

# Homogeneous catalytic synthesis of formic acid (salts) by hydrogenation of CO<sub>2</sub> with H<sub>2</sub> in the presence of ruthenium species

Jun Zhong Zhang<sup>\*</sup>, Zhong Li, Hui Wang, Chang You Wang

*C1 Chemistry Laboratory, Institute of Coal Chemical Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, PR China*

Received 20 September 1995; accepted 30 April 1996

## Abstract

The purpose of this investigation is to synthesize formic acid by hydrogenation of CO<sub>2</sub>. The catalysts or catalyst precursors employed in these studies under 6 MPa(CO<sub>2</sub>/H<sub>2</sub>) and at 60°C, were ruthenium chloride or ruthenium complexes. The turnover number obtained for formic acid production was ca. 200 by using ethanol/water (5:1) for a 5 h reaction period. In the reaction mechanism the CO<sub>2</sub> is activated by the ruthenium complex with formation of metal-formate intermediate HCO<sub>2</sub>RuH(CO)(PPh<sub>3</sub>)<sub>3</sub>, which releases formic acid by reductive elimination of the hydrido-formate ligands.

*Keywords:* Carbon dioxide hydrogenation; Formic acid; Ruthenium chloride; Ruthenium complexes

## 1. Introduction

In view of the increasing scarcity of organic carbon sources in the future, and of the unfavourable effects of carbon dioxide on climate, carbon dioxide is becoming increasingly attractive as a C<sub>1</sub> synthesis unit [1,2].

Formic acid is one of the fundamental chemical feedstocks in the organic chemical industry. It has been used as a starting material for the production of formate esters, which can be utilised in the production of a large variety of useful organic derivatives such as aldehydes, ketones, carboxylic acids and amides, and in the

perfume and fragrance industry. It has been used as a mordant, auxiliary agent in the dyeing industries, a neutraliser in the tanning process, a disinfectant and a preservative agent in sanitary stations [3].

Transition metal complexes have been widely used as catalysts for the activation of CO<sub>2</sub> [4–8]. The efficient production of formic acid has been described more recently, in a supercritical mixture of carbon dioxide and hydrogen containing a catalytic ruthenium(II)phosphine complex [9]. Previous studies of the synthesis of alkyl formate from CO<sub>2</sub>, H<sub>2</sub> and methanol using anion group 6 metal carbonyls catalysts [10] concluded that alkyl formates were derived directly from carbon dioxide rather than carbon monoxide from reverse water gas shift chemistry. Our studies of the synthesis of formic acid from CO<sub>2</sub>

<sup>\*</sup> Corresponding author. Present address: School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia. E-mail: s9500325@vmsuser.acsu.unsw.edu.au.

and  $H_2$  indicated that with  $RuCl_3$  used as catalyst precursor, dihydrocarbonyltris(triphenylphosphine)ruthenium(II), i.e.  $RuH_2(CO)(PPh_3)_3$ , was formed in the reaction [11] and the  $HCOOH$  was also directly formed from  $CO_2$  [12]. The reaction mechanism is not yet clear.

The purpose of this investigation is to continue our studies on the hydrogenation of  $CO_2$  to produce formic acid, emphasizing mechanistic aspects of the process.

## 2. Experimental section

### 2.1. Starting materials

$RuCl_3 \cdot nH_2O$  was purchased from Kongming Noble-metal Institute (Yongnan Province, China). Triphenylphosphine ( $PPh_3$ ) was purchased from Shanghai Chemical Reagents Plant No. 1. Reagent grade methanol, ethanol, propanol, *n*-butanol, formic acid and triethylamine were purchased from Beijing Chemical Reagent Plant and were used without further purification. The Institute of Shanxi Coal Chemistry (Academia Sinica) was the source of carbon monoxide, and carbon dioxide, whereas both nitrogen and hydrogen with a purity of 99.99% were obtained from Taiyuan Iron Steel Company. Oxalic acid and sodium carbonate were from Xian Chemical Reagent Plant and were used as received.

