Oxide Transfer Reaction from Carbonate to Metal-CO Complex, Affording Metal-η^1-CO_2 Complex and Carbon Dioxide

Hiroshi Nakajima, Kiyoshi Tsuge, and Koji Tanaka*
Institute for Molecular Science, Myodaiji, Okazaki 444

(Received January 30, 1997; CL-970077)

The unprecedented oxide transfer reaction from CO_3^{2-} to the carbonyl complex, $[Ru(bpy)_2(CO)_2]^{2+}$ in aprotic media is described. The oxide transfer proceeds via the 1:1 adduct formation, to afford $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ and CO_2.

The CO_2/CO conversion is a primary importance in the exploitation of CO_2 as C1 resources for synthesis of organic molecules.[1] Metal-carbonyl species derived from metal-CO_2 complexes are generally accepted as precursors for CO evolution in electro- and photochemical CO_2 reductions catalyzed by metal complexes.[2, 3, 4, 5] These metal-carbonyl species are generated from either an acid-base equilibrium among $[M\text{-}CO_2]^{n+}$, $[M\text{-}C(O)OH]^{(n+1)+}$, and $[M\text{-}CO]^{(n+2)+}$ (eq. 1)[2,3] or oxide transfer from $[M\text{-}CO_2]^{n+}$ to CO_2 (eq. 2).[5] The CO_2 / CO conversion of

$$[M\text{-}CO_2]^{n+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M\text{-}C(O)OH]^{(n+1)+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M\text{-}CO]^{(n+2)+} \quad (1)$$

$$[M\text{-}CO_2]^{n+} + CO_2 \longrightarrow [M\text{-}CO]^{(n+2)+} + CO_3^{2-} \quad (2)$$

eq. 1 has been successively utilized to multi-electron reduction of CO_2. The electrochemical CO_2 reduction by $[Ru(bpy)(trpy)(CO)]^{2+}$ (bpy = 2, 2'-bipyridine, trpy = 2, 2': 6, 2" -terpyridine) produces the multi-electron reduced species, such as HCHO, CH_3OH, HOOCCHO, and $HOOCCH_2OH$[6] under aqueous conditions. The oxide transfer of eq. 2 also serves catalytic formation of acetone and acetoacetic acid by double methylation of $[Ru(bpy)_2(qu)(CO)]^{2+}$ (qu = quinoline) in electrochemical CO_2 reduction in DMSO.[7] Thus, both reactions of eqs. 1 and 2 have fundamental importance in the CO_2 reduction affording not only CO but also highly reduced organic compounds.

Three complexes, $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$, $[Ru(bpy)_2(CO)(C(O)OH)]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ exist as equilibrium mixtures in H_2O [2] (eq. 1) and the molecular structures of these complexes have been determined by X-ray analysis.[8,9] The conversion between $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ and $[Ru(bpy)_2(CO)_2]^{2+}$ in aprotic conditions (eq 2) is of interest, since there is only two examples of oxide transfer from η^1-CO_2 complexes to CO_2.[5] In this study, we report the oxide transfer from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ as the first example of the reverse reaction of eq. 2, which is the key step of the reductive disproportionation of CO_2 affording CO and CO_3^{2-} in aprotic media.

An addition of $[Crown•K]_2CO_3$[10] to a CH_3CN solution of $[Ru(bpy)_2(CO)_2]^{2+}$ resulted in color change of the solution from colorless to yellow and then dark green. The ν(CO) band of $[Ru(bpy)_2(CO)_2]^{2+}$ (2091 and 2037 cm^{-1}) completely disappeared and two strong bands appeared at 1968 and 1620 cm^{-1} together with the 2342 cm^{-1} band of free CO_2 (Figure 1).

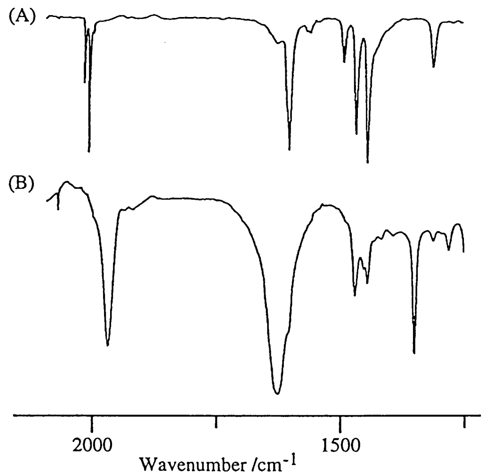


Figure 1. The IR spectra of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (A) and the reaction mixture of $[Ru(bpy)_2(CO)_2](PF_6)_2$ and $[Crown•K]_2CO_3$ (B) in CD_3CN; solvent bands are removed.

