The Carbonylation of Alcohols Catalyzed by Cu(I) Carbonyl

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In conc. H_2SO_4 containing the Cu(I) compound, alcohols react with carbon monoxide at room temperature and atmospheric pressure to produce *tert*-carboxylic acids in high yields. Primary carboxylic acid is not formed. It is assumed that the unstable Cu(I) tricarbonyl ion, $Cu(CO)_3^+$, is transiently formed in conc. H_2SO_4. An amount of the Cu(I) compound as small as 0.2 mol/l is sufficient. The catalyst is effective at H_2SO_4 concentrations above 80%. The reaction rate decreases with a decrease in the H_2SO_4 concentration. At H_2SO_4 concentrations of less than 80%, no carboxylic acids are obtained.

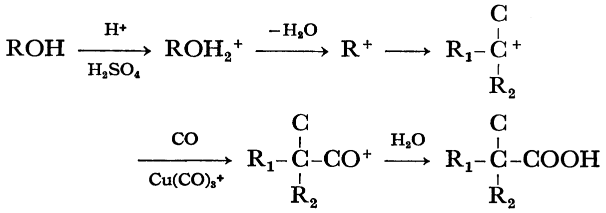
Many attempts to obtain carboxylic acid from alcohol and carbon monoxide have been made. Reppe *et al.*[1] reported the carbonylation of alcohols with the nickel carbonyl catalyst to give mixtures of straight-chain carboxylic acids and branched carboxylic acids. Adkins and Rosenthal[2] suggested that a possible course of the reaction was the dehydration of the alcohol to an olefin. These reactions proceed at high temperatures and under high pressures. Eidus *et al.*[3] reported the carbonylation of alcohols using an acid catalyst such as H_2SO_4 or H_3PO_4. Even in this reaction, however, an elevated pressure of carbon monoxide is necessary. Koch and Haff[4] reported the synthesis of branched carboxylic acids from alcohols using formic acid in conc. H_2SO_4.

To carry out the carbonylation reaction under mild conditions, the present authors previously attempted the use of the Cu(I) carbonyl catalyst, prepared from Cu(I) compounds and carbon monoxide in conc. H_2SO_4.[5] The unstable Cu(I) tricarbonyl ion, $Cu(CO)_3^+$, acts as a catalyst for this carbonylation reaction. The carbonylation of olefin using the Cu(I) catalyst was reported; *tert*-carboxylic acids were thus obtained in high yields.[6]

In this report, the carbonylation of alcohol using the Cu(I) carbonyl catalyst was studied at room temperature and atmospheric pressure. Reactions using the Cu(I) carbonyl catalyst will prove of wide-ranging synthetic utility for carbonylation reactions.

Results and Discussion

The results of the carbonylation of alcohols using the Cu(I) carbonyl catalyst are shown in Table 1. Various alcohols (normal, secondary, and tertiary alcohols) are converted to *tert*-carboxylic acids in high yields. Alcohol is protonated and dehydrated to the carbonium ion, which rearranges to the stable tertiary carbonium ion prior to the carbonylation. Hence, no primary carboxylic acid is obtained.



$$ROH \xrightarrow[H_2SO_4]{H^+} ROH_2^+ \xrightarrow{-H_2O} R^+ \longrightarrow R_1\text{-}\begin{array}{c}C\\|\\C^+\\|\\R_2\end{array}$$

$$\xrightarrow[Cu(CO)_3^+]{CO} R_1\text{-}\begin{array}{c}C\\|\\C\text{-}CO^+\\|\\R_2\end{array} \xrightarrow{H_2O} R_1\text{-}\begin{array}{c}C\\|\\C\text{-}COOH\\|\\R_2\end{array}$$

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

$R_2=H$, CH_3, C_2H_5, n-C_3H_7

The structures of the products were determined by a study of their NMR, IR, and mass spectra as well as by elemental analysis. In most cases, the products were mixtures of the isomers. When the mixtures were easily separable by glpc, each isomer was isolated by preparative glpc and was subjected to structure analysis. When the separation was not easy by glpc, the mixture was analyzed by means of ^{13}C NMR.

