Ruthenium Complex Catalysed Hydrogenation of Carbon Dioxide to Carbon Monoxide, Methanol and Methane

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A novel hydrogenation of carbon dioxide proceeds in the presence of a $Ru_3(CO)_{12}$–KI homogeneous catalytic system with successive formation of carbon monoxide, methanol and methane.

Hydrogenation is one of the most promising processes to convert carbon dioxide emitted through thermal power generation into raw materials for fuels and chemicals. Although a number of effective heterogeneous catalysts are known for the hydrogenation of carbon dioxide to carbon monoxide, methanol, methane *etc.*, only a few such homogenous catalysts have been reported so far.[1]

On the other hand, homogeneous Ru[2] or Ni[3] carbonyl complexes catalyse the hydrogenation of carbon monoxide to methanol, whereas using Rh[4] or Co[5] carbonyl complexes as

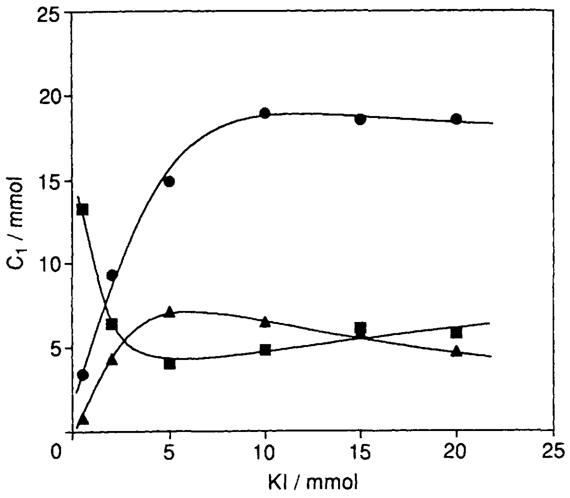

Fig. 1 Effect of the amount of KI added to the $Ru_3(CO)_{12}$–KI catalysed hydrogenation of CO_2. Solvent = NMP. See Table 1 for other conditions. ● = MeOH, ▲ = CO and ■ = CH_4 + C_2H_6

catalysts leads to the formation of methanol and other products including ethanol and ethylene glycol. Dombek reported that ethylene glycol was formed in significant yields using ruthenium catalysts with promoters such as carboxylic acids[6] or iodide anion[7] under high-reaction pressures (400–1000 atm, 1 atm = 101.3 kPa).

One of us has previously reported that the transition metal complex–base catalytic system was effective for the hydrogenation of carbon dioxide to formate derivatives under relatively mild reaction conditions (room temp.–140 °C, 50–100 atm).[8] We report here a novel hydrogenation of carbon dioxide to *methane via* carbon monoxide and methanol [eqn. (1)], which proceeds in the presence of a homogeneous $Ru_3(CO)_{12}$–KI catalytic system at a higher reaction temperature (240 °C) but under an almost equivalent pressure (90–140 atm).

$$CO_2 + H_2 \xrightarrow{Ru_3(CO)_{12}\text{–KI}} CO + MeOH + CH_4 \qquad (1)$$

In a typical experiment, an *N*-methylpyrrolidone (20 ml) solution of $Ru_3(CO)_{12}$ (0.2 mmol) and KI (10 mmol) was stirred in a 100 ml hastelloy autoclave for over 1 h and CO_2–H_2 (1 : 3) gas mixture was introduced under 80 atm at 30–32 °C. The autoclave was then heated so that its interior temperature was raised at the rate of 5 °C min^{-1} and kept at 240 °C for 3 h. The total pressure initially rose to *ca.* 140 atm but finally dropped to *ca.* 90 atm. GLC analyses of the resulting gas and solution revealed the formation of methanol (18.9 mmol or a 32 turnover number based on ruthenium atom), carbon monoxide (6.5 mmol), methane (4.7 mmol) and ethane (0.1 mmol). Water was formed in a yield of 37.2 mmol corresponding with the formation of deoxygenated products and carbon dioxide (38.1 mmol) was recovered unreacted. No significant amount of ethylene glycol was detected probably because of the low reaction pressure employed.

The addition of KI drastically suppresses the vigorous hydrogenation of carbon dioxide to hydrocarbons (methane and ethane) catalysed by the deposited ruthenium metal† as shown in Fig. 1. A gradual increase in the formation of hydrocarbons is again observed with additions of KI >10 mmol, whereas a decreases is shown in the yields of carbon monoxide and methanol. The reaction solutions have a clear red–orange colour and no deposition of ruthenium metal is observed for runs with > 5 mmol of KI. Thus, the homogeneous hydrogenation of methanol to methane may be catalysed by the ruthenium complex in the presence of an excess of KI, which is responsible for the gradual increase in the yield of hydrocarbons and the decrease in the amount of methanol.

