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THE WATER GAS SHIFT REACTION CATALYZED BY RUTHENIUM CARBONYL COMPLEXES

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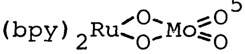
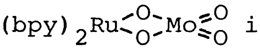
A new preparative method of $[Ru(bpy)_2(CO)Cl]^+$ (bpy = 2,2'-bipyridine) and the water gas shift reaction (WGSR) catalyzed by this complex are described. A cyclic mechanism for the WGSR is proposed to proceed *via* $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)(COOH)]^+$, and $[Ru(bpy)_2(CO)H]^+$ as intermediates successively; the former two were isolated.

Since the water gas shift reaction (WGSR); $CO + H_2O \longrightarrow H_2 + CO_2$, had been found more than 70 years ago, commercial methods for the reaction have been carried out under high pressures and high temperatures by using metal oxides as heterogeneous catalysts.[1)] Recently, much attention has been paid to transition metal complexes as homogeneous catalysts for the WGSR under mild conditions.[2-4)] This letter reports a new synthetic method of $[Ru(bpy)_2(CO)Cl]^+$ (bpy = 2,2'-bipyridine) and the WGSR by using it in an alkaline condition.

An ethylene glycol (20 cm^3) solution of $Ru(bpy)_2Cl_2$ (0.26 mmol) was refluxed in the presence of a catalytic amount of  $(bpy)_2Ru{<}^{O}_{O}{>}Mo{\leqq}^{O}_{O}$[5)] (0.02 mmol) for 6 h and evaporated to about a half volume *in vacuo*, followed by the addition of water (30 cm^3). The resulting solution was filtered and the filtrate was treated with NH_4PF_6 (1.2 mmol) to give a precipitate, which was chromatographed on alkaline alumina using CH_3CN/C_6H_6 (1:1 v/v) as an eluent and recrystallized from CH_3CN/C_6H_6, giving yellow prisms of $[Ru(bpy)_2(CO)Cl]PF_6$ in a 70% yield. This compound was prepared also by heating $Ru(bpy)_2Cl_2$ with a catalytic amount of  $(bpy)_2Ru{<}^{O}_{O}{>}Mo{\leqq}^{O}_{O}$ in $EtOH/H_2O$ (1:1 v/v) at 180°C for 40 h in a sealed tube, followed by the addition of NH_4PF_6, while the chloride salt $[Ru(bpy)_2(CO)Cl]Cl$ was obtained previously in a 40% yield by the prolonged reflux (7 d) of a dimethylformamide solution containing $RuCl_3$ and bpy.[6)]

Recently, $[Ru(bpy)_2(CO)Cl]^+$ has been shown to catalyze the WGSR under mild conditions (1 - 3 atm CO, 100 - 160°C) irradiated with white light.[7)] We have found, however, that $[Ru(bpy)_2(CO)Cl]^+$ is still active as a catalyst precursor for the WGSR without irradiation. Table 1 summarizes the results of the WGSR in the presence of $[Ru(bpy)_2(CO)Cl]^+$ in an aqueous alkaline medium. The turnover number of H_2 produced for 20 h is 112 under the pressure of 5 kg/cm^2 CO at 150°C, and attains 502 under 20 kg/cm^2 CO. The reaction temperature also has a remarkable

Table 1. The water gas shift reaction in an alkaline medium, 3.2 mmol KOH in 15 cm^3 H_2O

Catalyst[a)]	Temp	CO	Gaseous Product[b)]	
	°C	kg/cm^2	H_2	CO_2
$[Ru(bpy)_2(CO)Cl]^+$	150	5	112	46
$[Ru(bpy)_2(CO)Cl]^+$	150	10	197	75
$[Ru(bpy)_2(CO)Cl]^+$	150	20	502	203
$[Ru(bpy)_2(CO)Cl]^+$	100	10	106	62
$[Ru(bpy)_2(CO)_2]^{2+}$	150	10	198	75

a) PF_6 salt, 0.05 mmol. b) Mol / (Catalyst mol 20 h).