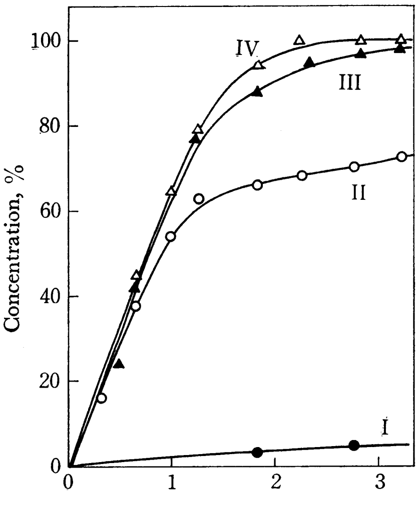


Fig. 1. Catalytic effect of Cu_2O.
98% H_2SO_4 10.5 ml and 1-hexanol 1.24 ml (10 mmol) at 30°
I: Cu_2O 0 mmol, II: Cu_2O 0.1 mmol, III: Cu_2O 1 mmol
IV: Cu_2O 4 mmol

Cuprous oxide was used as the Cu(I) compound. The effect of the amount of cuprous oxide is illustrated in Fig. 1. Without cuprous oxide, the rate of the reaction was very slow, and the yield of carboxylic acid was less than 10% after 3 hr. When cuprous oxide was added in conc. H_2SO_4, the rate of the reaction increased rapidly, and *tert*-carboxylic acid was obtained in a high yield.

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[1] W. Peppe, H. Kroper, N. Kutepow, and H. J. Pistor, *Ann. Chem.*, **582**, 72 (1953).

[2] H. Adkins and R. W. Rosenthal, *J. Amer. Chem. Soc.*, **72**, 4550 (1950).

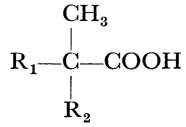
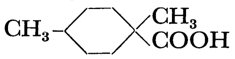
[3] Ya. T. Eidus, K. V. Puzitskii, and S. D. Pirozhkov, *Neftekhimiya*, **8**, 343 (1968).

[4] H. Koch and W. Haff, *Ann. Chem.*, **618**, 251 (1958).

[5] Y. Souma and H. Sano, *Nippon Kagaku Zasshi*, **91**, 625 (1970).

[6] Y. Souma and H. Sano, *J. Org. Chem.*, **38**, 2016 (1973).

TABLE 1. *tert*-CARBOXYLIC ACIDS DERIVED FROM ALCOHOLS AND CARBON MONOXIDE[a)]

Alcohol	 $R_1-\overset{\displaystyle CH_3}{\underset{\displaystyle R_2}{C}}-COOH$		Yield (%)
	R_1	R_2	
1-Propanol[b)]	CH_3	H	15
2-Propanol[b)]	CH_3	H	18
1-Butanol[b)]	CH_3	CH_3	22
	C_2H_5	H	23
2-Methylpropanol[b)]	CH_3	CH_3	56
2-Methyl-2-propanol[b)]	CH_3	CH_3	52
2-Butanol[b)]	CH_3	CH_3	28
	C_2H_5	H	19
1-Pentanol	C_2H_5	CH_3	62
1,1-Dimethylpropanol	C_2H_5	CH_3	30
	CH_3	CH_3	24
	C_3H_5	CH_3	7
	Other acids		8
1-Hexanol	C_3H_5	CH_3	60
	C_2H_5	C_2H_5	25
	C_2H_5	CH_3	4
	CH_3	CH_3	2
2-Hexanol	C_3H_5	CH_3	55
	C_2H_5	C_2H_5	38
	C_2H_5	CH_3	3
	CH_3	CH_3	1
4-Methyl-2-pentanol	C_3H_5	CH_3	56
	C_2H_5	C_2H_5	28
	Other acids		9
3-Methyl-3-pentanol	C_3H_5	CH_3	26
	C_2H_5	C_2H_5	30
	C_2H_5	CH_3	20
	CH_3	CH_3	10
Cyclohexanol			80
1-Octanol	n-C_5H_{11}	CH_3	72
	n-C_4H_9	C_2H_5	15
	n-C_3H_7	n-C_3H_7	5
2-Octanol	n-C_5H_{11}	CH_3	55
	n-C_4H_9	C_2H_5	30
	n-C_3H_7	n-C_3H_7	10
1-Decanol	n-C_7H_{15}	CH_3	75
	n-C_6H_{13}	C_2H_5	15
	n-C_5H_{11}	n-C_3H_7	5
2,5-Dimethylcyclohexanol			78

a) In most cases, 20 mmol of alcohol, 4 mmol of Cu(I) oxide, and 21 ml of 98 % H_2SO_4 were used, and the reaction temperature was approximately 30°, while the reaction time varied from 1 to 2 hr. The pressure of carbon monoxide was 1 atm.

b) 10 mmol of alcohol was used.

