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Aerobic oxidation of alcohol in aqueous solution catalyzed by gold

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Abstract—The heterogeneous oxidation catalyzed by supported gold nanoparticles has been relatively well studied. In comparison, the oxidation of alcohols catalyzed by ligand-supported gold complexes was rarely reported. Herein a general method is demonstrated to oxidize secondary and primary benzyl and allylic alcohols to carbonyl compounds via Au(I) catalyzed reaction in air and water. Primary mechanistic studies indicated that the catalytic pathway is different from those catalyzed by solid-supported gold nanoparticles.

1. Introduction

Organic transformation catalyzed by gold species has attracted considerable attention in the past several years.[1] Gold species have been utilized to mediate the formation of C–C bond and C–X (X=O, N) bond starting from alkenes and alkynes.[2] Recently direct functionalization of the C–H bond of electron rich arenes to form new C–C bonds mediated by gold species has also been developed.[3] During all of these processes, gold species has exhibited the dramatically catalytic reactivities as a 'soft' transition metal to initiate these reactions.[1–3] It was believed that gold species can be easily reduced but are difficult to be oxidized, suggesting that the oxidation chemistry catalyzed by gold complexes seems to be difficult to reach due to the necessary change of oxidation states.[1a]

However, this viewpoint has been relatively changed, partly due to many efforts made on the selective oxidation of CO with O_2 catalyzed by solid-supported gold nanoparticles.[4] Some previous results also indicated that gold nanoparticles loaded on different solid supports exhibited unique reactivities in the oxidation of alcohol under basic conditions, whereas the exact mechanism still remains elusive.[5] Meanwhile, selective oxidation via gold catalyzation in homogeneous solution has rarely been reported. Only one case in this field was demonstrated by Hill and co-workers, who first showed the oxidation of sulfide to sulfoxide with dioxygen (O_2) catalyzed by gold(III) salt in aqueous solution.[6] Very recently, we and the others found that alcohols can be selectively oxidized to carbonyl compounds in toluene with O_2 catalyzed by gold(I) complex supported by anionic ligands.[7] During preparation of this manuscript, Tsukuda et al. and Corma et al. independently reported the selective aerobic oxidation of alcohols to carbonyl compounds through different pathways catalyzed by gold nanoparticles.[8] Herein we intend to describe an aerobic oxidation of benzyl and allylic alcohols to carbonyl compounds catalyzed by gold complexes in water.

2. Results and discussion

An intensive literature search indicated that gold(I) complexes can be supported by different bidentated nitrogen ligands. The linear or four coordinated gold(I) complexes can be prepared fairly easily through known processes.[9] Our preliminary results also showed that gold(I) complexes supported by neocuproine (Neo **1**) could catalyze the oxidative cleavage of C=C double bond to produce two carbonyl compounds when TBHP was used as the oxidant.[10] Interestingly, some alcohols could also be oxidized to carbonyl compounds under the same condition with a 1:1 ratio of gold(I)–**1** as a catalyst (Table 1). However, only secondary benzyl alcohols could be oxidized to aryl ketones in excellent conversions and yields (entries 1–4, Table 1). Benzyl alcohol **2e** exhibited poor reactivity and only a small amount of benzaldehyde **3e** was produced with most of the starting materials recovered (entry 5, Table 1). Furthermore, primary and secondary allylic and aliphatic alcohols could not be oxidized at all. Hydrogen peroxide was also utilized as an

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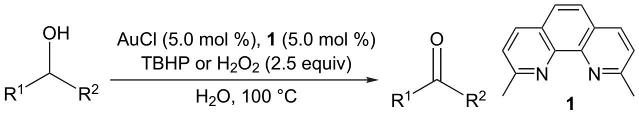
Table 1. Alcohol oxidation with TBHP/H_2O_2 catalyzed by gold(I)[a]



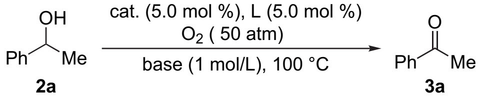
Entry	**2**	R^1	R^2	**3** (%)
1	**2a**	Ph	Me	**3a** 85 (22)
2	**2b**	Ph	Ph	**3b** 98 (72)
3	**2c**	*p*-MeC_6H_4	Me	**3c** 99 (38)
4	**2d**	*p*-BrC_6H_4	Me	**3a** 99 (75)
5[b]	**2e**	Ph	H	**3e** 31 (6)

[a] The yields in parentheses were obtained from the reactions with H_2O_2.
[b] The yields were determined by GC with *n*-decane as internal standard.

oxidant instead of TBHP, however, the efficiency of oxidation was dramatically decreased. Despite the oxidative reactivity of gold complexes toward secondary benzyl alcohols, the utilization of this method is very limited, due to the small scope of successful substrates.

