



Koch carbonylation using silver trifluoromethanesulfonate

Hajime Mori,^{*,†} Aya Mori, Qiang Xu and Yoshie Souma*

National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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Abstract—Koch carbonylation was carried out using silver trifluoromethanesulfonate (AgOTf). Tertiary alcohols were transformed into the corresponding carboxylic acids in good yield under carbon monoxide atmosphere (5 MPa: initial pressure) at 150°C. It can be assumed that under these reaction conditions, a strong acid, in which a silver(I) cation participates, would be generated from AgOTf. © 2002 Elsevier Science Ltd. All rights reserved.

The transformation from carbon monoxide with alcohols or olefins and H₂O to carboxylic acids is well known as Koch carbonylation¹ and is a glamorous process from the standpoint of atom economy. Although the reaction is usually carried out under severe conditions such as high CO pressure, high temperature and strong acid media, some modified methods have recently been developed. As milder reaction conditions, we have already found that at ambient temperature and pressure, the Cu(I), Ag(I), Au(I), Pd(I), Pt(I), and Rh(I) carbonyl cations generated in concentrated H₂SO₄ work well as a catalyst for Koch carbonylation.² From both the industrial and environmental points of view, we and other groups have also reported the carbonylation of alcohols over solid acids such as H-zeolite,³ sulfated zirconia,⁴ Nafion-H,⁵ and an acidic ion-exchange resin⁶ and much attention has focused on a convenient and environmentally benign process for Koch carbonylation.

Silver(I) salts have been widely used for the oxidation and the activation of carbon–halogen and carbon–sulfide bonds. Silver trifluoromethanesulfonate (AgOTf) is, in particular, a common reagent for *O*-glycosylation as a promoter and its application for glycoside chemistry has been significantly explored.⁷ Compared with the application described above, the utilization of AgOTf for acid-catalyzed reactions⁸ is quite limited, although the recent report on the enantioselective aldol

reaction catalyzed by the BINAP–AgOTf complex shows remarkable progress for its application.⁹ During the investigation of a new process for Koch carbonylation, we found that the carbonylation using a catalytic amount of AgOTf smoothly proceeded and AgOTf, weak and soft Lewis acid, gave better results than the common hard Lewis acids. Furthermore in this process no workup operation such as extraction and neutralization was required to obtain carboxylic acids, similar to the previous study using solid acids.^{3–5} In this report, as a new application of AgOTf and a novel and convenient process for Koch carbonylation, we describe the carbonylation of alcohols or olefins and H₂O with carbon monoxide over AgOTf to form carboxylic acids.

The activity of various Lewis acids for the conversion of *tert*-butyl alcohol to pivalic acid, was first investigated. The reaction was carried out in a stainless steel autoclave at 150°C under carbon monoxide (5 MPa: initial pressure) atmosphere for 18 h using hexane as the solvent. The obtained results are summarized in Table 1. The highest yield of carboxylic acids was achieved using AgOTf, while the other silver salts (AgOAc and Ag₂SO₄) completely lacked any catalytic activity (entries 1–3). These results suggest that the acidity of the conjugated acid of the silver salts would be of great importance. Among the common hard Lewis acids, BF₃·Et₂O gave moderate results, while AlCl₃ and TiCl₄ were inert for this reaction (entries 4–7). The Lewis acidity did not directly affect the yield of the carboxylic acids. The active species generated in situ from AgOTf will be discussed below.

The additives significantly contributed to the carbonylation (Table 2). Thus, the addition of 5 mmol H₂O, which promotes the formation of carboxylic acids from

Keywords: Koch reaction; silver trifluoromethanesulfonate; *tert*-carboxylic acid.

* Corresponding authors. Tel.: +81-73-477-1271; fax: +81-73-477-2880; e-mail: hmori@wakayama-kg.go.jp

† Present address: Industrial Technology Center of Wakayama Prefecture, Ogura 60, Wakayama 649-6261, Japan.

Table 1. Yield of carboxylic acids from *tert*-butyl alcohol over various Lewis acids^a

Entry	Catalysts	Yield of carboxylic acids/%			Selectivity ^d /%
		Total ^b		Pivalic acid ^c	
		Total ^b	Pivalic acid ^c		
1	AgOTf	26.5	23.4	88	
2	AgOAc	0	0	—	
3	Ag ₂ SO ₄	0	0	—	
4	BF ₃ ·Et ₂ O	15	11.6	77	
5	TiCl ₄	1	—	—	
6	AlCl ₃	1	—	—	
7	Sn(OTf) ₂	4.3	3.3	77	

^a Reaction conditions: 120 mL autoclave, *tert*-butyl alcohol (5 mmol), catalyst (1 mmol). Hexane (50 mL), CO (5 MPa; initial pressure), 150°C, 18 h.