### 2.2. Catalytic reactions

In a typical run, 0.2 mmol of the catalyst was dissolved in 20 ml solvent. After the addition of the  $PPh_3$  and triethylamine the solution was transferred to a 100 ml stainless steel autoclave and the vessel was flushed with  $CO_2$  three times to remove air and was pressurized up to a final pressure of 6 MPa (at room temperature) with  $CO_2/H_2$  (1:1). The reactor was heated by means of a mantle equipped with a temperature controller. When the temperature inside the reactor (measured with a thermocouple) reached 60°C

in a few minutes, stirring began and the reaction time was recorded from that point. At the end of the reaction period (normally 3–5 h) the heating was discontinued and the reactor was placed in a cold water bath until it reached room temperature. At this time a gas sample was analyzed by the on line chromatography. After depressurizing, the vessel was opened and the reaction solution was collected. The formic acid produced in the liquid was esterified completely for the GC analysis. The column used for analysis of the liquid samples was 10% PEG20M over Chromsorb W (3 m × 3 mm), at 80°C, and a ionisation detector was used. For gas sample analysis, the column was packed with carbon molecular sieve (2 m × 3 mm), and a therm conductivity detector was used.

The GC analyses were carried out with a Shimadzu Model 9A Chromatography, equipped with a Shimadzu recorder CR3A. IR spectra were recorded on a Shimadzu FTIR 8001 spectrometer. NMR measurements were carried out on a Varian Model FT-300 spectrometer. Elemental analyses were performed by the Elemental Analysis Laboratory of the Institute of Shanxi Coal Chemistry (Academia Sinica).

## 3. Results and discussion

### 3.1. Hydrogenation of $CO_2$ with $H_2$ in the presence of additives

$RuCl_3$  was found to be an active catalyst precursor for the hydrogenation of  $CO_2$  with  $H_2$  under moderate conditions (loading pressure 6 MPa of  $CO_2/H_2$  (1:1), 60°C) to produce formic acid (Eq. (1)). In the absence of  $PPh_3$  the turnover number was only 86.5 mol  $HCOOH$ /mol cat. (Table 1, entry 1). This demonstrates that  $PPh_3$  plays an important role in the catalysis. The catalyst recovered at the end of the reaction was characterized by IR, NMR and chemical analysis to be  $RuH_2(CO)(PPh_3)_3$  (Table 1, entry 2). If  $Et_3N$  was not added or added in the form of  $Et_3N \cdot$

Table 1  
Effects of additives on the hydrogenation of CO<sub>2</sub> to produce formic acid<sup>a</sup>

Expt	Catalyst <sup>b</sup>	Additives	Turnover No. <sup>d</sup>	Catalyst form <sup>e</sup>
9211	RuCl <sub>3</sub>	Et <sub>3</sub> N	86.5	—
9212	RuCl <sub>3</sub> , PPh <sub>3</sub>	Et <sub>3</sub> N	200.1	RuH <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>3</sub>
9213	RuCl <sub>3</sub> , PPh <sub>3</sub>	—	14.5	—
9214 <sup>c</sup>	RuCl <sub>3</sub> , PPh <sub>3</sub>	Et <sub>3</sub> N·HCl	15.8	—
9215	RuCl <sub>3</sub> , PPh <sub>3</sub>	NH <sub>3</sub>	11.5	black crystals
9216	RuCl <sub>3</sub> , PPh <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	8.25	black crystals
9217	RuCl <sub>3</sub> , PPh <sub>3</sub>	CO	2.15	Ru(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>

<sup>a</sup> Temp. 60°C; 5 h reactions; 6 MPa pressure (CO<sub>2</sub>/H<sub>2</sub> (1:1)) at room temperature; EtOH/H<sub>2</sub>O (5:1) as solvent.

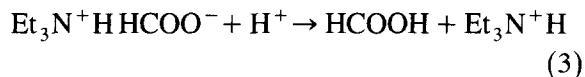
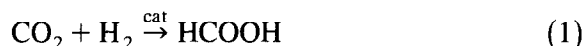
<sup>b</sup> [cat.] = 8 × 10<sup>-3</sup> M.