To further explore the new oxidation of alcohol with gold complexes, much more attention was paid to environmentally benign aerobic oxidation.[11] We chose gold(I)–Neo **1** as the catalytic system and the oxidation of 1-phenethanol **2a** under different conditions was screened. The oxidation of 1-phenethanol **2a** was first carried out at 1 atm of air in the presence of 5 mol % of AuCl and **1** in water. Unfortunately, this process could not perform well and only a small amount of **2a** was converted into acetophenone **3a**. Comparably, this oxidation could not run well under an atmospheric pressure of O_2 with AuCl–**1** as catalyst in either the presence or absence of $NaHCO_3$ (Table 2, entries 1 and 2). Increment of the pressure of O_2 to 50 atm did not enhance the yield (Table 2, entry 3). As the references reported, strong basic condition is very important for aerobic oxidation of alcohol catalyzed by gold nanoparticles.[5] However, the use of NaOH (1.0 mol/L) is not very helpful for this oxidation under 1 atm of either air or O_2. Remarkably, the aerobic oxidation of **2a** ran very smoothly when the pressure of oxygen was increased to 50 atm in the presence of 1 M $NaHCO_3$ (Table 2, entry 4). To our surprise, the oxidation could not run very efficiently in the presence of NaOH (1.0 mol/L) under 50 atm of O_2 (Table 2, entry 13). Conversely, organic base, such as Et_3N, was very inefficient for this oxidation (Table 2, entry 14). Moreover, the other nitrogen ligands were also investigated in this reaction. The efficiency of oxidation decreased very obviously with pyridine and bipyridine as ligands (Table 2, entries 5 and 6). Only 1,10-phenanthroline **4** and 4,7-diphenyl-1,10-phenanthroline **5** could play the critical role due to the same scaffold as **1** (Table 2, entries 7 and 8). $AuCl_3$ supported by **1** could also catalyze this oxidation but the efficiency of this reaction was much lower (Table 2, entry 9). Similarly, the oxidation could not perform well under 50 atm of O_2 in the absence of either AuCl or any ligand in water (Table 2, entries 10 and 11). Finally, the catalyst loaded could be decreased to 1.0 mol % and the completion of the oxidation took longer time at higher temperature in order to achieve high yield.

Table 2. Aerobic oxidation of phenethanol under different conditions[a]

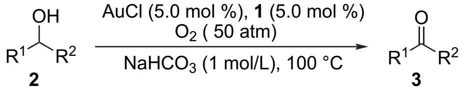


Entry	Cat.	L	Base	**3a**[b] (%)
1[c]	AuCl	**1**	—	<10
2[c]	AuCl	**1**	$NaHCO_3$	<10
3	AuCl	**1**	—	<10
4[d]	AuCl	**1**	$NaHCO_3$	95
5	AuCl	py	$NaHCO_3$	50
6	AuCl	bipy	$NaHCO_3$	60
7[d]	AuCl	**4**	$NaHCO_3$	94
8[d]	AuCl	**5**	$NaHCO_3$	96
9	$AuCl_3$	**1**	$NaHCO_3$	46
10	AuCl	—	$NaHCO_3$	<5
11	—	1	$NaHCO_3$	<10
12[d]	AuCl	**1**	Na_2CO_3	88
13[d]	AuCl	**1**	NaOH	48
14	AuCl	**1**	Et_3N	<10

[a] All the reactions were carried out in the scale of 1 mmol of **2a**.
[b] The yields were determined by GC with *n*-decane as internal standard.
[c] All the reactions were performed under the bubble pressure of dioxygen.
[d] Isolated yields.

