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Carbonylation of Alcohols, Olefins, and Saturated Hydrocarbons by CO in the Ag(I)-H_2SO_4 System

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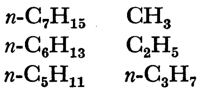
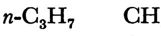
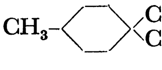
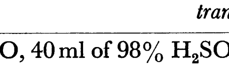
In the presence of an Ag carbonyl-ion catalyst, prepared *in situ* from the Ag compound and carbon monoxide in H_2SO_4, olefins or alcohols reacted with carbon monoxide at room temperature and atmospheric pressure to produce exclusively tertiary carboxylic acids in high yields. The amount of Ag compound sufficient for carrying out the reaction is *ca.* 0.2 mol/l. The optimum reaction temperature is 0—40 °C. The reaction proceeds practically at above a 90% H_2SO_4 concentration. Saturated hydrocarbons, containing a tertiary hydrogen, also reacted with carbon monoxide in the presence of alcohols or olefins as carbonium ion precursors, thus producing tertiary carboxylic acids.

In our previous papers, we have reported the carbonylation reactions of olefins,[1)] alcohols,[2)] and saturated hydrocarbons[3)] by the catalysis of the Cu(I) carbonyl ion[4)] to produce tertiary carboxylic acids in high yields at room temperature and atmospheric pressure. The present investigation will deal with the use of the Ag compound as a catalyst for the same reaction.

Results

Olefins or alcohols react with carbon monoxide in the presence of the Ag carbonyl ion catalyst in a concd H_2SO_4 solution at room temperature and atmospheric pressure to produce tertiary carboxylic acids exclusively, because olefins or alcohols are protonated and rearrange to the most stable tertiary carbonium ion prior to the carbonylation. The results are shown in Table 1.

Table 1. Carbonylation of olefin or alcohol[a)]

Substrates	Temp. (°C)	Time (min)	Products  $R_1-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle R_2}{\vert}}{C}}-COOH$ R_1	R_2	Yield (%)
1-Hexene	30	40	n-C_3H_7	CH_3	80
			C_2H_5	C_2H_5	16
1-Octene	30	40	n-C_5H_{11}	CH_3	61
			n-C_4H_9	C_2H_5	24
			n-C_3H_7	n-C_3H_7	12
1-Decene	30	60	n-C_7H_{15}	CH_3	60
			n-C_6H_{13}	C_2H_5	24
			n-C_5H_{11}	n-C_3H_7	10
Cyclohexene	10—12	55			84
1-Butanol	30	3 hr	CH_3	CH_3	29
			C_2H_5	H	17
1-Hexanol	30	2 hr	n-C_3H_7	CH_3	79
			C_2H_5	C_2H_5	19
Cyclohexanol	30	1 hr			81
2,5-Dimethyl-cyclohexanol	30	1 hr			*cis* 33 *trans* 33

a) In all cases, 8 mmol of Ag_2O, 40 ml of 98% H_2SO_4, and 20 mmol of olefins or alcohols were used. The pressure of carbon monoxide was 1 atm.

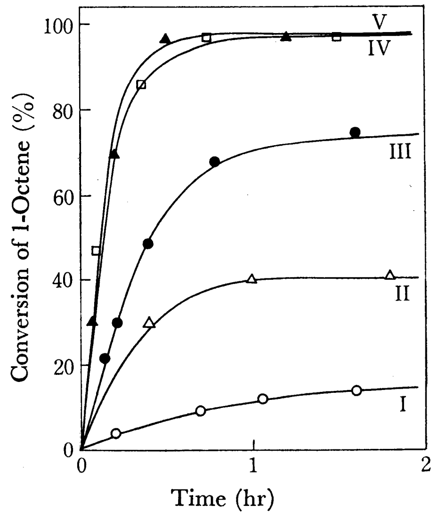


Fig. 1. The catalytic effect of Ag_2O.
1-Octene 5 mmol and 98% H_2SO_4 10 ml were used at 30 °C.
I: Ag_2O 0 mmol, II: Ag_2O 0.1 mmol, III: Ag_2O 1 mmol, IV: Ag_2O 2 mmol, V: Ag_2O 4 mmol.