<sup>c</sup> Et<sub>3</sub>N·HCl was obtained by neutralisation of Et<sub>3</sub>N with HCl.

<sup>d</sup> Turnover No. = moles of HCOOH/moles of catalyst.

<sup>e</sup> Catalysts were characterised via FTIR and NMR at the end of reactions.

HCl (Table 1 entry 2 and 3) a trace amount of formic acid was produced and the spectra show that RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> was not formed in the reaction. The presence of Et<sub>3</sub>N not only served as a base to neutralise HCOOH (Eq. (2)) but also affected the catalyst structure formed in the reaction process. In the literature [13] triethylamine was used as the basic reducing agent in place of sodium borohydride for the synthesis of RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> from RuCl<sub>3</sub>, H<sub>2</sub>, PPh<sub>3</sub> and formaldehyde. It is possible that in this study Et<sub>3</sub>N acts the same way, as shown in the catalytic cycle, which will be presented later.



When Et<sub>3</sub>N was replaced by inorganic bases such as NH<sub>3</sub>·H<sub>2</sub>O or Na<sub>2</sub>CO<sub>3</sub> (Table 1 entry 5, 6), black crystals were recovered from the liquid after the reaction was finished. Their structure has not been identified. The data show that very little formic acid is produced in this case. Carbon monoxide caused a drastic decrease of activity. When ten percent of CO was

introduced into the reactor as co-gas, the recovered complex was Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, which was found to be catalytically inactive as shown in Table 1 entry 7.

In all of the reactions reported in this section, almost no ethyl formate was detected in the reaction solution by GC analysis.

Fig. 1 shows the results of the hydrogenation of CO<sub>2</sub> to formic acid by ruthenium chloride with different amounts of PPh<sub>3</sub> added. Their corresponding infrared spectra in the ν(C–O) region are illustrated. As PPh<sub>3</sub> increases, the intensity of the band at 1944 cm<sup>-1</sup> increases (Fig. 2). The results indicate that RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> is the real form of the catalyst for hydrogenation. Reactions carried out in an excess of PPh<sub>3</sub> (P/Ru = 10) or with undissolved PPh<sub>3</sub> remaining in the reaction solution showed a decrease of the catalytic activity. Their turnover number dropped slightly. The complex with high P/Ru ratio such as in RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> was not formed despite a large amount of PPh<sub>3</sub> being used. Fig. 2 shows that only one complex, RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>, was formed in the reactions with different amounts of PPh<sub>3</sub> added.

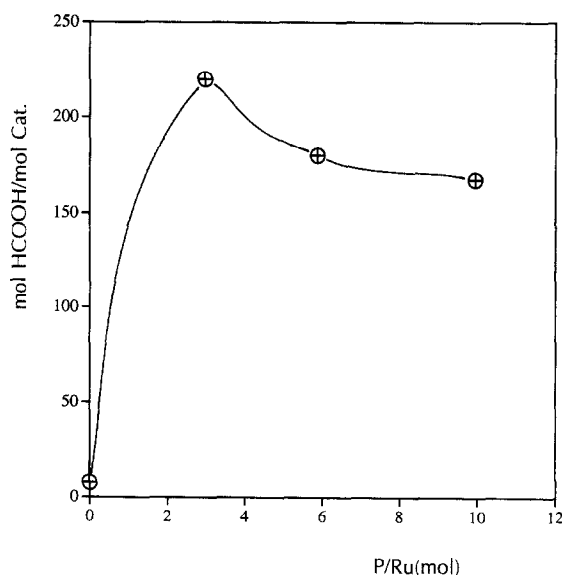


Fig. 1. Effect of PPh<sub>3</sub> on the hydrogenation of CO<sub>2</sub> with H<sub>2</sub>.

