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Carbonylation of Olefins, Alcohols, and Saturated Hydrocarbons Using $Cu(CO)_n^+$ and $Ag(CO)_2^+$ Catalysts in BF_3–H_2O

Yoshie Souma and Hiroshi Sano
Government Industrial Research Institute, Osaka, Midorigaoka, Ikeda, Osaka 563

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Olefins, alcohols, and saturated hydrocarbons reacted with carbon monoxide to give *t*-carboxylic acids in high yields using copper carbonyl and silver carbonyl catalysts at room temperature and in carbon monoxide at atmospheric pressure in BF_3–H_2O solutions. Dienes and diols also reacted with carbon monoxide to give mixtures of monocarboxylic acids, dicarboxylic acids and lactones. The concentration ratio of H_2O/BF_3 was maintained between 1 and 2 during the carbonylation reaction. There was no difference between the catalytic behavior of $Cu(CO)_n^+$ and that of $Ag(CO)_2^+$. The reaction rates for primary alcohols were very low in BF_3–H_2O, although they increased with the addition of H_2SO_4. The reaction rates for *s*-alcohol, *t*-alcohol and olefins in BF_3–H_2O remained unchanged upon the addition of H_2SO_4.

In previous papers, the authors have reported that olefins, alcohols, and saturated hydrocarbons reacted with carbon monoxide and produced *t*-carboxylic acids in the presence of $Cu(CO)_n^+$ catalysts in H_2SO_4 at room temperature and at atmospheric pressure.[1–4)] Similarly, carbonylation reactions of diisobutylene and 1-octene have been reported by Yoneda *et al.* using $Cu(CO)_n^+$ catalysts in BF_3–H_2O.[5)] It has been reported that Ag_2O was not effective in the carbonylation.[6)] In this case, no silver carbonyl ions appear to be formed, because silver compounds are easily reduced to metal silver when BF_3–H_2O is added to Ag_2O in a CO atmosphere at room temperature. However, the formation of $Ag(CO)_2^+$ was possible by adding Ag_2O to cold BF_3–H_2O.[7)] Therefore, it was clarified that the catalysis of $Ag(CO)_2^+$ was the same as that of $Cu(CO)_n^+$ in BF_3–H_2O. This paper describes the carbonylation of olefins, alcohols, and saturated hydrocarbons using $Ag(CO)_2^+$ and $Cu(CO)_n^+$ catalysts in BF_3–H_2O.

Results and Discussion

Cu(I) compounds absorb carbon monoxide and form unstable copper carbonyl ions $Cu(CO)_4^+$, in BF_3–H_2O, as described in a preceding paper.[7)]

$$Cu^+ + CO \rightleftharpoons Cu(CO)_4^+ \qquad (1)$$

$$Cu(CO)_4^+ \rightleftharpoons Cu(CO)^+ + 3CO \qquad (2)$$

In BF_3–H_2O, $Cu(CO)_4^+$, and $Cu(CO)^+$ coexist in equilibrium. The effect of temperature and BF_3 concentration on the formation of $Cu(CO)_4^+$ has been reported by Matsushima *et al.*[8)] As the temperature decreases, the equilibruim is shifted toward the left hand side of Reaction 2.

As has been described previously, Ag carbonyl ions are also formed by the absorption of carbon monoxide by silver compounds in cold BF_3–H_2O solutions.[7)]

$$Ag^+ + CO \rightleftharpoons Ag(CO)_2^+ \qquad (3)$$

$Ag(CO)_2^+$ and Ag^+ also coexist in equilibrium. The effect of the temperature and concentration of BF_3–H_2O on the formation of $Ag(CO)_2^+$ is shown in Fig. 1. Silver carbonyl ions are formed in concentrated BF_3–H_2O solutions, when the H_2O/BF_3 molar ratio of the solution is between 1 and 2. The equilibirum is shifted toward the right hand side of Reaction 3 as the temperature decreases. IR absorption ($\nu_{C=O}$) of $Cu(CO)_4^+$, $Cu(CO)^+$, and $Ag(CO)_2^+$, in BF_3–H_2O occur at 2185, 2160, and 2193 cm^{-1}, respectively.[7)] The ^{13}C NMR chemical shifts of $Cu(CO)_4^+$, $Cu(CO)^+$, and $Ag(CO)_2$ are 169.5, 169.0, and 173.4 ppm, respectively.[7)]