The effect of the amount of Ag compound is illustrated in Fig. 1. Without Ag_2O, the rate of reaction is very slow and the yield of carboxylic acid is less than 15%. When Ag_2O is added in concd H_2SO_4, the rate of reaction and the yield increase considerably. The amount of Ag_2O sufficient for carrying out carbonylation is *ca.* 0.2 mol/l. In concd. H_2SO_4, the polymerization reaction proceeds in competition with the carbonylation reaction of olefin. When the amount of Ag_2O is not enough, the CO concentration enriched by Ag^+ in the solution is not sufficient for its reaction with the carbonium ion. Therefore, polymerization predominates over carbonylation.

Saturated hydrocarbons bearing tertiary hydrogen also react with carbon monoxide in the presence of olefins or alcohols, which form carbonium ions and which can abstract hydride from branched hydrocarbons. The results are shown in Table 2. The added olefins or alcohols in the reaction mixture also yield tertiary carboxylic acid.

As shown in Table 3, the effect of the H_2SO_4 concentration upon the carbonylation is parallel to its

TABLE 2. THE CARBONYLATION OF SATURATED HYDROCARBON IN THE PRESENCE OF OLEFIN OR ALCOHOL[a]

Substrates	Olefin or alcohol	Reaction time (min)	Products	Yield (%)
Methylcyclohexane	1-Hexene	40	Methylcyclohexanecarboxylic acid	45
			tert-C_7 acids	33
Methylcyclohexane	1-Hexanol	90	Methylcyclohexanecarboxylic acid	42
			tert-C_7 acids	31
Methylcyclohexane	1-Octene	60	Methylcyclohexanecarboxylic acid	72
			tert-C_9 acids	23
1,4-Dimethylcyclohexane	1-Octene	60	1,4-Dimethylcyclohexanecarboxylic acid (*cis*: *trans*=1: 1)	60
			tert-C_9 acids	30
Methylcyclopentane	1-Octanol	120	Methylcyclopentanecarboxylic acid	60
			tert-C_9 acids	27
n-Octane	1-Hexanol	90	*tert*-C_9 acids	0
			tert-C_7 acids	75

a) In all cases, 1.856 g of Ag_2O, 40 ml of 98% H_2SO_4, 20 mmol of saturated hydrocarbons, and 20 mmol of olefins (or alcohols) were used. The reaction temperature was approximately 30 °C. The CO pressure was 1 atm. The components of *tert*-C_7 acids and *tert*-C_9 acids were the same as in Table 1.

effect upon the formation of the unstable Ag carbonyl ion, $Ag(CO)_n^+$, in the H_2SO_4 solution. As was shown in our previous paper, Ag^+ does not absorb carbon monoxide in H_2SO_4 of less than an 80% concentration.

TABLE 3. THE EFFECT OF THE H_2SO_4 CONCENTRATION UPON THE CARBONYLATION[a]

Concn of H_2SO_4 (wt%)	$Ag(CO)^+/Ag^+$ mol ratio	Conversion of 1-octene, %	Reaction time (min)
100	0.14	97	20[b]
95	0.07	90	25[b]
90	0.04	80	90[c]
85	0.01	17	150[c]
80	0	0	—

a) 0.928 g of Ag_2O, 1.57 ml of 1-octene, and 20 ml of H_2SO_4 were used at 30°C. The 1-octene was added drop by drop in order to prevent polymerization. b) In concd H_2SO_4, 1-octene reacted with CO immediately after the addition of 1-octene. c) The reaction rate became slower when the concentration of H_2SO_4 was less than 90%.