### 3.2. The effects of carbon monoxide on the hydrogenation of CO<sub>2</sub> with H<sub>2</sub> to produce formic acid

As indicated in Table 2 the addition of carbon monoxide retarded the formic acid production with 7.5% of CO introduced in the reaction atmosphere. The activity of the catalyst decreased to 2.15 mol/mol cat. Infrared spectra (Fig. 3) showed that on adding CO, the structure of the complex formed in the reaction changed. The band at 1944 cm<sup>-1</sup> which belongs to the stretching vibration of CO in RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> [14] disappeared, and a new band at 1900 cm<sup>-1</sup> was formed, which corresponds to the formation of Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> [15]. The results of expt. 3, 4 and 5 show Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> to be neither catalytically active under an atmosphere of CO<sub>2</sub>/H<sub>2</sub> (1:1), nor active for the hydrogenation of carbon monoxide with H<sub>2</sub>.

In conclusion, Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> is much more easily formed than RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> in the presence of Et<sub>3</sub>N and EtOH as the solvent and carbon monoxide is the poison to the hydrogenation of CO<sub>2</sub> with H<sub>2</sub> to produce formic acid for RuCl<sub>3</sub> as a catalyst.

### 3.3. Mechanism

In order to get detailed information on catalysts formed in the reaction, a 1 l autoclave was used, which made it possible to separate some reaction liquid to be analysed by IR. Based on the results mentioned above and the IR data in the reaction process, a general catalytic cycle

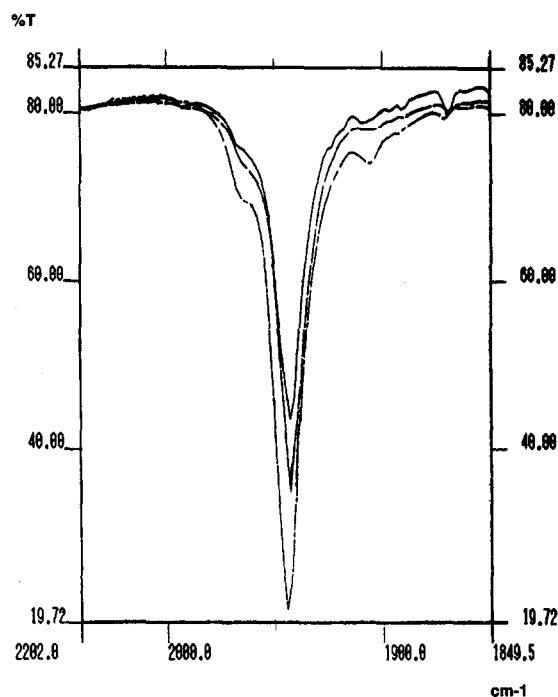


Fig. 2. IR spectra of catalyst with different PPh<sub>3</sub> added.

for the production of formic acid starting from CO<sub>2</sub> and H<sub>2</sub> is proposed. It is shown in Scheme 1, and is similar to the process proposed by Darensbourg for the synthesis of alkyl formate from CO<sub>2</sub>, H<sub>2</sub> and alcohols [16].

In the atmosphere of CO<sub>2</sub> and H<sub>2</sub> ruthenium chloride is converted into RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>, A, which will take part in the cycle. The CO<sub>2</sub> insertion reaction with ruthenium triphenylphosphine complex to produce the formate complex is a well-documented reaction [17,18]. The IR band at 1637 cm<sup>-1</sup>, which appeared during reaction process, shows the formation of for-

Table 2

Effects of CO in the reaction atmosphere on the hydrogenation and catalyst structures

Expt	Atmosphere	Turnover No.	Catalyst form
1	CO <sub>2</sub> /H <sub>2</sub> (1:1)	210	RuH <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>3</sub>
2	CO <sub>2</sub> /H <sub>2</sub> /CO (1:1:0.01)	50.3	Ru(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> and RuH <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>3</sub>
3	CO <sub>2</sub> /H <sub>2</sub> /CO (1:1:0.15)	2.15	Ru(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>
4	CO <sub>2</sub> /H <sub>2</sub> /CO (1:1:0.3)	0.750	Ru(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>
5	CO/H <sub>2</sub> (1:1)	0.001	Ru(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>

Temp. = 60°C, 5 h reaction, final pressure 6 MPa.  
EtOH/H<sub>2</sub>O/Et<sub>3</sub>N = 5:1:2.5, [cat.] = 8 × 10<sup>-3</sup> M.