Cuprous oxide absorbs carbon monoxide in conc. H_2SO_4 and forms an equilibrium mixture of Cu(I) carbonyl ions, $Cu(CO)^+$ and $Cu(CO)_3^+$:[5)]

$$Cu_2O + CO \overset{H^+}{\rightleftharpoons} Cu(CO)^+ + Cu(CO)_3^+$$

Only $Cu(CO)_3^+$ acts as a catalyst in the carbonylation reaction. With the absorption of carbon monoxide, the reddish color of cuprous oxide gradually changes to white. Every Cu^+ ion changes to a $Cu(CO)_3^+$ ion in conc. H_2SO_4 at −10 °C, under 7 atm of carbon monoxide. However, $Cu(CO)_3^+$ is unstable, and it exists as an equilibrium mixture with $Cu(CO)^+$ at the atmospheric pressure of carbon monoxide and at room temperature:

$$Cu(CO)_3^+ \rightleftharpoons Cu(CO)^+ + 2CO$$

In the presence of CO acceptors such as carbonium ions, CO is liberated from $Cu(CO)_3^+$ and reacts with the carbonium ion immediately. Carbon monoxide is continuously absorbed by the $Cu(CO)^+$ in the solution from the gas phase, and a constant amount of $Cu(CO)_3^+$, which acts as a catalyst, exists in conc. H_2SO_4. In the reaction system, Cu^+ acts as a "CO carrier" from the gas phase to the reaction species in the solution.

TABLE 2. THE EFFECT OF THE H_2SO_4 CONCENTRATION UPON THE CARBONYLATION[a)]

H_2SO_4 concn		Conversion of alcohol (%)		
Wt.%	Mole ratio H_2O/H_2SO_4	1-Hexanol	2-Hexanol	3-Methyl-3-pentanol
100.0	0.0	91	90	90
98.2	0.10	50	90	90
95.6	0.25	28	90	90
91.5	0.50	8	74	89
88.0	0.75		31	47
84.4	1.00		10	21
73.0	2.00		0	0

a) In most cases, 10.5 ml of H_2SO_4, 0.286 g of Cu_2O, and 1.25 ml of alcohol were used. The reaction temperature was 30°C, and the reaction time was 3 hr.

The influence of the H_2SO_4 concentration upon the carbonylation was also examined. The results are shown in Table 2. With the increase in the concentration above 80%, the reaction rate and the yield increased. No carboxylic acid was obtained at concentrations below 80%.

As to Cu(I) carbonyl, only $Cu(CO)^+$ exists in H_2SO_4 concentrations below 80%. It is known that $Cu(CO)_3^+/Cu(CO)^+$ gradually increases with an increase in the H_2SO_4 concentration above 80%.[5)] The effect of the H_2SO_4 concentration upon the carbonylation is parallel with the effect upon the formation of the unstable $Cu(CO)_3^+$ in the system.

Alcohol was added slowly to the Cu(I) carbonyl suspension. The absorption of carbon monoxide by the alcohol was then measured. The results are shown in Fig. 2. Among normal, secondary, and tertiary alcohols, the rates of CO absorption are different at every H_2SO_4 concentration (100, 91.5, and 84.4%). The rate increases in the following order; normal<secondary<tertiary. In normal alcohol, dehydration is difficult compared with that in secondary or tertiary alcohols. In 91.5% H_2SO_4 and 84.4% H_2SO_4, the rate of CO absorption became slower. This shows that dehydration and isomerization become more difficult with the decrease in the H_2SO_4 concentration. Roebuck and Evering studied the relation between the isomerization of the alkyl cation and the H_2SO_4 concentration,

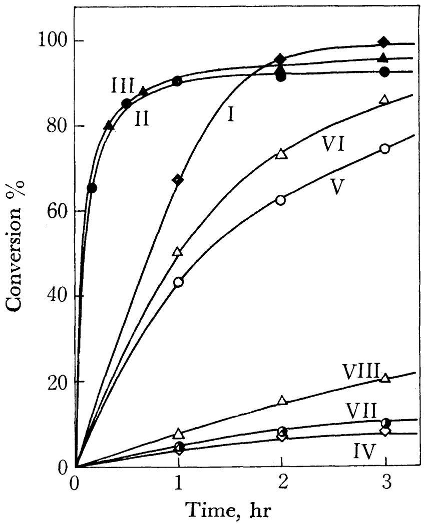


Fig. 2. The rate of CO absorption by alcohols (*n*, *sec*, *tert*). Alcohols (10 mmol) and H_2SO_4 (10 ml) were used at 30°. I: 1-hexanol in 100% H_2SO_4, II: 2-hexanol in 100% H_2SO_4, III: 3-methyl-3-pentanol in 100% H_2SO_4, IV: 1-hexanol in 91.5% H_2SO_4, V: 2-hexanol in 91.5% H_2SO_4, VI: 3-methyl-3-pentanol in 91.5% H_2SO_4, VII: 2-hexanol in 84.4% H_2SO_4, VIII: 3-methyl-3-pentanol in 84.4% H_2SO_4.

