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CATALYTIC FIXATION OF CARBON DIOXIDE TO FORMIC ACID BY TRANSITION-METAL COMPLEXES UNDER MILD CONDITIONS

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Formic acid was catalytically synthesized from carbon dioxide and hydrogen by a combination of group VIII transition-metal complexes and bases in the presence of water far less than the equivalent amount of the catalyst.

It is known that CO_2 is reduced electrochemically to formic acid in aqueous solution, but the synthesis of formic acid directly from CO_2 and H_2 has not been reported except for the recent work on the catalytic formation of magnesium formate from H_2 and CO_2 by a $TiCl_4$-Mg system.[1] We have previously reported the synthesis of alkyl formates from CO_2, H_2, and primary alcohols by a combination of group VIII transition-metal complexes and tertiary amines.[2]

We now wish to report the catalytic formation of formic acid from CO_2 and H_2 in the presence of water under mild conditions by a combination of group VIII transition-metal complexes and some bases.

$$CO_2 + H_2 \xrightarrow[\text{Base, } H_2O]{\text{Cat.}} HCO_2H$$

Typically, a 100 ml stainless steel autoclave equipped with a magnetic stirrer was charged with $Pd(diphos)_2$ 0.1 mmol[diphos=$Ph_2PCH_2CH_2PPh_2$], benzene 10 ml, water 500 mmol, and triethylamine 50 mmol, then the mixture was stirred constantly at room temperature under pressure of CO_2(25 atm) and H_2(25 atm). After reaction for 20 hr, the formic acid yielded was quantitatively analyzed by NMR using disodium telephthalate as an internal standard. Table 1 shows the catalytic formation of formic acid from CO_2 and H_2 in the presence of water. Complexes of most group VIII transition-metals can be used as the catalyst component. As shown in Fig. 1, a very small quantity of water is effective enough to accelerate the reaction.

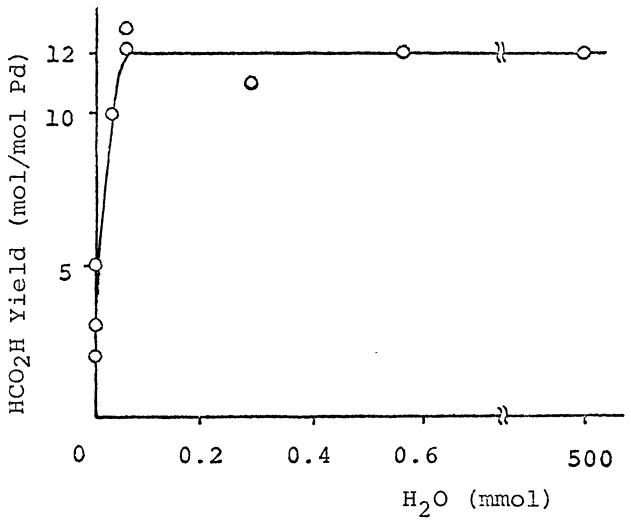

Fig. 1 Effect of water added

$Pd(diphos)_2$ 0.1 mmol, triethylamine 50 mmol, benzene 10 ml, CO_2 25 atm, H_2 25 atm; r.t. 20 hr.

Table 1 Catalytic formation of formic acid[a)]

Complex	Base	Temp. (°C)	HCO_2H Yield (mol/mol complex)
$Pd(diphos)_2$	None	r.t.	0
	Trimethylamine	r.t.	12
	Triethylamine	r.t.	12
		66	40
		110	62
		140	70
		160	50
	Tripropylamine	r.t.	14
	N-Methylpyrrolidine	r.t.	12
	1,4-Diazabicyclo[2.2.2]octane	r.t.	24
	Dipropylamine	r.t.	7
	Tetramethylammonium hydroxide[b)]	r.t.	5
	Sodium hydroxide	r.t.	11
	Sodium hydrogencarbonate[c)]	r.t.	3
$Ni(diphos)_2$	Triethylamine	r.t.	7
$Pd(PPh_3)_4$	Triethylamine	r.t.	3
$RhCl(PPh_3)_3$	Triethylamine	r.t.	22
$H_2Ru(PPh_3)_4$	Triethylamine	r.t.	87
$H_3Ir(PPh_3)_3$	Triethylamine	r.t.	15

a) Any other organic products were not detected by GLC and NMR analyses. Reaction conditions: complex 0.1 mmol, base 50 mmol, water 500 mmol, benzene 10 ml, CO_2 25 atm, H_2 25 atm; reaction time 20 hr. b) Tetramethylammonium hydroxide 27.5 mmol, water 1250 mmol. c) Without CO_2.

Although the mechanism for this reaction is not fully understood the following may be a possible one.[3)]

$$LnM\text{-}H + CO_2 \longrightarrow LnMOCH(=O) \xrightarrow{H_2O(Base)} LnMOH + HOCH(=O)$$

$$LnMOH + H_2 \longrightarrow LnM\text{-}H + H_2O$$

In the sodiun hydrogencarbonate system, however, formic acid was obtained in some yields even in the absence of CO_2. Therefore, the following route via hydrogencarbonate cannot be excluded at the moment.

$$CO_2 + H_2O + NR_3 \rightleftharpoons HOC(=O)CONHR_3 \xrightarrow[Cat.]{H_2} HOCH(=O) + HONHR_3 \text{ (or } H_2O + HC(=O)CONHR_3)$$

Controlled experiments ruled out the route that CO_2 was reduced to carbon monoxide which in turn reacted with the water to form formic acid.

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References

1) B. Jezowska-Trzebiatowska and P. Sobota, J. Organometal. Chem., 76, 43 (1974). idem, ibid., 80, C27 (1974).
2) Y. Inoue, Y. Sasaki, and H. Hashimoto, J. C. S. Chem. Comm., 718 (1975).
3) Intermediate formation of formic acid is supposed in the preparation of $RhCl(CO)(PPh_3)_2$ from $RhCl(PPh_3)_3$, H_2, and CO_2 in the presence of water; H. Koinuma, Y. Yoshida, and H. Hirai, Chem. Lett., 1223 (1975).

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