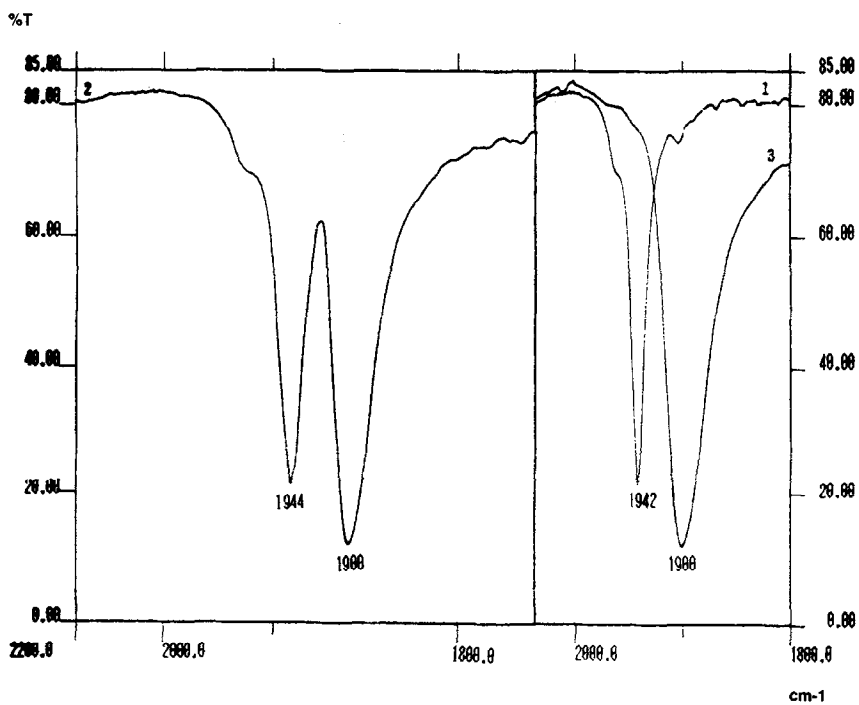
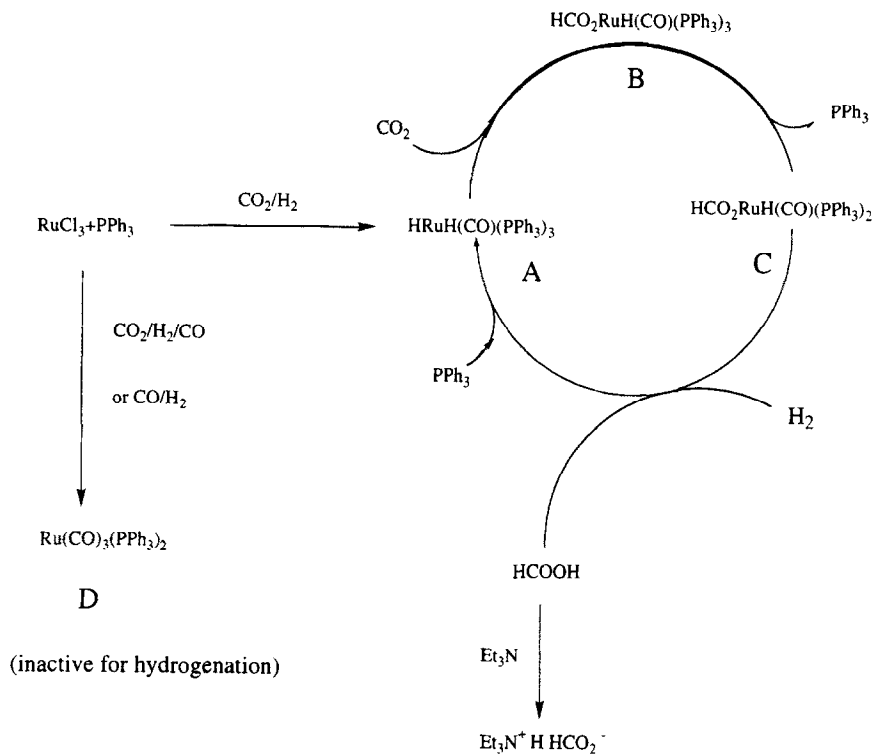


