Homogeneous Bimetallic Catalysts for Production of Carboxylic Acids from Carbon Dioxide, Hydrogen, and Organic Iodides

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(Received April 4, 1995)

Carboxylic acids RCOOH (R = Me, Et, Ph) are catalytically produced from carbon dioxide, dihydrogen, and the corresponding organic iodides in the presence of homogeneous Ru/Co or Ni/Co bimetallic catalysts.

Fixation of carbon dioxide into organic chemicals has attracted much attention, since CO_2 is a potential C_1 starting material.[1] In the reduction of CO_2 with H_2 with transition metal complexes, formic acid is catalytically formed and its derivatives are obtained when alcohol and amine are present.[2] In the reaction of CO_2, H_2, and alkyl halides, Darensbourg reported a catalytic formation of alkyl formates,[3] but carboxylic acid was not obtained. The production of carboxylic acids using CO_2 is well known in industry, i.e., the Kolbe-Schmitt process, but this is only applicable to phenol derivatives. In organometallic chemistry, insertion of CO_2 into metal-carbon bond is known for many transition and non-transition metal alkyl complexes, and protonolysis of the resulting metal carboxylates gives carboxylic acids.[1,4] However, these are usually stoichiometric reactions. One example of the catalytic formation of carboxylic acid using CO_2 is the generation of C_9-carboxylic acids from 1,3-butadiene with Pd(0) complexes.[5] A Rh-catalyzed reaction of ethylene and CO_2 to produce propionic acid was also reported, but ca. 700 atm of pressure was necessary.[6] Benzoic acid was formed from benzene and CO_2 with Pd(II) salts, but the yield was low (127 %/Pd).[7] In this communication we report a catalytic production of carboxylic acids from CO_2, H_2, and organic iodides by homogeneous Ru/Co or Ni/Co bimetallic catalysts [Eq. (1)].

$$RI + CO_2 + H_2 \xrightarrow[\substack{Ru_3(CO)_{12}/Co_2(CO)_8 \\ \text{or } Ni(cod)_2/Co_2(CO)_8}]{} RCOOH \qquad (1)$$

In a typical experiment (Table 1, Run 3), $Ru_3(CO)_{12}$ (0.050 mmol) and $Co_2(CO)_8$ (0.075 mmol) were dissolved in *N*-methylpyrrolidone (NMP, 10 ml) under Ar, and then methyl iodide (5.0 mmol) was added. The red brown solution was transferred to a 50 ml stainless steel autoclave with a glass liner under Ar. The autoclave was pressurized to 80 atm with CO_2/H_2 (1:3) at room temperature. The autoclave was heated at 240 °C for 8 h, then cooled to room temperature. The resulting gas and orange solution were analyzed by GC and GC-MS,[8] showing the complete consumption of MeI and the formation of acetic acid (1.2 mmol, corresponding to 8 TON per Ru atom) (TON = turnover number). Neither methanol nor methyl formate was detected. In the reaction gas, carbon monoxide (3.0 mmol) and methane (7.5 mmol) were observed.

The striking feature of the present reaction is the synergistic effect of $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ on catalytic production of AcOH. No AcOH was formed with the Ru or Co single catalyst (Runs 1 and 2). The formation of AcOH was pronounced when $Co_2(CO)_8$ was increased (Run 4), where the yield of AcOH based on MeI was 32 %. The recovered solutions in Runs 3-9 were homogeneous, and no deposition of metals was observed. HI formed in the reactions was probably trapped by NMP to form HI-NMP salts. By-products detected in GC were CO and CH_4. Presumably, CO originated from the reverse water-gas shift reaction, and CH_4 from the hydrogenation of MeI. Small parts of CH_4 may also be produced from CO + H_2. Concerning the reverse water-gas shift reaction, Sasaki et al. reported a homogeneous alcohol synthesis catalyzed by Ru and Ru/Co complexes.[9] Under milder conditions of 150 °C and 40 atm (Run 6), the formation of CO and CH_4 was suppressed but that of AcOH was unchanged at TON of 12 per Ru atom. *N,N*-Dimethylformamide (DMF) was also an effective solvent (Run 7), and in this case the largest TON of 17 was obtained and the yield based on MeI was 50 %. In contrast, toluene and water were not effective as solvents.