effect on the H_2 formation; the amount of H_2 obtained at 150°C is about 2 times larger than at 100°C. The discrepancy between the amounts of H_2 and CO_2 produced in the gaseous phase comes from not only the higher solubility of CO_2 than H_2 but also the formation of carbonate ions in alkaline media, as pointed out previously.8) In fact, the amount of CO_2 dissolved in the final solution of the WGSR was determined as 20 - 30 wt.% of that in the gaseous phase by the gas chromatography. On the other hand, the WGSR in water without KOH scarcely proceeded, and a known compound $[Ru(bpy)_2(CO)_2](PF_6)_2$6) was isolated in a 70% yield by the addition of excess NH_4PF_6 to a colorless solution obtained after heated $[Ru(bpy)_2(CO)Cl]^+$ in water under 10 kg/cm^2 CO at 150°C for 20 h. The WGSR by using $[Ru(bpy)_2(CO)_2]^{2+}$ was thus conducted in aqueous KOH solutions. The result shows that the amount of H_2 produced is almost identical with the case of $[Ru(bpy)_2(CO)Cl]^+$ under the same condition (Table), suggesting that the WGSR is catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$.

A colorless aqueous solution of $[Ru(bpy)_2(CO)_2]^{2+}$ rapidly changes to a yellow one on addition of aqueous KOH and the solution changes from yellow to colorless on reacidification reversibly. The electronic spectra of an aqueous solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ at various pH is depicted in Fig. 1, which shows no absorption in the visible region in neutral and acidic media. In alkaline solutions, however, there appears a weak shoulder around 400 nm, which is obscured by an absorption around 430 nm newly appeared over pH 9.0. The intensity of the 430 nm band increases with increasing the pH value and reaches a maximum around pH 12.0. These results indicate that two equilibrium reactions exist in alkaline solutions. In addition, slow evaporation of an aqueous solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ at pH 9.5 ± 0.5 under reduced pressures yielded a novel9) $[Ru(bpy)_2(CO)(COOH)](PF_6)$ (100°C > decomp. $\nu(O\text{-}H)$ 3070 cm^{-1}, $\nu(C\equiv O)$ 1960 cm^{-1}, $\nu(C=O)$ 1605 cm^{-1}, and $\nu(C\text{-}O)$ 1140 cm^{-1}) as a precipitate. Thus, the equilibrium reactions may be expressed as Eqs. 1 and 2. The equilibrium constants of Eqs. 1 and 2, K_1 and K_2, obtained by the potentiometric method are 1.32×10^5 and 2.27×10^4 $mol^{-1}dm^3$, respectively. The reaction rate constant of Eq. 110) was obtained by monitoring the rise of the absorbance at 440 nm under the pseudo-first-order condition with at least a 5-fold

