 8.73 mol/cathmol⋅2h.

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