Subsequently, the scope of this method was illustrated with a range of secondary benzyl and allylic alcohols under the standard condition (Table 3). With the attachment of different electron donating groups to the phenyl rings, aerobic oxidations ran smoothly and ketones were produced as the sole products in good to excellent yields (Table 3, entries 3 and 6–9). However, the reaction rate was decreased noticeably when electron withdrawing groups, such as nitro, were induced into the phenyl ring and starting materials could not be completely converted into ketones (Table 3, entry 11). It implies that electron density on phenyl ring plays an important role in affecting the reactivity of the substrates. Further studies also indicated that the electronic effect is not the sole factor. The increase of steric hindrance can also observably decrease the efficiency of oxidation. For example, when bulky groups were induced into either aryl part or alkyl part, conversions and yields decreased dramatically (Table 3, comparing entries 9 and 10 with entries 8 and 1). Even when a harsher condition with high pressure of O_2 and high temperature was employed, the oxidation of alcohols bearing

Table 3. Aerobic oxidation of secondary alcohols[a]



Entry	**2**	R^1	R^2	**3**	Yield[b] (%)
1	**2a**	C_6H_5	CH_3	**3a**	99
2	**2b**	C_6H_5	C_6H_5	**3b**	100
3	**2c**	*p*-$CH_3C_6H_4$	CH_3	**3c**	95
4	**2d**	*p*-BrC_6H_4	CH_3	**3d**	100
5	**2f**	*p*-ClC_6H_4	C_6H_5	**3f**	97
6	**2g**	*p*-$CH_3OC_6H_4$	CH_3	**3g**	100
7	**2h**	*p*-$C_4H_9C_6H_4$	*n*-C_4H_9	**3h**	91
8	**2i**	*p*-$CH_3OC_6H_4$	C_2H_5	**3i**	84
9	**2j**	*p*-$CH_3OC_6H_4$	*c*-C_6H_{11}	**3j**	11
10[c]	**2k**	2-$C_{10}H_7$	CH_3	**3k**	58 (84)
11[c]	**2l**	*p*-$NO_2C_6H_4$	CH_3	**3l**	30 (45)
12	**2m**	*trans*-$C_6H_5CH{=}CH$	C_6H_5	**3m**	99

[a] All the reactions were carried out in the scale of 1 mmol of **2**.
[b] Isolated yields.
[c] Isolated yields reported in parentheses were obtained under 60 atm of dioxygen at 120 °C for 48 h.

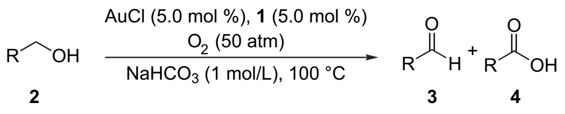
strong electron withdrawing group could not perform completely at all (Table 3, entry 11).

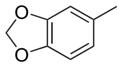
Moreover, the oxidation reactions of primary benzyl and allylic alcohols were studied (Table 4). Under the same conditions, both aldehydes and acids were produced. Similarly, electron donating groups are beneficial to this oxidation and interestingly the aldehydes were observed as major products in most cases (Table 4, entries 1–3). Entry 3 also demonstrated another feature of this reaction, functional group compatibility with allyl phenyl ether, and 3,3-Claisen rearrangement was not observed. One exception was listed in entry 9 with (benzo[*d*][1,3]dioxol-6-yl)methanol with relatively lower yield. When halides were induced into phenyl group, the oxidation still performed well and acids were observed as major products (Table 4, entries 5 and 6). Nevertheless, there are no clear clues to predict the major product from any given substrate. For instance, 4-methylbenzoic acid was obtained in 74% isolated yield with a weak electron donating methyl group on phenyl ring (Table 4, entry 4). Moreover, allylic alcohol could be oxidized to acid in excellent yield under the same condition (Table 4, entry 8).

Previous studies indicated that gold(I) complexes could not catalyze the oxidation smoothly in the absence of either base or O_2. Under the atmosphere of O_2, the oxidation is insufficient under either neutral or basic condition. Studies on relationship between the rate of oxidation and the pressure of oxygen showed us that the reaction is retarded obviously by the pressure of oxygen. On the other hand, the concentration of $NaHCO_3$ is helpful to increase the reaction rate under 50 atm of O_2.

However, strong alkali could obviously decrease the efficiency of oxidation under the same condition. Thus, both the pressure of O_2 and the pH value of the reaction solution are key factors to determine the rate of oxidation. Furthermore, the primary benzyl alcohol showed better reactivity than that of the secondary benzyl alcohol under the same condition. In 2001, Gupta and co-workers reported the oxidation of alcohols with stoichiometric gold(III) salts as oxidants.[12] They have proposed a radical process based on their mechanistic studies. Apparently, all of our primary results indicated that the catalytic process during this oxidation is different from not only the process that Gupta presented, but also the previous reported results catalyzed by gold nanoparticles.[5]

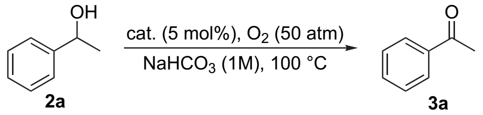
Table 4. Aerobic oxidation of primary alcohols