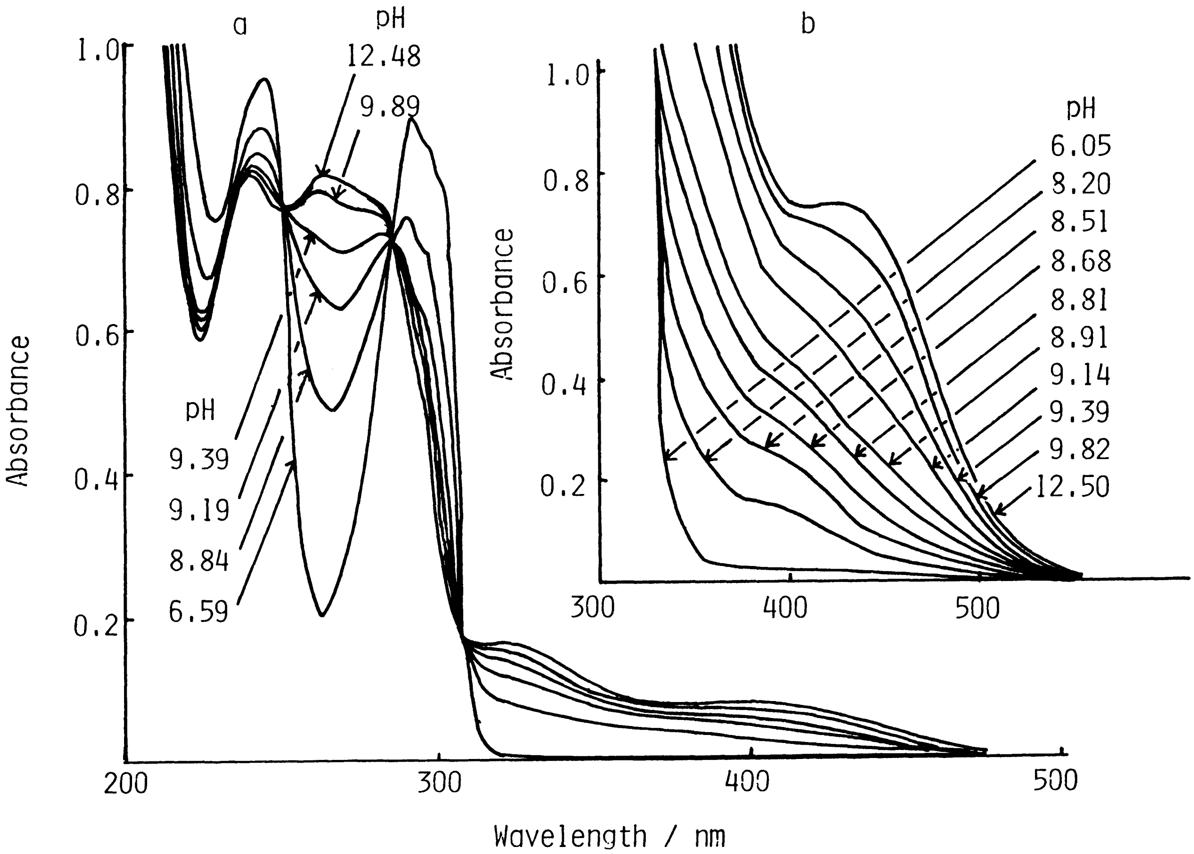


Fig. 1. Electronic spectra of $[Ru(bpy)_2(CO)_2](PF_6)_2$ ((a) 2.84×10^{-5} mol dm^{-3} and (b) 2.84×10^{-4} mol dm^{-3}) in H_2O at various pH.

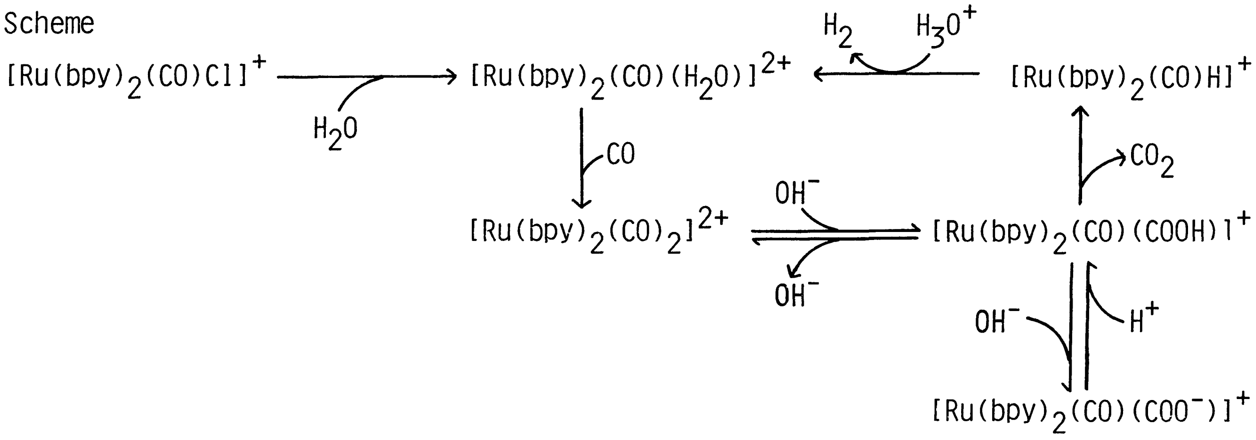
$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Ru(bpy)_2(CO)(COOH)]^+ \qquad (1)$$

$$[Ru(bpy)_2(CO)(COOH)]^+ + OH^- \overset{K_2}{\rightleftharpoons} [Ru(bpy)_2(CO)(COO^-)]^+ + H_2O \qquad (2)$$

excess amount of NaOH at 25°C. The plot of k_{obsd} *vs.* the concentration of NaOH yielded a straight line with an intercept being close to zero, suggesting that the rate constant of the backward reaction is very small. The rate constant of the forward reaction in Eq. 1 (k_1) is 2.3×10^4 s^{-1}mol^{-1}dm^3, and that of the backward reaction (k_{-1}) calculated from K_1 and k_1 is 0.17 s^{-1}.