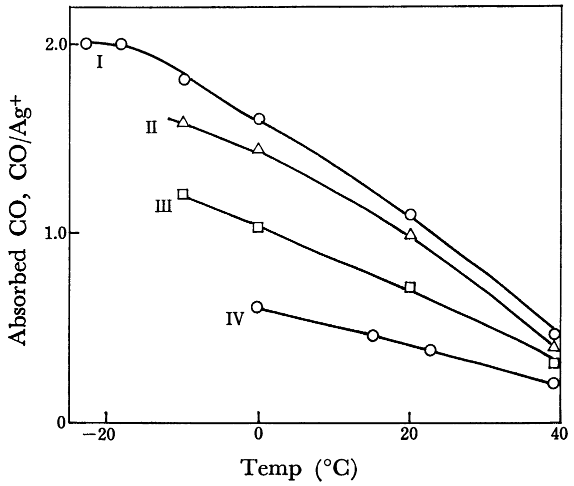


Fig. 1. The formation of $Ag(CO)_2^+$ in BF_3-H_2O solution.
I: BF_3-H_2O, II: BF_3-$1.2H_2O$, III: BF_3-$1.5H_2O$, IV: BF_3-$2.0H_2O$.

Table 1. Carbonylation of 1-octene catalyzed by $Cu(CO)_n^+$ and $Ag(CO)_2^+$ in BF_3-H_2O[a)]

H_2O/BF_3 mole ratio	$Cu(CO)_n^+/Cu^+$	Yield of C_9-*t*-acid	$Ag(CO)_2^+/Ag^+$	Yield of C_9-*t*-acid
1.0	2.8	92	1.2	93
1.2	2.5	95	1.1	96
1.5	1.8	68	0.7	80
1.7	1.4	50	0.6	55
2.0	1.1	7	0.4	5

a) In all cases, 20 ml of BF_3-H_2O, 572 mg of Cu_2O, 928 mg of Ag_2O and 3.15 ml of 1-octene were used. The reaction was carried out at 20°C in 1 atm of carbon monoxide. b) The product was a 4 : 2 : 1 mixture of 2,2-dimethylheptanoic acid, 2-methyl-2-ethylhexanoic acid and 2-methyl-2-propylpentanoic acid.

The results of the carbonylation reaction of 1-octene in various concentrations of BF_3–H_2O using $Cu(CO)_n^+$ and $Ag(CO)_2^+$ catalysts are shown in Table 1.

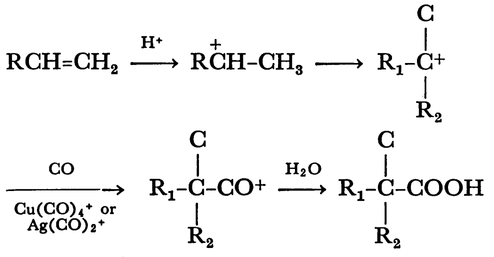
TABLE 2. THE CARBONYLATION OF OLEFINS, ALCOHOLS, AND SATURATED HYDROCARBONS[a]

Compound	Catalyst	Time	Products	Yield	(total)
1-Hexene	$Cu(CO)_4^+$	1 h	2,2-Dimethylpentanoic acid	60	80
			2-Methyl-2-ethylbutanoic acid	20	
1-Octene	$Ag(CO)_2^+$	1 h	2,2-Dimethylheptanoic acid	55	92
			2-Methyl-2-ethylhexanoic acid	26	
			2-Methyl-2-propylpentanoic acid	13	
1-Decene	$Ag(CO)_2^+$	1 h	2,2-Dimethylnonanoic acid	47	86
			2-Methyl-2-ethyloctanoic acid	23	
			2-Methyl-2-propylheptanoic acid	11	
			2-Methyl-2-buthylhexanoic acid	5	
Cyclohexene	$Cu(CO)_4^+$	1 h	1-Methylcyclopentanecarboxylic acid		75
2-Propanol	$Cu(CO)_4^+$	3 d	2-Methylpropionic acid		15
2-Methyl-2-propanol	$Cu(CO)_4^+$	2 h	2,2-Dimethylpropionic acid		94
1-Hexanol	$Ag(CO)_2^+$	1 d	2,2-Dimethylpentanoic acid	12	16
			2-Methyl-2-ethylbutanoic acid	4	
2-Hexanol	$Ag(CO)_2^+$	2 h	2,2-dimethylpentanoic acid	72	95
			2-Methyl-2-ethylbutanoic acid	23	
3-Methyl-3-pentanol	$Ag(CO)_2^+$	2 h	2,2-Dimethylpentanoic acid	16	95
			2-Methyl-2-ethylbutanoic acid	79	
1-Octanol	$Ag(CO)_2^+$	7 d	2,2-Dimethylheptanoic acid	20	35
			2-Methyl-2-ethylhexanoic acid	10	
			2-Methyl-2-propylpentanoic acid	5	
		1 d	same as above		16
Methylcyclohexane	$Cu(CO)_4^+$	2 h	1-Methylcyclohexanecarboxylic acid		30
(Coexist. with 1-octene)			C_9 *t*-carboxylic acid		60
Methylcyclopentane	$Ag(CO)_2^+$	2 h	1-Methylcyclopentanecarboxylic acid		30
(Coexist. with 2-hexanol)			C_7 *t*-carboxylic acid		50