Entry	2	R	3[a] (%)	4[a] (%)
1	**2e**	C_6H_5	**3e** (81)	**4e** (16)
2	**2n**	*o*-$CH_3OC_6H_4$	**3n** (61)	**4n** (21)
3	**2o**	*p*-AllylOC_6H_4	**3o** (49)	**4o** (35)
4	**2p**	*p*-MeC_6H_4	**3p** (11)	**4p** (74)
5	**2q**	*p*-BrC_6H_4	**3q** (38)	**4q** (54)
6	**2r**	*p*-FC_6H_4	**3r** (0)	**4r** (76)
7	**2s**	2-$C_{10}H_7$	**3s** (51)	**4s** (41)
8	**2t**	*trans*-$C_6H_5CH{=}CH$	**3t** (0)	**4t** (99)
9	**2u**		**3u** (59)	**4u** (13)

[a] Isolated yields.

Furthermore, the oxidation could also perform with the use of some pre-synthesized and more stable gold complexes as catalysts under the completely homogeneous condition (Scheme 1). With the use of 5 mol % of Ph_3PAuCl and [(Neo)$AuPPh_3$]Cl, product **3a** was acquired in 48% and 47% isolated yields, respectively (Scheme 1, entries 1 and 2). Interestingly, when 5 mol % of (THT)AuCl (THT= tetrahydrothiophene) was employed as a catalyst, the oxidation could not run at all because gold complex was obviously decomposed into particles. It implied that gold particles without any support could not catalyze this oxidation under the same condition. Thus, we hypothesized that gold complexes were the efficient catalytic species in solution. Completely understanding this process is still underway in our lab.



entry	cat.	yield (%)[a]
1	Ph_3PAuCl	48%
2	(Neo)$AuPPh_3Cl$	47%
3	(THT)AuCl	<5%

[a] GC yields with *n*-decane as internal standard.

Scheme 1. Oxidation of **2a** catalyzed by stable gold complexes.

3. Conclusion

In summary, we reported the novel and successful process of aerobic oxidation of benzyl and allylic alcohols in aqueous solution with gold complexes as catalysts. A range of alcohols could be oxidized to produce the different carbonyl compounds under the pressure of oxygen in good to excellent yields. Primary mechanistic studies showed that the rate of oxidation was related to the pressure of O_2 and the pH value of the solution. The results also indicated that this catalytic process was mechanistically different from those catalyzed by solid-supported gold nanoparticles, and gold complexes were assumed as catalytic species in solution. Here we contribute to develop new catalytic system of oxidative transformation from alcohol to carbonyl compound based on gold catalyzation. Further studies to probe the mechanism of these transformations, to unambiguously identify the catalytically active species and broaden the scope of these reactions, are currently under investigation and will be reported in due course.

4. Experimental

4.1. General

All reagents were obtained commercially and used without further purification unless otherwise noted. The substrates were commercially available or were prepared according to the literature.[1] Flash chromatographic purification of products was performed on silica gel 200–300 mesh. Thin-layer chromatography (TLC) was performed by visualizing with UV light (245 and 365 nm) or by iodine vapor staining. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on a Varian YH200/300, and are referenced internally according to residual proton solvent signals or internal TMS standard. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), integration. *Caution*: the oxidation of alcohol under 50 atm of O_2 must be carried out in a high-pressure kettle with care.

4.1.1. General procedure for oxidation of alcohols with TBHP as oxidant. Neocuproine (11.0 mg, 0.05 mmol) and 12.0 mg of gold(I) chloride (0.05 mmol) were dissolved into 4 mL of aqueous solution. The corresponding alcohol (1 mmol) was added, followed by 4 equiv of TBHP under air. After the addition, the reaction mixture was heated to 100 °C and stirred for 24 h. The reaction was completed after 24 h in good yield.

4.1.2. General procedure for oxidation of alcohols with AuCl and neocuproine and O_2 as oxidant. To the reactor loaded with 1 mmol of corresponding alcohol, 11.0 mg of neocuproine (0.05 mmol), and 12.0 mg of gold(I) chloride (0.05 mmol) was added 4 mL of 1 M $NaHCO_3$ aqueous solution. The reaction system was degassed three times and refilled by O_2 and kept under O_2 atmosphere at 50 atm pressure. The reaction mixture was heated to 100 °C and stirred for 24 h. The reaction was completed in good yield.

Acknowledgements

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