In conclusion, a possible mechanism for the present WGSR is presented in Scheme; $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ resulting from solvolysis of $[Ru(bpy)_2(CO)Cl]^+$ in H_2O undergoes a substitution reaction by CO under pressures to afford $[Ru(bpy)_2(CO)_2]^{2+}$, followed by the nucleophilic attack of OH^- on one of coordinated CO, giving $[Ru(bpy)_2(CO)(COOH)]^+$, as described above. Although no direct evidence for the generation of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ from $[Ru(bpy)_2(CO)(COOH)]^+$ *via* $[Ru(bpy)_2(CO)H]^+$ has been obtained,11) β-hydrogen elimination of the hydrocarboxyl complexes giving metal-hydrides and CO_2 are generally accepted in the homogeneous WGSR.4) Moreover, the photo-assisted WGSR catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ has been proposed to afford $[Ru(bpy)_2ClH]$ thermally *via* the hydrocarboxyl complex $[Ru(bpy)_2Cl(COOH)]$ as an intermediate.7) Thus, $[Ru(bpy)_2(CO)H]^+$ formed in the present reaction would

Scheme



react with H_3O^+ to evolve H_2 with regenerating $[Ru(bpy)_2(CO)(H_2O)]^{2+}$.[12)]

References

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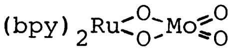
2) C. H. Cheng, D. E. Hendriksen, and R. Eisenherg, *J. Am. Chem. Soc.*, 99, 2791 (1977).
3) C. Ungermann, V. Landis, S. A. Moya, H. Cohen, M. Walker, R. G. Pearson, R. G. Rinken, and P. C. Ford, *J. Am. Chem. Soc.*, 101, 5922 (1979).
4) T. Yoshida, T. Okano, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, 103, 3411 (1981) and refs. therein.
5) An $EtOH/H_2O$ (1:1 v/v, 50 cm^3) solution containing $Ru(bpy)_2Cl_2$ (0.81 mmol) and Na_2MoO_4 (0.82 mmol) was heated at 120°C for 18 h in a sealed tube to afford a black precipitate of  $(bpy)_2Ru\overset{O}{\underset{O}{\lessgtr}}Mo\overset{O}{\underset{O}{\lessgtr}}$ in a 50% yield.
6) D. Choudhury, R. F. Jones, G. Smith, and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1982, 1143.
7) D. Choudhury and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1982, 1885.
8) A. D. King Jr., R. B. King, and D. B. Yang, *J. Am. Chem. Soc.*, 102, 1028 (1980).
9) Only three hydrocarboxyl transition metal complexes with metal to carbon bonds have been isolated so far; M. Cattelani and J. Halpern, *Inorg. Chem.*, 19, 556 (1980) for $PtCl(COOH)(PEt_3)$, A. J. Deeming and B. L. Shaw, *J. Chem. Soc., A*, 1969, 443 for $IrCl_2(COOH)(PMe_2Ph)_2$, and T. G. Appleton and M. A. Bennett, *J. Organomet. Chem.*, 55, C88 (1973) for $PtR(COOH)(Ph_2PCH_2CH_2PPh_2)$ ($R = CH_3$, C_6H_9).
10) The reaction of Eq. 2 is too fast to follow since the rate may be diffusion controlled.
11) Several attempts to obtain $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ by heating (100 - 150°C) $[Ru(bpy)_2(CO)_2]^{2+}$ in an aqueous alkaline solution under N_2 instead of CO for 2 - 3 h has been unsuccessful, and then $[Ru(bpy)_2(CO)(COOH)]^+$ and $[Ru(bpy)_2(CO)(COO^-)]^+$ were obtained together with small amounts of the decomposition product. This result suggests that these cations are stable in N_2, though they may undergo a facile reaction under CO.
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