and reported that increasing the initial acid concentration from 95.5 to 99.8% increased the rate of isomerization as much as 64 fold.[7)]

In the carbonylation of 3-methyl-3-pentanol, considerable amounts of 2,2-dimethylbutanoic acid and 2,2-dimethylpropionic acid are obtained as by-products. Möller[8)] and Yoneda *et al.*[9)] reported the same type of reactions. They explained the reaction as the disproportionation of the dimerized alkyl group in strong acid. On the other hand, Olah and Lukas[10)] reported the formation of a very stable *tert*-butyl cation from C_5—C_{16} alkanes in a very strong acid medium at room temperature.

The effect of the amount of alcohol on the yield of *tert*-carboxylic acid was studied in the presence of constant amounts of 98% H_2SO_4 and Cu_2O. The results are shown in Table 3. When the amount of alcohol increases, the rate of reaction becomes very slow, and the yield of carboxylic acid decreases.

TABLE 3. THE EFFECT OF THE AMOUNT OF ALCOHOL ON THE YIELD OF *tert*-CARBOXYLIC ACID[a)]

1-Hexanol	98% H_2SO_4	Mole ratio 1-hexanol/ H_2SO_4	Yield of *tert*-C_7 acid
1.24 ml(10 mmol)	10.5 ml(200 mmol)	0.05	85%
2.24 (18 mmol)		0.09	79
5.24 (42 mmol)		0.21	53
7.24 (58 mmol)		0.29	41

a) The reaction temperature was 30°C, and 0.286 g of Cu_2O was used.

Experimental

The infrared spectra were taken as neat samples on a Hitachi EPI-S2 apparatus. The ^1H NMR spectra were taken on a JEOL PS-100 apparatus at 100 MHz in the CCl_4 solvent. The chemical shifts are given in δ units (ppm) downfield from the internal TMS. The mass spectra were measured on the Shimadzu-LKB-9000 gaschromatograph-mass spectrometer with a 70 eV ionizing current. The glpc analyses were performed using a 3 m FFAP column (10% on Chromosorb WAW). The elemental analyses were done on a Yanagimoto CHN MT-2 apparatus.

All the alcohols used in the experiment were commercial reagents and were purified by distillation. The Cu_2O, H_2SO_4, and carbon monoxide were all commercial reagents and were used without further purification.

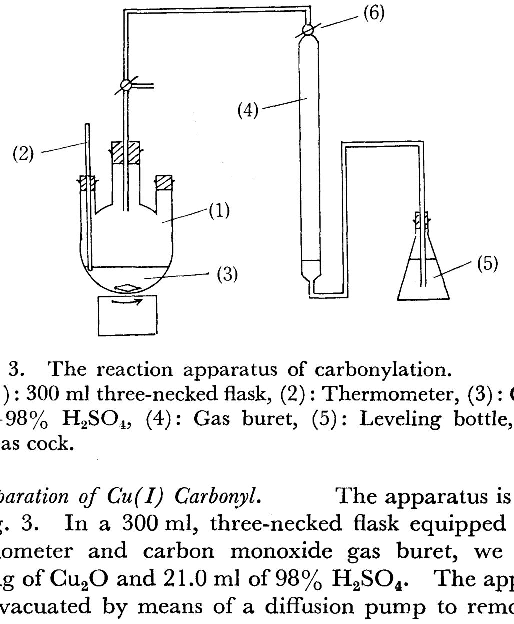


Fig. 3. The reaction apparatus of carbonylation.
(1): 300 ml three-necked flask, (2): Thermometer, (3): Cu_2O +98% H_2SO_4, (4): Gas buret, (5): Leveling bottle, (6): Gas cock.

Preparation of Cu(I) Carbonyl. The apparatus is shown in Fig. 3. In a 300 ml, three-necked flask equipped with a thermometer and carbon monoxide gas buret, we placed 572 mg of Cu_2O and 21.0 ml of 98% H_2SO_4. The apparatus was evacuated by means of a diffusion pump to remove the air; then carbon monoxide was introduced from the gas buret. The mixture of Cu_2O and H_2SO_4 was then stirred vigorously. The carbon monoxide was absorbed by the Cu^+ in about 40 min. The CO/Cu^+ ratio reached 1.35 at 30°, CO 1 atm.