The IR spectrum of the final product indicates the formation of $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$, since 1968 cm^{-1} and 1620 cm^{-1} band is assignable to ν(CO) band and $\nu_{asym}(CO_2)$ band, respectively.[1] Moreover, $[Ru(bpy)_2(CO)_2]^{2+}$ was regenerated in an almost quantitative yield when the dark green CH_3CN solution was treated with CF_3COOH (eq. 1). These results indicate that the reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with CO_3^{2-} produces $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ and CO_2.

The same reaction occurred on the treatment of $[Ru(bpy)_2(CO)_2]^{2+}$ with $(Me_4N)_2CO_3$[11] in DMSO, in which the yellow intermediate was more clearly observed because the rate of the reaction is considerably slower than that with $[Crown•K]_2CO_3$ in CH_3CN. Figure 2 shows the time dependent electronic absorption spectra of the mixture of $[Ru(bpy)_2(CO)_2](PF_6)_2$ and $(Me_4N)_2CO_3$ in DMSO.

Right after the mixing, a weak broad band appears around 540 nm together with a stronger band at wavelength shorter than 480 nm. Then, two absorption bands at 396 and 590 nm emerge and gradually increase in the intensities with isosbestic point at 355 nm. These spectral change almost ceased in 5 min. The detection of the yellow intermediate in the initial stage of the reaction (Figure 2) indicates that $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ is formed via adduct formation (eq. 3) and subsequent CO_2 dissociation (eq. 4).

$$[Ru(bpy)_2(CO)_2]^{2+} + CO_3^{2-} \xrightarrow{k_1} [Adduct] \quad (3)$$

$$[Adduct] \xrightarrow{k_2} Ru(bpy)_2(CO)(\eta^1\text{-}CO_2) + CO_2 \quad (4)$$

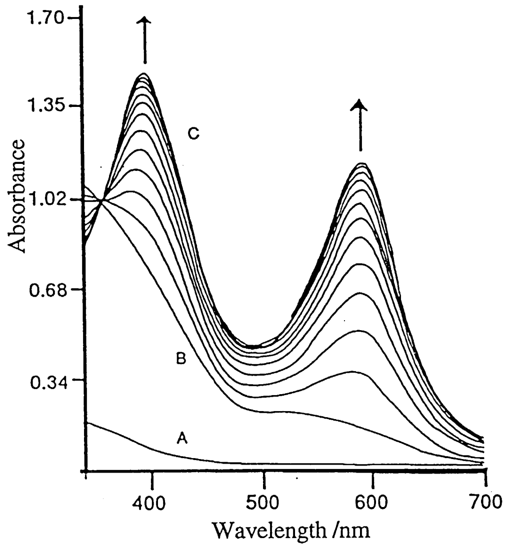
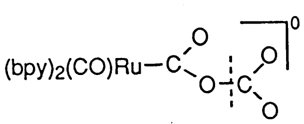


Figure 2. Time dependent electronic absorption spectra in DMSO at 25 °C: (A), $[Ru(bpy)_2(CO)_2](PF_6)_2$ (1.6 x 10^{-2} mol•l^{-1}; (B) and (C), after the addition of $(Me_4N)_2CO_3$ (4.8 x 10^{-2} mol•l^{-1}), t = 1 and 300 s, respectively.

The rates of the reactions of eqs. 3 and 4 were separately determined by monitoring the increase in the absorbance at 355 and 590 nm, respectively, under pseudo first-order reaction conditions of 10 - 50 molar excess of $(Me_4N)_2CO_3$ in DMSO.[12] The rate constant of the first step was determined by a stopped flow method. Plots of the observed rate constant against the concentration of $(Me_4N)_2CO_3$ gave a straight line with the zero intercept, suggesting that the contribution of the backward reaction of eq. 3 is negligible. The rate constant of the first step (k_1) is 3.5 x 10^2 mol^{-1}•l•s^{-1} (25 °C). Under pseudo-first order reaction conditions, the observed rate constant of the second step was essentially independent on the concentration of $(Me_4N)_2CO_3$, and the rate constant of the second step (k_2) is determined as 1.1 x 10^{-2} s^{-1} (25 °C). The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ calculated from the k_2 values at 25, 30, 35 and 40 °C were 1.3 x 10^5 J•mol^{-1} and +1.8 x 10^2 J•K^{-1}•mol^{-1}, respectively. The large difference in k_1 and k_2 is explained by a smooth nucleophilic attack of CO_3^{2-} to a carbonyl carbon of $[Ru(bpy)_2(CO)_2]^{2+}$ and slow dissociation of CO_2 from the RuC(O)O-CO_2 moiety. The relatively large $\Delta S^{\neq}$ value in the latter also reflects the RuC(O)O-CO_2 bond breaking in the rate determining step (eq. 4 and scheme 1).



