

Published on Web 10/20/2006

Non-Nanogold Catalysis of Carbon Monoxide Oxidative Amination

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In recent years, numerous papers have described the use of supported nanogold particles for catalysis of the reaction of CO and O₂ to form CO₂, as well as a variety of other reactions.¹⁻³ Several factors control the activities of nanogold catalysts: (a) the size of the Au particle (less than 5 nm), (b) the metal oxide support, (c) the oxidation state of the Au, and (d) the method of catalyst preparation and pretreatment.¹⁻⁷ We recently reported⁸ bulk gold catalysis of the oxidative amination of isocyanides to give carbodiimides according to eq 1. The catalyst was gold powder with a

$$\begin{array}{cccc} R-N \equiv C &+ & NH_2 - R' &+ & \frac{1}{2}O_2 & \xrightarrow{Au} & \\ R-N \equiv C \equiv N - R' &+ & H_2O'' & \end{array}$$
(1)

particle size of approximately 1 μ m (10³ nm). On the basis of studies of the adsorption of isocyanides on the Au powder,⁹ identification of the carbodiimide product, and kinetic studies, we proposed a mechanism (Scheme 1) in which the rate-determining step (a) is amine attack on the adsorbed isocyanide carbon. Intermediate **A** or **B** then reacts by transferring hydrogen atoms to O₂ to give the presumed H₂O byproduct. Step (a) is analogous to the well-known attack of amines on isocyanide ligands in transition metal complexes.¹⁰ It is also known¹¹ that the C=O ligand, which is isoelectronic with isocyanides, is attacked by amines (eq 2) when ν (CO) is greater than

$$_{x}M-C=0 + 2 NH_{2}-R \longrightarrow$$

 $L_{x}M-C' + NH_{3}-R \qquad (2)$
NHR

approximately 2000 cm⁻¹. Although CO is not detectably adsorbed on bulk gold at room temperature,^{1c} CO adsorbed at low temperatures on bulk¹² Au or on Au nanoparticles¹³ gives ν (CO) values of approximately 2100 cm⁻¹, which suggests that CO adsorbed on Au should be susceptible to attack by amines. If the reaction of CO with primary amines were to follow the pathway for the reaction of isocyanides with primary amines and O₂ (eq 1 and Scheme 1), one would expect the product to be an isocyanate (O=C=N-R), which in many cases would react with another primary amine molecule to give the final urea product (eq 3). Herein, we report that this new

$$C=O + NH_2 - R + \frac{1}{2}O_2 \xrightarrow{Au} O=C=N-R + "H_2O" \quad (3)$$
$$O=C(NHR)_2 \xrightarrow{NH_2 - R}$$

reaction of CO does occur, and it is catalyzed by bulk gold powder (\sim 1000 nm particles) that does not have nanosized dimensions, under mild temperatures (45 °C) and at atmospheric pressures of the CO and O₂ gases.

The reactions were performed by stirring (magnetic stir bar) 1.00 g of shiny gold powder with 5 mL of a solution containing 0.50 mmol of the primary amine in a glass tube. Syringe needles attached

Scheme 1



Table 1. Gold Metal-Catalyzed Reactions of Primary Amines with CO and O_2 According to eq 3^a

		Products	
entry	amine/mmol	urea (%)	isocyanate (%)
1	<i>n</i> -BuNH ₂ (0.5)	46	<1, trace
2	s-BuNH ₂ (0.5)	12	0
3	t-BuNH ₂ (0.5)	2	0
4	$PhNH_2(0.5)$	21	3
5	$p-MeC_6H_4NH_2(0.5)$	24	3
6	$o-MeC_6H_4NH_2(0.5)$	11	1
7	$(n-Pr)_2NH(0.5)$	0	
8	PhNH ₂ /(n-Pr) ₂ NH (0.5/0.5)	19^{b}	3, PhNCO
9	n-BuNH ₂ /(n-Pr) ₂ NH (0.5/0.5)	$39^c, 5^d$	0, n-BuNCO
10	<i>n</i> -BuNH ₂ /PhNH ₂ (0.5/0.5)	41 ^d , 25 ^e	trace, <i>n</i> -BuNCO 2, PhNCO

^{*a*} At 45 °C in 5 mL of MeCN solvent for 24 h with 1.00 g of Au powder; CO and O₂ total pressure = ~ 1 atm. ^{*b*} PhNH(C=O)N(*n*-Pr)₂. ^{*c*} (*n*-Bu)NH(C=O)N(*n*-Pr)₂. ^{*d*} (*n*-BuNH)₂CO. ^{*e*} PhNH(C=O)N(*n*-Bu).

to balloons containing an approximately 2.5:1 ratio of CO and O_2 (~1 atm total pressure) were inserted into the septum covering the opening of the tube; the amounts of CO and O_2 were in excess as compared with that of the amines. Products of these reactions (Table 1) were identified by their GC-mass spectra, and the yields were determined by GC using authentic samples of the products as calibrants. Under the standard reaction conditions (1.00 g of Au powder, 45 °C, 24 h, MeCN solvent), the straight chain primary amine *n*-BuNH₂ gives the highest yield (46%) of the urea product; the branched chain amine (*s*-BuNH₂) gives a much lower yield (12%); and *t*-BuNH₂ gives a very low yield (2%). Aniline and *p*-MeC₆H₄NH₂ give 21–24% yields, while *o*-MeC₆H₄NH₂ gives a lower yield (11%). The above results indicate that the highest yields are achieved by the most basic, least sterically hindered aliphatic amines.