Fig. 3. The effects of CO on the structure of catalysts. (1)  $\text{CO}_2/\text{H}_2$  (1:1); (2)  $\text{CO}_2/\text{H}_2/\text{CO}$  (1:1:0.3); (3)  $\text{CO}/\text{H}_2$  (1:1).



Scheme 1.

mate complex, B, which can also be detected sometimes at the end of the reaction period. The oxidative addition of hydrogen appears to be the rate-determining step of the process and it must be preceded or followed by dissociation of phosphine ligand to produce the active unsaturated species, C. However, the importance of the dissociation is shown by the decrease in rates, on addition of excess of triphenylphosphine (Fig. 1).

Reactions performed in the presence of carbon monoxide displayed greatly diminished activity toward formic acid production since ruthenium chloride was converted into inactive species, D, as showed in Scheme 1.

### Acknowledgements

The investigation was supported by Shanxi Natural Sciences Foundation for Young Scientists. We thank Dr. Qingnian Dong, Institute of Shanxi Coal Chemistry (China Academia Sinica) for his skilful help with the interpretation of the spectra. We also thank Professor R.F. Howe, and Professor A.M. Long, University of New South Wales, Sydney, who have provided many useful comments.

### References

- [1] D. Walther, *Coord. Chem. Rev.* 79 (1987) 136.
- [2] *Greenhouse Issues* 12 (1992) 6.
- [3] Zhonggou Huagong Shangpin Daquan, Vol. 1 (Chinese Commodity Press, Beijing, 1988).
- [4] J.-C. Tsai and K.M. Nicholas, *J. Am. Chem. Soc.* 114 (1992) 5117.
- [5] Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, *Chem. Lett.* 863 (1976).
- [6] M.M.T. Khan, S.B. Halligudi and S. Shuka, *J. Mol. Catal.* 51 (1989) 47.
- [7] E. Graf and W. Leiter, *J. Chem. Soc. Chem. Commun.* 623 (1992).
- [8] F. Gassner and W. Leiter, *J. Chem. Soc. Chem. Commun.* 1465 (1993).
- [9] P.G. Jessop, T. Ikariya and R. Noyori, *Nature* 368 (1994) 231.
- [10] D.J. Darensbourg, *J. Am. Chem. Soc.* 106 (1984) 3750.
- [11] J.Z. Zhang, Z. Li and C.Y. Wang, *Trans. Metal Chem.* 20 (1995) 118.
- [12] J.Z. Zhang, Z. Li and C.Y. Wang, *J. Mol. Catal.* 1 (1994) 76 (in Chinese).
- [13] W.P. Griffith, *The Chemistry of the Rarer Platinum Metals* (Wiley, New York, 1967).
- [14] P.S. Hallman, B.R. McGarvey and G. Wilkinson, *J. Chem. Soc. A* 3143 (1968).
- [15] F.L. Eplattener and F. Calderazzo, *Inorg. Chem.* 7 (1968) 1290.
- [16] D.J. Darensbourg and C. Ovalles, *J. Am. Chem. Soc.* 109 (1987) 3330.
- [17] R.P.A. Sneed, G. Wilkinson, F.G.A. Stone and E.W. Abel, *Comprehensive Organometallic Chemistry*, Vol. 8 (Pergamon Press, Oxford, 1982).
- [18] S. Inoue and N. Yamazaki, *Organic and Bio-organic Chemistry of Carbon Dioxide* (Kodansha Ltd., Tokyo, 1982).