Carbonylation of Alcohol. By a syringe, 20 mmol of alcohol was added, drop by drop, to a Cu(I)-carbonyl suspension over a 20 min. The CO absorption by alcohol finished in from 1 to 3hr. The amount of CO absorption was measured using a CO gas buret. The amount of the conversion of alcohol to acid is equal to that of the CO absorption. The reaction mixture was then poured over ice-water. The products were extracted by benzene, and excess alkali was added to the benzene extract. The aqueous phase was acidified by H_2SO_4. The carboxylic acid was then again extracted by the use of benzene. In order to determine the yield of *tert*-carboxylic acid, a 1/10 volume of the benzene extract was titrated with a 1/10M NaOH ethanol solution. The yield of the carboxylic acid was also determined by gas chromatography by adding a known amount of the internal standard.

1,4-Dimethylcyclohexanecarboxylic Acid. This was obtained by the carbonylation of 2,5-dimethylcyclohexanol. The *cis* and *trans* isomers were separated by preparative glpc, the *trans* isomer as a white solid and the *cis* isomer as a liquid component. (lit,[4,11)]) Bp 135—137°C/16—20 mmHg;

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7) A. K. Roebuck and B. L. Evering, *J. Amer. Chem. Soc.*, **75**, 1631 (1953). H. Pines and N. E. Hoffmann, "Friedel-Crafts and Related Reactions," Vol. II, part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., (1964) Chapter 28.

8) K. E. Möller, *Brennst. Chem.*, **45**, 129 (1964).

9) T. Yoneda, Y. Matsushima, M. Matsubara, and H. Otsuka, *Nippon Kagaku Kaishi*, **1972**, 1475.

10) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227, 4739 (1967).

$n_D^{25}=1.4576$.

trans-Isomer. Mp 69°; IR (cm^{-1}) 2950, 1703 (C=O), 1458, 1235, 1178; NMR δ 0.90 (d, 3, $J=6$ Hz, $\mathrm{C\underline{H}_3}$-$\overset{|}{\mathrm{C}}\mathrm{H}$), 1.22 (s, 3, $\mathrm{C\underline{H}_3}$-$\overset{|}{\mathrm{C}}$-COOH) 1.64 (m, 4, -$\mathrm{CH_2}$-), 0.70—1.26 (m, 3, -$\mathrm{\underline{H}}\overset{|}{\mathrm{C}}\mathrm{H}$, -$\overset{|}{\mathrm{C}}\mathrm{\underline{H}}$), 2.0—2.40 (m, 2, -$\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{\underline{H}}$), 11.66 (br. s, 1, $\mathrm{COO\underline{H}}$); mass spectrum (70 eV) *m/e* (rel. intensity) 156 (25, M$^+$), 111 (45), 87 (72), 70 (100), 69 (70). Found: C, 69.02; H, 10.09%. Calcd for $\mathrm{C_9H_{16}O_2}$: C, 69.19; H, 10.32%.

cis-Isomer. IR (cm^{-1}) 2950, 1703 (C=O), 1470, 1295, 1130; NMR δ 0.98 (d, 3, $J=7$ Hz, $\mathrm{C\underline{H}_3}$-$\overset{|}{\mathrm{C}}\mathrm{H}$), 1.26 (s, 3, $\mathrm{C\underline{H}_3}$-$\overset{|}{\mathrm{C}}$-COOH), 0.75—1.50 (m, 3, -$\mathrm{\underline{H}}\overset{|}{\mathrm{C}}\mathrm{H}$, -$\mathrm{C\underline{H}}$-), 1.73 (m, 6, -$\mathrm{C\underline{H}_2}$-), 11.58 (br. s, 1, $\mathrm{COO\underline{H}}$); mass spectrum (70 eV) *m/e* 156 (10, M$^+$), 111 (100), 110 (73), 69 (94), 55 (53). Found: C, 69.25; H, 10.42%. Calcd for $\mathrm{C_9H_{16}O_2}$: C, 69.19; H, 10.32%.

The 2-methylpropionic acid, 2,2-dimethylpropionic acid, 2-methylbutanoic acid, 2,2-dimethylbutanoic acid, 2,2-dimethylpentanoic acid, 2-methyl-2-ethylbutanoic acid, and 1-methylcyclopentanecarboxylic acid were identified by comparing their retention time and "spiking" with those of authentic samples. The authentic samples were obtained by the carbonylation of olefins.[6] The ratios of all the isomers of the *tert*-$\mathrm{C_9}$ and *tert*-$\mathrm{C_{11}}$ carboxylic acids were determined by ^{13}C NMR according to the method described in a previous paper.[6]

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11) W. G. Schindel and R. E. Pincock, *J. Org. Chem.*, **35**, 1789 (1970).