a) The reaction was carried out using 20 ml of BF_3-H_2O, 572 mg of Cu_2O, 928 mg of Ag_2O, and 20 mmol of the compound, at 25 °C in carbon monoxide, at 1 atm.

The yield of *t*-carboxylic acids and the reaction rate decrease with a decrease in the BF_3 concentration. This tendency of the yield to decrease corresponds to the decrease of the amount of $Cu(CO)_4^+$ or $Ag(CO)_2^+$ present in the BF_3–H_2O solution. The carbonylation does not proceed at H_2O/BF_3 molar ratio larger than 2. The best results were obtained at H_2O/BF_3 molar ratios of 1.0—1.2.

The reaction scheme is the same as that for H_2SO_4. The olefin is protonated in the BF_3–H_2O solution and is rearranged to a tertiary carbonium ion with the migration of an alkyl group. The tertiary carbonium ion reacts with carbon monoxide and forms *t*-carboxylic acid in the presence of $Cu(CO)_4^+$ or $Ag(CO)_2^+$ as a catalyst.



$R_1 = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, n\text{-}C_5H_{11}, n\text{-}C_6H_{13}, n\text{-}C_7H_{15}$
$R_2 = CH_3, C_2H_5, n\text{-}C_3H_7$

The results of the carbonylation of olefins, alcohols, and saturated hydrocarbons are shown in Table 2.

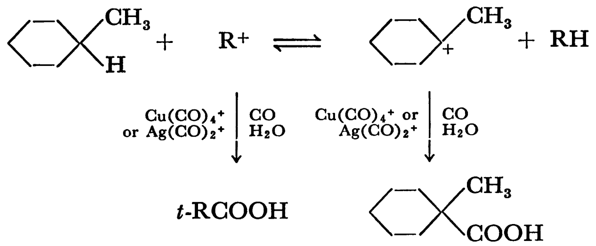
The rate and the conversion of the reaction with primary alcohols were low, and most of the primary alcohol was recovered. The dehydration of primary alcohol appears to be difficult.

TABLE 3. THE INFLUENCE OF THE BF_3-H_2O CONCENTRATION ON THE CARBONYLATION OF SATURATED HYDROCARBONS[a]

Yield of carboxylic acid	H_2O/BF_3 molar ratio			
	1.0	1.2	1.5	1.7
1-Methylcyclohexane-carboxylic acid	30	8	1	0
C_9 *t*-carboxylic acid	60	84	65	57

a) The reactions were carried out using 20 ml of BF_3-H_2O, 527 mg of Cu_2O, 2.56 ml of methylcyclohexane, and 3.14 ml of 1-octene at 20 °C.