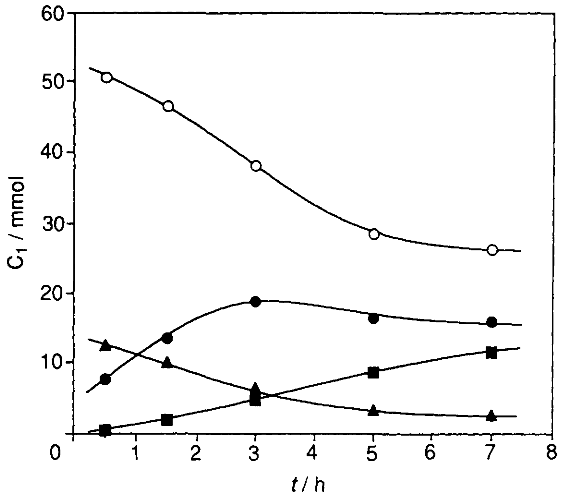

Fig. 2 Time-course of the hydrogenation of CO_2. Solvent NMP. See Table 1 for other conditions. ○ = CO_2, ● = MeOH, ▲ = CO and ■ = CH_4 + C_2H_6

Table 1 Hydrogenation of carbon dioxide with $Ru_3(CO)_{12}$ and salt[a]

Solvent[b]	Salt	Products yield/mmol CO	MeOH	CH_4	C_2H_6	CO_2 recovered/ mmol
NMP	KI	6.5	18.9	4.7	0.1	38.1
NMP	NaI	6.1	17.3	5.6	0.0	39.0
NMP	LiI	4.1	15.1	11.0	0.1	36.1
NMP	I_2[c]	5.3	0.4	15.2	0.1	43.7
NMP	ZnI_2[c]	14.5	0.8	0.7	0.0	55.3
NMP	KBr	6.4	3.7	15.6	0.3	48.3
NMP[d]	KI	6.9	28.7	10.5	0.0	44.9
DMI	KI	5.5	18.7	4.7	0.0	37.9
NEP[e]	KI	5.8	18.4	4.1	0.2	37.8

[a] $Ru_3(CO)_{12}$ (0.2 mmol), salt (10 mmol), solvent (20 ml), 80 atm (at 30–32 °C) of CO_2–H_2 (1 : 3), 240 °C, 3 h. [b] NMP = *N*-methyl-2-pyrrolidone; DMI = 1,3-dimethyl-2-imidazolidinone; NEP = *N*-ethyl-2-pyrrolidone. [c] 5 mmol. [d] Methanol (20 mmol) was initially added. [e] A small amount of ethanol (0.4 mmol) was detected which may be caused by slight hydrolysis of NEP.

The time course of the hydrogenation of carbon dioxide (Fig. 2) clearly shows the successive formations of carbon monoxide, methanol and methane. The yield of carbon monoxide reaches its maximum in the early stages of the reaction. The yield of methanol increases with a decrease in carbon monoxide up to 3 h and then gradually decreases. A constant increase in the yield of hydrocarbons may be due to the homogeneous hydrogenation of methanol to methane, which was verified by the enhanced formation of methane in a control experiment with additional methanol (Table 1).

The most important feature of this reaction is that the ruthenium complex remains dissolved in the solvent even at high reaction temperatures. This must be because of the iodide salts which stabilizes the complex and thus enables it to catalyse a rapid reverse water gas shift reaction. Among the anions examined only iodide (and bromide to some extent) exhibited this ability. Furthermore, a significant effect is observed on the formation of methanol depending on the cation used. The reactions with some alkaline metal cations give satisfactory yields of methanol, while carbon monoxide and methane are preferentially formed with ZnI_2 and I_2 respectively. Effective solvents for this reaction seem to be

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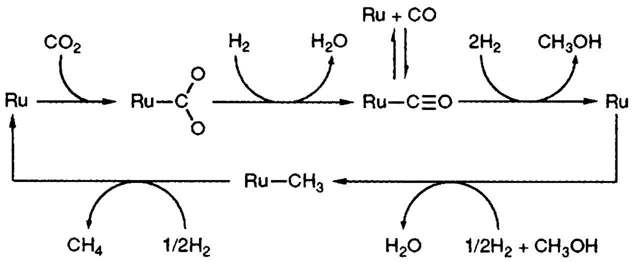
† An adequate removal of plated ruthenium metal was achieved through washing with dilute sodium hypochlorite solution followed by careful polishing.



Scheme 1 ('Ru' = carbonylated and/or iodide coordinated ruthenium complexes)

limited to some cyclic carbamate or urea derivatives as shown in Table 1.

The entire role of the salt is not yet clear, but some ionic ruthenium species may be produced in the presence of the iodide anion which either coordinates to it or not, as indicated in Dombec's report.[7] Scheme 1 shows a possible overall reaction mechanism. Although formation of an intermediate ruthenium formate complex was implied in the hydrogenation of cabon dioxide to alkyl formate catalysed by the ruthenium carbonyl complexes,[9] the η^1-coordinated CO_2 complex may not be excluded from the mechanism of hydrogenation of carbon dioxide to carbon monoxide. The formation of such complexes were assumed in a stoichiometric reduction of carbon dioxide to carbon monoxide induced by anionic ruthenium carbonyl complex[10] and have also been isolated.[11] Hydrogenation of carbon monoxide to methanol may be followed by further hydrogenation to methane which is co-catalysed by iodide anion.

As a liquid phase methanol synthesizing process is considered favourable for heat elimination and temperature control of the reactor in comparison with a fixed-bed type process containing heterogeneous catalysts, the present reaction may be applicable in the industrial disposal of carbon dioxide on a large scale.

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