Scheme 1.

Preparation of metal-η^1-CO_2 complexes are usually conducted under strict exclusion of oxygen and water at low temperature, since the metal-η^1-CO_2 complexes are thermally unstable and easily oxidized. Cooper et. al., have reported that thermally labile η^1-CO_2 complexes, $[W(CO)_5(\eta^1\text{-}CO_2)]^{2-}$ and $[CpFe(CO)_2(\eta^1\text{-}CO_2)]^-$, smoothly react with CO_2 produce CO_3^{2-} and $[W(CO)_6]$, and $[CpFe(CO)_3]^+$, respectively (eq. 2).[5] On the other hand, the ruthenium-η^1-CO_2 complex, $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ is as stable as the carbonyl complex, $[Ru(bpy)_2(CO)_2]^{2+}$ since both complexes are smoothly converted into each other in aqueous solution (eq 1).[2] Moreover, $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ spontaneously forms from $[Ru(bpy)_2(CO)_2]^{2+}$ in aprotic media (eqs. 3 and 4), as described above. This oxide transfer reaction is the first example of the reverse oxide transfer reaction of eq. 2, which should be correlated with the stability and less basicity of $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$. In the case of tungsten and iron complex, the highly basic η^1-CO_2 ligand gives its oxide ion to CO_2. However, the basicity of $Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)$ seems to be weaker than CO_3^{2-}, since the pK_a value of $[Ru(bpy)_2(CO)(COOH)]^+$ (9.5)[2] is less than that of HCO_3^- (10.3)[13] in aqueous solution. Since the basicity of the metal-η^1-CO_2 and CO_3^{2-} can be regarded as reflecting their oxide donating ability, the difference of the basicity between metal-η^1-CO_2 and CO_3^{2-} is likely to control the direction of the oxide transfer reaction.

References and Notes

1 *Chemical Fixation of Carbon Dioxide*, ed by M. M. Halmann, CRC Press, London(1993), and References therein.
2 H. Ishida, F. Katsuyuko, T. Ohba, K. Ohkubo, T. Tanaka, T. Terada, and K. Tanaka, *J. Chem. Soc., Dalton Trans.*, **1990**, 2115; H. Ishida, K. Tanaka, M. Morimoto, and T. Tanaka, *Organometallics*, **5**, 725(1986).
3 H. Ishida, T. Terada, K. Tanaka, and T. Tanaka, *Inorg. Chem.*, **29**, 905(1990).
4 *Electrochemical and Electrocatalytic reduction of Carbon Dioxide,* ed by B. P. Sullivan, Elsevier, Amsterdam(1993), p 58.
5 G. R. Lee, J. H. Maher, and N. J. Cooper, *J. Am. Chem. Soc.*, **109**, 2956(1987); G. R. Lee and N. J. Cooper, *Organometallics*, **4**, 794(1985).
6 H. Nagao, T. Mizukawa, and K. Tanaka, *Inorg. Chem.*, **33**, 3415(1994).
7 H. Nakajima, T. Mizukawa, H. Nagao, and K. Tanaka, *Chem. Lett.*, **1995**, 251.
8 H. Tanaka, B.-C. Tzeng, H. Nagao, S.-M. Peng, and K. Tanaka, *Inorg. Chem.*, **32**, 1508(1993).
9 K. Toyohara, H. Nagao, T. Adachi, T. Yoshida, and K. Tanaka, *Chem. Lett.*, **1996**, 27.
10 The oxide transfer reaction from CO_3^{2-} to $[Ru(bpy)_2CO)_2]^{2+}$ in CH_3CN was conducted by using $[Crown•K]_2(CO_3)$ to solubilize CO_3^{2-} in the solvent.
11 The reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with $(Me_4N)_2CO_3$ was conducted in DMSO since the $(Me_4N)_2CO_3$ was not soluble to CH_3CN.
12 Solubility of $[Crown•K]_2CO_3$ is not enough to measure the reaction rate in CH_3CN under pseudo-first conditions.
13 D. M. Kern, *J. Chem. Educ.* , **37**, 14(1960).