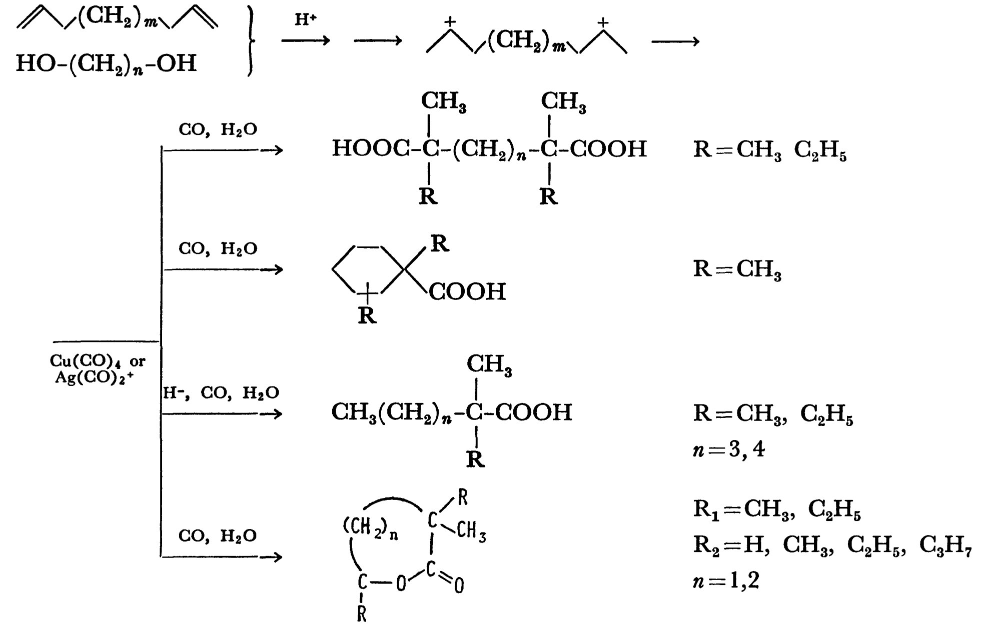
Saturated hydrocarbons react with carbon monoxide in the presence of olefins and alcohols. The hydride ion is abstracted from the saturated hydrocarbon by the carbonium ion formed from the olefin or alcohol. Then the carbonium ion forms *t*-carboxylic acid. Saturated hydrocarbons which have no tertiary hydrogens do not react with carbon monoxide.



Hydride transfer takes place only in concentrated BF_3–H_2O solutions. The results of the carbonylation of 1-methylcyclohexane in the presence of 1-octene in various concentrations of BF_3–H_2O are shown in Table 3.

The results of carbonylation reactions of diene and diol are shown in Table 4. Mixtures of *t*-monocarboxylic acids or *t*-dicarboxylic acids and lactones were obtained. The lactones have alkyl branches on α-carbon. The structural analysis of each compound will be reported elsewhere.[9]

The reaction scheme proposed is as follows.



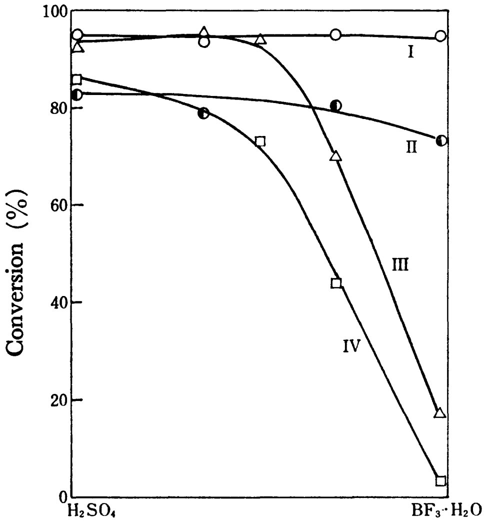


Fig. 2. Carbonylation in BF_3-H_2O∼H_2SO_4 system. I: 1-Octene, II: 1,9-decadiene, III: 1-octanol, IV: 1,2-dodecanediol.

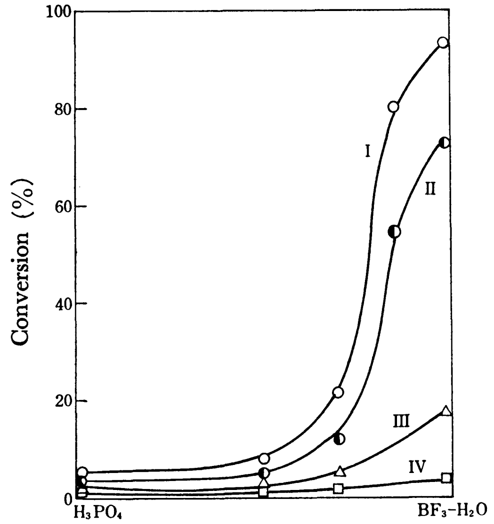


Fig. 3. Carbonylation in BF_3-H_2O∼H_3PO_4 system. I: 1-Octene, II: 1,9-decadiene, III: 1-octanol, IV: 1,12-dodecanediol.