^b Titration yield of total carboxylic acids.

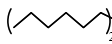
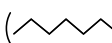










^c GC yield.

^d 100×(yield of pivalic acid/yield of total carboxylic acids).

the intermediate acyl cation rather than the oligomerization of *iso*-butene produced by dehydration of *tert*-butyl alcohol, improved the yields of the carboxylic acids, and even the addition of 15 mmol H₂O, which is the 15 times amount of AgOTf, did not significantly degrade the catalytic activity (entries 2 and 3, Table 2). Furthermore, the reaction under 0.1 MPa air and 4.9 MPa carbon monoxide doubled the yields of the carboxylic acids (entry 4). This remarkable effect would result from the participation of molecular oxygen during the reoxidation of the silver salts, which are reduced under reducing atmosphere. Unfortunately, synergism between H₂O and air did not appear (entry 5).

The effect of solvents was also examined under the same reaction conditions (no additive) and it was found that the employment of the halogen-containing solvent CH₂Cl₂ caused little decrease of the yield of total carboxylic acids (22.8%) and a low selectivity of pivalic acid (25%). Variation of the reaction temperature (120–

Table 3. Results of the carbonylation of various alcohols and olefins over AgOTf^a

Entry	Subs.	Main Product	Yield of products /%	
			Main product	Total carboxylic acids ^g
1	1-Hexanol		72 ^e	—
2	1-Octanol		65 ^e	—
3	2-Butanol	—	—	—
4	2-Hexanol	—	—	—
5 ^{b,c}			44 ^f	56
6 ^{b,c}			64 ^e	69
7 ^{b,c}			35 ^f	46
8 ^{b,d}			14 ^f	27
9 ^{b,d}			10 ^f	13

^a Reaction conditions: 120-mL autoclave, substrates (20 mmol), AgOTf (1 mmol), Hexane (50 mL), CO (5 MPa; initial pressure), 150 °C, 18 hrs,

^b Substrates (5 mmol), ^c Carried out under 0.1 MPa air and 4.9 MPa CO.

^d In the presence of 5 mmol H₂O. ^e Isolated yields, ^f GC yields.

^g Titration yields.

170°C) and the carbon monoxide (1–5 MPa) pressure showed no significant contribution to the yield of the carboxylic acids. The best yield of pivalic acid was achieved at 150°C and 5 MPa carbon monoxide.

In order to evaluate the potential of AgOTf, we carried out the carbonylation with various alcohols and olefins (Table 3). Primary alcohols such as 1-hexanol, 1-octanol and tertiary alcohols such as *tert*-butyl alcohol, 1-adamantanol, and 2-methyl-2-butanol, were transformed into the corresponding ethers and carboxylic acids in good yield, respectively (entries 1, 2 and 5–7). For secondary alcohols, complex mixtures, which contain neither ethers nor carboxylic acids, were obtained (entries 3 and 4). Under the reaction conditions, the alkyl cation, which reacts with carbon monoxide and

Table 2. Additive effect on the carbonylation of *tert*-butyl alcohol^a

Entry	Additives (mmol)	Yield of carboxylic acids/%		Selectivity ^d /%
		Total ^b	Pivalic acid ^c	
1	None	26.5	23.4	88
2	H ₂ O (5)	36.5	30.7	84
3	H ₂ O (15)	24.0	18.4	77
4	Air (0.1 MPa)	55.5	44.0	79
5	Air (0.1 MPa) H ₂ O (5)	54.0	44.8	83

^a Reaction conditions: 120 mL autoclave, *tert*-butyl alcohol (5 mmol), AgOTf (1 mmol), hexane (50 mL), CO (5 MPa; initial pressure), 150°C, 18 h.

^b Titration yield of total carboxylic acids.

^c GC yield.

^d 100×(yield of pivalic acid/yield of total carboxylic acids).

H₂O to form carboxylic acids, was generated only from the tertiary alcohols, while a substitution and an oligomerization were the main reactions for the primary and secondary alcohols, respectively. The results using Nafion-H under similar conditions,⁵ in which the smooth conversion from primary and secondary alcohols to a carboxylic acid was observed, apparently indicate that the acidity of the reaction media would not be enough for the generation of the carbocation from the primary and secondary alcohols. Olefins with an equal amount of H₂O were also converted to the corresponding carboxylic acid under the same reaction conditions, although the yields of the carboxylic acids were lower than that of the alcohol due to the significant oligomerization (entries 8 and 9).