It seems that Ag compounds form the unstable Ag carbonyl ion by absorbing carbon monoxide in concd H_2SO_4, as in the case of the Cu(I) carbonyl ion:[5]

$$Ag^+ + nCO \overset{H_2SO_4}{\rightleftarrows} Ag(CO)_n^+ \qquad n=1\sim2$$

The $Ag(CO)_n^+$ is very unstable, and in the presence of such CO acceptors as carbonium ions, CO is liberated from $Ag(CO)_n^+$ and combines with the carbonium ion immediately. That Ag^+ seems to act as a CO carrier to keep a high CO concentration in solution.

Among the compounds, Ag_2O, Ag_2SO_4, and $AgClO_4$ are effective in this reaction. On the other hand, AgCl, AgBr, AgI, and AgCN do not show any catalytic activity. The presence of the halogen atom and CN^- may be supposed to prevent the formation of silver carbonyl ions.

The influence of the reaction temperature was also studied. The results are shown in Table 4.

1-Hexanol reacts with carbon monoxide at 0—30 °C and gives tertiary C_7 carboxylic acids in high yields. The rate of reaction becomes rapid with an increase in the temperature. A linear relationship between $\log k$ and $1/T$ was observed. However, the total yield of carboxylic acids and the proportion of tertiary C_7 carboxylic acid decrease with the increase in the temperature. The explanation of this is that the formation of unstable silver carbonyl ion decreases and the polymerization predominates over carbonylation. In addition, the β scission of carbonium ions begins to proceed with the increase in the temperature. In the reaction of 1-hexene or cyclohexene, the influence of the temperature is almost the same as that in the case of 1-hexanol. However, the rate of reaction is very rapid

TABLE 4. THE INFLUENCE OF THE TEMPERATURE ON THE REACTION OF 1-HEXANOL[a]

Reaction temp., °C	The total yield of carboxylic acids, %	The component of carboxylic acids				Rate constant $k\times 10_5\,s^{-1}$ [b]	$\frac{Ag(CO)^+}{Ag}$
		t-C_5	*t*-C_6	*t*-C_7	higher acids		
0	99	0	0	100	0	2.78	0.37
10	99	0	0	100	0	4.63	0.30
30	99	0	1	99	0	18.50	0.14
40	83	7	10	77	6	56.0	0.08
55	32	57	25	15	3	—[c]	0.02

a) 1-Hexanol (10 mmol), Ag_2O (4 mmol), and 98% H_2SO_4 (20 ml) were used. b) The first-order rate constant was calculated from $-d[ROH]/dt=k[ROH]$. c) The rate constant could not be measured because the rate of reaction was too rapid and because the reaction proceeded immediately after the addition of 1-hexanol.

and depends on the rate of the addition of the reactant. The reactant must be added drop by drop to prevent polymerization.

Experimental

Preparation of the Ag Carbonyl Catalyst Solution. In a 300 ml three-necked flask, equipped with a thermometer and a CO gas buret, we placed 1.856 g of Ag_2O and 40 ml of 98% H_2SO_4. The apparatus was evacuated by means of a vacuum pump to remove the air, and then carbon monoxide was introduced from the gas buret. When the mixture was stirred, CO was absorbed by the Ag^+ solution in 10 min.

Carbonylation of Olefins, Alcohols, and Saturated Hydrocarbons. From a syringe, 20 mmol portion of olefins (or alcohols or equimolar mixtures of saturated hydrocarbons and alkylcation sources) was added, drop by drop, to the Ag carbonyl catalyst solution. The carbon monoxide was soon absorbed. After the reaction, the reaction mixture was poured over ice water, and the products were extracted by benzene. The yield of tertiary carboxylic acid was determined by the titration of the benzene extract with a 1/10 M NaOH ethanol solution, and also by gas chromatography by adding a known amount of the internal standard. Glpc analysis was performed using a 3 m FFAP column (10% on Chromosorb WAW).

All the identifications were carried out using authentic samples which had been obtained and characterized by the carbonylation of olefins, alcohols, or saturated hydrocarbons using a Cu(I) carbonyl catalyst.[1-3] The ratios of each isomer of *tert*-C_9 acids and *tert*-C_{11} acids were determined by ^{13}C NMR according to the method described in a previous paper.[2]

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