The effect of the addition of H_2SO_4 or H_3PO_4 to the BF_3–H_2O solution is shown in Figs. 2 and 3. The addition of H_2SO_4 accelerates the carbonylation reaction of primary alcohols such as 1-octanol and 1,12-dodecanediol, but is not effective in the reactions of olefins and *s*- or *t*-alcohols. The addition of H_2SO_4 appears to promote the dehydration of primary alcohols. The addition of H_3PO_4 decreases the carboxylic acid yield and the reaction rate.

The catalytic behavior of $Ag(CO)_2^+$ and $Cu(CO)_4^+$ are the same for the carbonylation reactions in BF_3–H_2O.

Experimental

Preparation of $Cu(CO)_n^+$ *and* $Ag(CO)_2^+$ *in* BF_3-H_2O. The BF_3-H_2O solution was preparared by introducing BF_3 gas into water.

In a 300 ml three-necked flask, equipped with a thermometer and a CO gas burette, 572 mg of Cu_2O were placed. The apparatus was evacuated by a vacuum pump and CO was introduced from the gas burette. The mixture was stirred after the addition of BF_3–H_2O. Colorless copper(I) carbonyl ions were formed by the absorption of CO by the Cu_2O.

TABLE 4. CARBONYLATION OF DIENES AND DIOLS[a)]

Compound	Catalyst	Temp, °C	Time, h	Products	Yield, %
1,5-Hexadiene	$Cu(CO)_4^+$	5—10	2	2-Ethyl-4-pentanolide	35
1,7-Octadiene	$Ag(CO)_2^+$	20—30	2	1,4-Dimethylcyclohexanecarboxylic acid	30
				2,2-Dimethyl-4-heptanolide	35
				2,2-Dimethyl-5-heptanolide	8
1,9-Decadiene	$Cu(CO)_4^+$	6—10	2	2,2,7,7-Tetramethyloctanedioic acid	30
				2-Ethyl-2,6,6-trimethylheptanedioic acid	5
				2-Methyl-2-ethyl-4-octanolide	40
				2-Methyl-2-ethyl-5-octanolide	20
1,12-Dodecanediol	$Cu(CO)_4^+$	20—30	3	No reaction	
1,12-Dodecanediol	$Cu(CO)_4^+$	20—25	3	2,2,9,9-Tetramethyldecanedioic acid	30
				2-Ethyl-2,8,8-trimethylnonanedioic acid	10
				1,4- and 1,5-Lactone	45

a) The reactions were carried out using 30 ml of BF_3-H_2O, 6 mmol of Cu_2O or Ag_2O, and 30 mmol of the compound. b) An additional 30 ml of 98% H_2SO_4 were used.

For the preparation of silver carbonyl ions, 928 mg of Ag_2O were placed in a three-necked flask containing ice-cold BF_3–H_2O. Colorless silver carbonyl ions were formed by the absorption of CO by the Ag_2O for a period of 10 min.

Carbonylation of Olefins, Alcohols, and Saturated Hydrocarbons. From a syringe, 20 mmol of an olefin (an alcohols or an equimolar mixture consisting of saturated hydrocarbons and an alkyl cation source) were added drop by drop to the copper(I) carbonyl (or silver carbonyl) catalyst solution. Immediately, carbon monoxide reacted with these compounds. The reaction mixture was poured into ice-water, and the product was extracted with hexane.

The yields of monocarboxylic acid, dicarboxylic acid and lactone in the mixtures were determined as follows. First, a 1/5 volume of an hexane extract of the mixture was titrated with a 1/10 N NaOH ethanol solution to determine the total amount of carboxylic acid. The amount of monocarboxylic acid was determined by gas chromatography in the presence of a known amount of prim-carboxylic acid as an internal standard. The amount of dicarboxylic acid was found from the difference between the total amount of carboxylic acids and the amount of monocarboxylic acid. The amount of lactone was determined by measuring the saponification value as follows. The excess of the 1/10 N NaOH ethanol solution was added to the hexane extract, and the mixture was refluxed for 3 h and then titrated using a standard 1/10 N HCl solution. The amount of lactone was calculated from the difference between the saponification value and the total amount of carboxylic acid. GLPC analysis was performed using a 3-m FFAP column (10% on chromosorb WAW).

All identifications were carried out using authentic samples obtained and characterized previously by the carbonylation of olefins, alcohols, and saturated hydrocarbons in H_2SO_4 systems.[1—3,9)]

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