Taking the Lewis acidity of AgOTf into consideration, it is curious that AgOTf was effective for Koch carbonylation which is usually performed under a strong Brønsted-acid media such as concentrated H₂SO₄. In general, silver(I) compounds show an easily reduced character and under the carbon monoxide atmosphere, the generation of a Brønsted-acid from the silver-exchanged zeolites, have already been proposed.¹⁰ Judging from the previous report, in our case, the reduction of AgOTf, which causes the generation of an acid such as trifluoromethanesulfonic acid (TfOH), probably occurred.¹¹ In order to compare the acid generated in situ with TfOH, we carried out the carbonylation of *tert*-butyl alcohol, using TfOH under several reaction conditions (Table 4). Although the reaction using TfOH under the same conditions gave better results than that of AgOTf, the effect of additives was completely different between TfOH and AgOTf. Thus, the addition of water and air was advantageous for AgOTf, while for TfOH the opposite effects due to the additives appeared. Generally speaking, the addition of H₂O, which reduces the acidity of a strong acid, and of air, which causes the side reactions such as oxygenation by molecular oxygen, are unfavorable for Koch carbonylation as shown in the reaction by TfOH. The results obtained here suggest that not trifluoromethanesulfonic acid but an acid, in which a silver(I) cation would participate, would be generated in situ under the reaction media. Ono and co-workers reported that the silver

salts of heteropoly acids supported on silica showed high catalytic activity for the isomerization of hexane in the presence of hydrogen rather than the parent acids,¹² which are commonly used for various acid-catalyzed reactions as a solid acid catalyst. Based on the detailed investigation of their behavior under hydrogen atmosphere, they explained the unique phenomenon that the generation of a Brønsted-acid from the silver salts of heteropoly acids easily occurred and the mobility of protons in them was greater than that in the parent acids. From AgOTf, as described above, a strong acid and reduced silver metal would be generated. Taking the difference between AgOTf and metal oxide clusters on silica into consideration, the mobility of protons is not an important factor in our case. In the presence of air, reduced silver metal would be partly reoxidized to silver(I) cations and the formation of cationic silver(I) carbonyl complexes, which effectively catalyze Koch reaction in H₂SO₄,^{2a} is expected in the reaction media. In fact, the carbonyl complexes were observed by IR measurement in the silver salts of heteropoly acids and the silver-exchanged zeolites under low carbon monoxide pressure.^{10,12,13} Judging from the consideration described above, it seems that in our reaction conditions (4.9 MPa carbon monoxide and 0.1 MPa air), a strong acid produced from AgOTf cooperates with silver(I) carbonyl complexes to catalyze Koch reaction. Although we performed IR measurement to catch the carbonyl complexes generated in situ, any such active species have not been trapped yet. The positive effect of water on the redox behavior of silver cations in silver exchanged zeolites was also reported^{10,13} and in the present case, water would work at the promotion of the formation of carboxylic acids from acyl cation and might contribute to the acceleration of the reduction of a silver(I) cation, along with the formation of a Brønsted-acid.

In conclusion, we have demonstrated the novel application of AgOTf for Koch carbonylation and found that it worked well for the synthesis of *tert*-carboxylic acids from tertiary alcohols and of ethers from primary alcohols. The attempt described here provides a new insight into its use in synthetic organic chemistry.

Table 4. Comparison of the additive effect between AgOTf and TfOH^a

Catalysts	Additives	Yield of carboxylic acids/%		Selectivity ^d /%
		Total ^b	Pivalic acid ^c	
AgOTf	None	26.5	23.4	88
	Air 1 atm	55.5	44.0	79
	H ₂ O (5 mmol)	36.5	30.7	84
CF ₃ SO ₃ H	None	64.5	46.5	72
	Air 1 atm	42.5	31.1	73
	H ₂ O (5 mmol)	23.5	15.9	68

^a Reactions conditions: 120 mL autoclave, *tert*-butyl alcohol (5 mmol), catalyst (1 mmol). Hexane (50 mL). CO (5 MPa: initial pressure), 150°C, 18 h.

^b Titration yield of total carboxylic acids.

^c GC yield.

^d 100×(yield of pivalic acid/yield of total carboxylic acids).

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