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Ethylene Oxide-mediated Reduction of CO₂ to CO and Ethylene Glycol catalysed by Ruthenium Complexes

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In the presence of ethylene oxide, CO₂ is efficiently hydrogenated to give CO and ethylene glycol in good yields using ruthenium complexes as homogeneous catalysts.

One of the problems with utilizing CO_2 as a chemical carbon source is how to eliminate the oxygens. Hydrogenation is an efficient method which produces the deoxygenated compounds such as CO, methanol and hydrocarbons as well as H₂O. Several kinds of heterogeneous catalysts have been used, but they usually require a reaction temperature over 200 °C. During the course of our investigations on CO₂ hydrogenation using transition-metal complexes as catalysts,¹⁻³ we have found that ruthenium cluster anions effectively catalyse the hydrogenation of CO₂ to CO (reverse water-gas shift reaction) under relatively mild conditions [140-180 °C, 100-120 atm (1 atm = 101.3 kPa).³ However, this reaction is unfavourable at lower temperatures because of its endothermicity. (Calculated thermodynamic equilibrium predicts only 8% yield of CO at 140 °C.) We now report a novel CO₂ hydrogenation effected by RuCl₂(PPh₃)₃ and tertiary amines in the presence of ethylene oxide affording CO and ethylene glycol in good yields, even under mild conditions [eqn. (1)].

$$H_{2} + CO_{2} + \bigwedge^{O} \xrightarrow{\text{RuCl}_{2}(\text{PPh}_{3})_{2}} CO + HO OH (1)$$
80 atm 30 mmol 30 mmol \bigvee^{N-Me} 71% 75%
140 °C. 15 h. NMP

This reaction is exothermic and, therefore, is expected to proceed even at lower temperatures. Indeed, a high CO₂ conversion (>80%) and CO yield (>70%) are attained in the presence of the ruthenium catalyst at a relatively low temperature (140 °C). Koinuma *et al.* previously reported the formation of glycol formates using RhCl(PPh₃)₃ without amines,⁴ however, no CO formation was reported during this reaction, indeed, we observed that RhCl(PPh₃)₃ is not effective for CO formation.

In a typical experiment, an *N*-methylpyrrolidone (NMP) solution of RuCl₂ (PPh₃)₃ (0.1 mmol) and *N*-methyl-pyrrolidine (1.0 mmol) was placed in a 50 ml autoclave. Ethylene oxide (30 mmol) and CO₂ (30 mmol) were introduced into the autoclave through an accumulated flow meter at -30 °C. After being pressurized with hydrogen at 80 atm, the autoclave was heated to 140 °C and kept at this temperature for 15 h. The resulting gas mixture was recovered with a sampling bag equipped with an accumulated flow meter and analysed with the liquid products by GLC.

When RuCl₂(PPh₃)₃ and *N*-methylpyrrolidine were used as catalysts, CO and ethylene glycol were obtained in yields of 71 and 75%, respectively; the turnover number for these products was more than 200 based on the ruthenium complex. Also formed were ethylene glycol monoformate (5%) and ethanol (3%). No epoxide or ethylene carbonate were detected, but 12% of the CO₂ was recovered.

Some typical results are summarized in Table 1. A reaction without amine gave ethylene carbonate as the main product (56%, run 1). Other tertiary amines tested gave almost the same result as *N*-methyl-pyrrolidine (runs 3-5) when used with RuCl₂(PPh₃)₃. Other ruthenium complexes proved to be slightly less effective for the formation of CO and ethylene glycol (runs 6 and 7). The corresponding complexes of rhodium (run 8), nickel, cobalt, and palladium were much less effective for this reaction.

Because ruthenium complexes have been known to decarbonylate alkyl formates at higher temperature (>180 °C),⁵ the decarboxylation of ethylene glycol monoformate is a possible pathway for the CO formation. However, the contribution of this path seems limited, since only a 7% yield of CO was achieved by the decarbonylation of ethylene glycol monoformate under our reaction conditions at 140 °C [eqn. (2)].

Another possible reaction mechanism involves the direct hydrogenation of ethylene carbonate using ruthenium complexes. This reaction path is strongly supported by the time course of this reaction (Fig. 1) which clearly indicates that ethylene carbonate formed during the early stage of the reaction is then hydrogenated to CO and ethylene glycol. When the hydrogenation of ethylene carbonate was carried out using the



Fig. 1 Time course of the CO₂ hydrogenation in the presence of ethylene oxide, RuCl₂(PPh₃)₃ and *N*-methyl-pyrrolidine. See Table 1 for other conditions. $\bullet =$ ethylene glycol, $\blacksquare =$ CO, $\blacklozenge =$ ethylene carbonate, $\blacktriangle =$ ethylene glycol monoformate.



| | | | Yield (%) ^b | | | | |
|-----|--|---------------------|------------------------|----|----|----------|----|
| Run | Complex | Base | со | ОН | он | ~0 ~0 | |
| 1 | RuCl ₂ (PPh ₃) ₃ | None | 23 | 29 | 2 | 56 | 1, |
| 2 | RuCl ₂ (PPh ₃) ₃ | N-Methylpyrrolidine | 71 | 75 | 5 | 0 | |
| 3 | $RuCl_2(PPh_3)_3$ | N-Methylpiperidine | 69 | 76 | 7 | 0 | |
| 4 | RuCl ₂ (PPh ₃) ₃ | Triethylenediamine | 64 | 72 | 12 | 1 | |
| 5 | $RuCl_2(PPh_3)_3$ | Et ₃ N | 70 | 56 | 5 | 0 | |
| 6 | RuCl ₃ ·3H ₂ O | N-Methylpyrrolidine | 66 | 58 | 4 | 0 | |
| 7 | Ru ₃ (CO) ₁₂ | N-Methylpyrrolidine | 54 | 60 | 15 | 0 | |
| 8 | RhCl(PPh ₃) ₃ | N-Methylpyrrolidine | 9 | 12 | 0 | 24 | |

Table 1 Hydrogenation of CO_2 in the presence of ethylene oxide^{*a*}

^a Complex (0.1 mmol), base (1.0 mmol), N-methylpyrrolidone (8 ml), CO₂ (30 mmol), ethylene oxide (30 mmol), H₂ (80 atm), 140 °C, 15 h. ^b Based on ethylene oxide, except for CO (based on CO₂).



same catalytic system, the corresponding yield of CO (82%) and ethylene glycol (79%) was obtained [eqn. (3)].

Therefore, we propose the following reaction mechanism as shown in Scheme 1. First, ethylene oxide reacts with CO_2 to produce ethylene carbonate in the presence of the ruthenium complex. Ethylene carbonate then adds oxidatively to the ruthenium hydride complex with cleavage of the OCO–O bond



to form a carboxylate complex. Following migration of CO, ethylene glycol is liberated. Little is known about the decarbonylation of carbonate esters by transition-metal complexes, but a similar decarbonylation of alkyl phenyl esters has been reported with a low valent nickel complex which nucleophilically attacks the carbonyl group of the esters cleaving the CO–O bonds.⁶ Since ethylene carbonate has a carbon bonded to three oxygen atoms, it should be more susceptible to nucleophilic attack. The last step is the oxidative addition of H₂ to the ruthenium carbonyl complex, regenerating the ruthenium hydride complex with liberation of CO.

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