We propose that the mechanism (Scheme 2) for reaction 3 is similar to that (Scheme 1) for the reaction of isocyanides with amines and O₂ (eq 1). This proposal is based on evidence for the intermediacy of the isocyanate (R-N=C=O) in reaction 3. Of course, this mechanism requires that secondary amines not give urea, which is observed in the reaction of $(n-Pr)_2NH$ (Table 1, entry 7). On the other hand, when equimolar PhNH₂ and $(n-Pr)_2NH$ are reacted with CO and O₂, a 19% yield of the mixed urea PhNH(C= O)N(n-Pr)₂ is obtained, but diphenylurea ((PhNH)₂C=O) is not formed (entry 8). This result is consistent with the mechanism in



which Ph-N=C=O is formed initially, and it reacts faster with $(n-Pr)_2NH$ than with PhNH₂, a known trend $(R_2NH > RNH_2 >$ $NH_3 > PhNH_2$)¹⁴ in isocyanate reactions with amines. We also find that when 0.10 mmol of PhNCO is reacted in the absence of gold with 0.50 mmol of both (n-Pr)₂NH and PhNH₂ under the conditions in Table 1, the only product is $PhNH(C=O)N(n-Pr)_2$. Also consistent with the intermediacy of an isocyanate is the reaction of equimolar n-BuNH₂ and (n-Pr)₂NH, which gives (entry 9) a ratio (39/5 = 7.8) of the *n*-BuNH(C=O)N(*n*-Pr)₂/(*n*-BuNH)₂C=O products, which is nearly the same as the ratio (7.2) of products obtained from the reaction of 0.10 mmol of n-BuN=C=O with 0.50 mmol of both n-BuNH₂ and (n-Pr)₂NH in the absence of gold under the standard reaction conditions. Also consistent with an isocyanate intermediate is the observation (entry 10) that the reaction of equimolar *n*-BuNH₂ and PhNH₂ gives a yield of (*n*-BuNH)₂C= O (41%) that is higher than that of the mixed urea product PhNH(C=O)NH(n-Bu) (25%), while no (PhNH)₂C=O is produced because of the weakly nucleophilic character of PhNH₂ as compared with n-BuNH₂ in its reaction with the Ph-N=C=O intermediate. Further evidence for the formation of isocyanates as intermediates in reaction 3 is the detection of small amounts of the isocyanates in reactions of the anilines (entries 4-6, 8, and 10).

Bulk gold catalysis of the oxidative amination of carbon monoxide is surprising in view of the long-known low catalytic activity of gold powder for the oxidation of CO.^{1-3,15} We were, therefore, concerned that the powdered gold used in these studies contained some nanogold particles, which were the actual catalyst. Because it is known^{1-3,15} that nanogold catalyzes the reaction of CO and O₂ to form CO₂ even below room temperature, we studied this reaction under the conditions in Table 1; however, no CO₂ (detectable if the yield were even only 0.1%) was produced, which suggests that nanogold is not involved in the catalysis of reaction 3. To check for possible soluble catalytic gold species, a reaction of n-BuNH₂, CO, and O₂ with 1.0 g of Au powder under the standard conditions was stopped after 6 h when the urea yield was 13%. The reaction solution was decanted from the Au powder and put under the standard CO/O2 atmosphere. Reheating the solution to 45 °C and stirring the solution for 15 h gave no additional urea (beyond the 13% produced in the presence of the Au powder). This result indicates that soluble species (ligated nanogold particles or Au complexes) are not the catalytically active species.

An earlier report¹⁶ showed that the reaction of anilines with CO and O_2 to give diaryl ureas was catalyzed by nanogold particles

supported on an anion exchange styrene divinylbenzene polymer (Amberlite IRA-400). However, these reactions were conducted under much more strenuous conditions (175 °C, 4.0 MPa (40 atm) of CO and 1.0 MPa (10 atm) of O_2) than were used in the current studies with gold powder. On the basis of this report, it appears that nanogold is less active as a catalyst in reaction 3 than bulk gold.

Considering the high catalytic activity of bulk gold, we explored the possibility that its less expensive congeners would also be catalysts of reaction 3. However, when 1.0 g of commercial Ag $(2-3.5 \ \mu\text{m})$ or Cu $(1-5 \ \mu\text{m})$ powder was stirred with *n*-BuNH₂ and CO/O₂ under the conditions in Table 1, the *n*-BuNH₂ did not react and no urea product was detected. Although the primary purpose of this communication is to note the high catalytic activity of bulk gold in an oxidative reaction of CO, the application of these results to a practical synthesis of ureas would make more efficient use of the gold metal by supporting it on high surface area materials; this is currently being explored.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences under Contract W-7405-Eng-82 with Iowa State University.

Supporting Information Available: Experimental procedures for the catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA065706T