Other Ru complexes such as $[PPN][HRu_3(CO)_{11}]$ (PPN = $(Ph_3P)_2N$) and $Ru(CO)_4I_2$ showed low activity, but $Ni(cod)_2$ was useful in place of $Ru_3(CO)_{12}$ (Runs 8 and 9). On the other hand, $Co_2(CO)_8$ was indispensable; $RhCl_3 \cdot 3H_2O$, $Rh_4(CO)_{12}$,

Table 1. Reaction of CH_3I, CO_2, and H_2 with homogeneous bimetallic catalysts[a]

Run	Catalyst	Co/Ru or Co/Ni[b]	$P(CO_2)$/ atm[c]	$P(H_2)$/ atm[c]	Reaction temp. / °C[d]	Reaction time / h	Product / mmol (TON[e])		
							AcOH	CO	CH_4
1	$Ru_3(CO)_{12}$	-	20	60	240	8	0	5.6 (37)	6.6 (44)
2	$Co_2(CO)_8$[f]	-	20	60	240	8	0	0	2.2 (15)
3	$Ru_3(CO)_{12} + Co_2(CO)_8$	1	20	60	240	8	1.2 (8)	3.0 (20)	7.5 (50)
4	$Ru_3(CO)_{12} + Co_2(CO)_8$	10	20	60	240	8	1.6 (11)	8.7 (58)	4.6 (31)
5	$Ru_3(CO)_{12} + Co_2(CO)_8$	10	20	60	150	24	1.3 (9)	0.6 (4)	1.4 (9)
6	$Ru_3(CO)_{12} + Co_2(CO)_8$	10	20	20	150	24	1.8 (12)	0.6 (4)	1.4 (9)
7	$Ru_3(CO)_{12} + Co_2(CO)_8$[g]	10	20	20	150	24	2.5 (17)	2.5 (17)	0.9 (6)
8	$Ni(cod)_2 + Co_2(CO)_8$	10	20	20	150	24	1.7 (11)	1.4 (9)	0.5 (4)
9	$Ni(cod)_2 + Co_2(CO)_8$[g]	10	20	20	150	24	1.7 (11)	0.9 (6)	0.6 (4)

[a] $Ru_3(CO)_{12}$ (0.050 mmol) or $Ni(cod)_2$ (0.150 mmol), CH_3I (5.0 mmol), NMP (10 ml) as a solvent. [b] Atomic ratio. [c] Initial pressure at room temperature. [d] Oil bath temperature. [e] TON per Ru (or Ni) atom. [f] $Co_2(CO)_8$ (0.075 mmol). [g] DMF (10 ml) as a solvent.

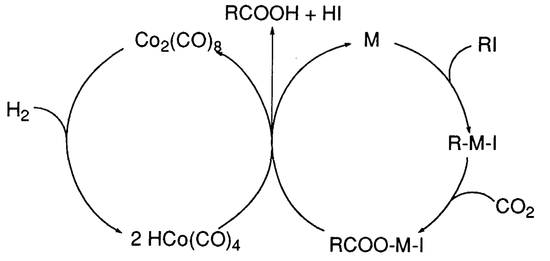
and $Fe_3(CO)_{12}$ were not effective as a cocatalyst of $Ru_3(CO)_{12}$.

The $Ru_3(CO)_{12}/Co_2(CO)_8$ system also catalyzed the carboxylation of EtI and PhI to give the corresponding carboxylic acids, i.e., EtCOOH and PhCOOH. Under the same reaction conditions of Run 4 in Table 1, EtCOOH and PhCOOH were obtained in TON's of 7 and 2 per Ru atom, respectively. In these reactions, ethane and benzene were also formed by simple hydrogenation of the organic iodides in addition to CO and CH_4.

The mechanism of the present catalytic reactions is not yet clear. The addition of HCOOMe to the $MeI/CO_2/H_2$ system was not effective, which may exclude the formation of HCOOMe[3] and isomerization to AcOH.[10] Considering the formation of CO, the mechanism involving reverse water-gas shift reaction and successive carbonylation of RI[11] [Eq. (2)] seems possible. However, the addition of CO (or MeOH) to the $MeI/CO_2/H_2$ system had little effect on the formation of AcOH, and no CH_3CHO was observed in the products. Thus, at present we favor the mechanism involving CO_2 insertion (Scheme 1).

$$RI + CO + H_2O \xrightarrow{\qquad\qquad} RCOOH + HI \qquad (2)$$

In Scheme 1, the reaction begins with the oxidative addition of RI to M (M = Ru, Ni) center to give M-R species. CO_2 inserts into M-R bond to form M-OCOR, where the insertion of CO_2 into Ru-H or Ru-C bond has been well known.[12] On the other hand, $Co_2(CO)_8$ reacts with H_2 to give $HCo(CO)_4$, which is a strong acid[13] and protonates the M-OCOR complex to produce RCOOH. Concerning the protonolysis step, the model reactions were performed: $HRu(OAc)(PPh_3)_3$ was reacted with excess $HCo(CO)_4$ in CH_2Cl_2 at 0 °C for 11 h to give AcOH in 22 % yield based on Ru. Similar reaction of $Ni(\eta^3\text{-}C_4H_7)(OAc)(PPh_3)$ with $HCo(CO)_4$ gave AcOH in 40 % yield. We are now studying the detailed reaction mechanism.



Scheme 1. M = Ru, Ni
R = Me, Et, Ph

We thank Prof. K. Osakada for useful discussion and Nissan Science Foundation for financial support.

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