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Non-Nanogold Catalysis of Carbon Monoxide Oxidative Amination

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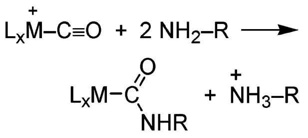
In recent years, numerous papers have described the use of supported nanogold particles for catalysis of the reaction of CO and O_2 to form CO_2, as well as a variety of other reactions.[1−3] Several factors control the activities of nanogold catalysts: (a) the size of the Au particle (less than 5 nm), (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 reported[8] bulk gold catalysis of the oxidative amination of isocyanides to give carbodiimides according to eq 1. The catalyst was gold powder with a

$$\text{R–N}{\equiv}\text{C} + \text{NH}_2\text{–R}' + \tfrac{1}{2}\,\text{O}_2 \xrightarrow{\text{Au}} \text{R–N=C=N–R}' + \text{"H}_2\text{O"} \qquad (1)$$

particle size of approximately 1 μm (10^3 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 O_2 to give the presumed H_2O byproduct. Step (a) is analogous to the well-known attack of amines on isocyanide ligands in transition metal complexes.[10] It is also known[11] that the C≡O ligand, which is isoelectronic with isocyanides, is attacked by amines (eq 2) when ν(CO) is greater than



$$\text{L}_x\overset{+}{\text{M}}\text{–C}{\equiv}\text{O} + 2\,\text{NH}_2\text{–R} \longrightarrow \text{L}_x\text{M–C(=O)NHR} + \overset{+}{\text{N}}\text{H}_3\text{–R} \qquad (2)$$

approximately 2000 cm^{-1}. Although CO is not detectably adsorbed on bulk gold at room temperature,[1c] CO adsorbed at low temperatures on bulk[12] Au or on Au nanoparticles[13] 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 O_2 (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

$$\begin{aligned} &\text{C}{\equiv}\text{O} + \text{NH}_2\text{–R} + \tfrac{1}{2}\,\text{O}_2 \xrightarrow{\text{Au}} \text{O=C=N–R} + \text{"H}_2\text{O"} \\ &\text{O=C(NHR)}_2 \xleftarrow{\text{NH}_2\text{–R}} \text{O=C=N–R} \end{aligned} \qquad (3)$$

reaction of CO does occur, and it is catalyzed by bulk gold powder (∼1000 nm particles) that does not have nanosized dimensions, under mild temperatures (45 °C) and at atmospheric pressures of the CO and O_2 gases.

Scheme 1

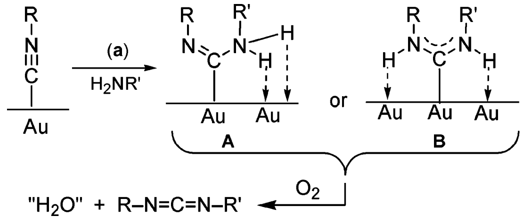


Table 1. Gold Metal-Catalyzed Reactions of Primary Amines with CO and O_2 According to eq 3[a]

entry	amine/mmol	Products urea (%)	 isocyanate (%)
1	n-$BuNH_2$ (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	$(n\text{-Pr})_2NH$ (0.5)	0	
8	$PhNH_2/(n\text{-Pr})_2NH$ (0.5/0.5)	19[b]	3, PhNCO
9	n-$BuNH_2/(n\text{-Pr})_2NH$ (0.5/0.5)	39[c], 5[d]	0, n-BuNCO
10	n-$BuNH_2/PhNH_2$ (0.5/0.5)	41[d], 25[e]	trace, n-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 O_2 total pressure = ∼1 atm. [b] $PhNH(C{=}O)N(n\text{-Pr})_2$. [c] $(n\text{-Bu})NH(C{=}O)N(n\text{-Pr})_2$. [d] $(n\text{-BuNH})_2CO$. [e] $PhNH(C{=}O)NH(n\text{-Bu})$.

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 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-$BuNH_2$ gives the highest yield (46%) of the urea product; the branched chain amine (s-$BuNH_2$) gives a much lower yield (12%); and t-$BuNH_2$ gives a very low yield (2%). Aniline and p-$MeC_6H_4NH_2$ give 21−24% yields, while o-$MeC_6H_4NH_2$ 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 O_2 (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 $(n\text{-Pr})_2NH$ (Table 1, entry 7). On the other hand, when equimolar $PhNH_2$ and $(n\text{-Pr})_2NH$ are reacted with CO and O_2, a 19% yield of the mixed urea $PhNH(C{=}O)N(n\text{-Pr})_2$ is obtained, but diphenylurea ($(PhNH)_2C{=}O$) is not formed (entry 8). This result is consistent with the mechanism in

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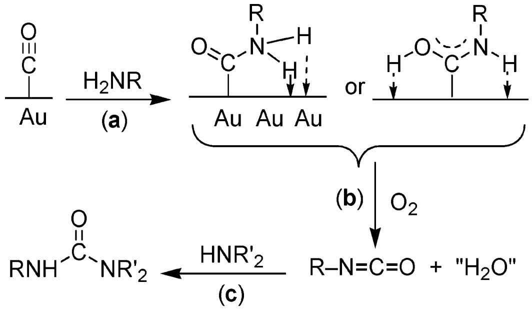
Scheme 2



which Ph−N═C═O is formed initially, and it reacts faster with $(n\text{-Pr})_2NH$ than with $PhNH_2$, 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 $(n\text{-Pr})_2NH$ and $PhNH_2$ under the conditions in Table 1, the only product is $PhNH(C{=}O)N(n\text{-Pr})_2$. Also consistent with the intermediacy of an isocyanate is the reaction of equimolar $n\text{-BuNH}_2$ and $(n\text{-Pr})_2NH$, which gives (entry 9) a ratio (39/5 = 7.8) of the $n\text{-BuNH}(C{=}O)N(n\text{-Pr})_2/(n\text{-BuNH})_2C{=}O$ products, which is nearly the same as the ratio (7.2) of products obtained from the reaction of 0.10 mmol of $n\text{-BuN}{=}C{=}O$ with 0.50 mmol of both $n\text{-BuNH}_2$ and $(n\text{-Pr})_2NH$ 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 $n\text{-BuNH}_2$ and $PhNH_2$ gives a yield of $(n\text{-BuNH})_2C{=}O$ (41%) that is higher than that of the mixed urea product $PhNH(C{=}O)NH(n\text{-Bu})$ (25%), while no $(PhNH)_2C{=}O$ is produced because of the weakly nucleophilic character of $PhNH_2$ as compared with $n\text{-BuNH}_2$ 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 O_2 to form CO_2 even below room temperature, we studied this reaction under the conditions in Table 1; however, no CO_2 (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 $n\text{-BuNH}_2$, CO, and O_2 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/O_2 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 report[16] 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 μm) or Cu (1−5 μm) powder was stirred with $n\text{-BuNH}_2$ and CO/O_2 under the conditions in Table 1, the $n\text{-BuNH}_2$ 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.

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

References

(1) (a) Bond, G. C.; Thompson, D. T. *Appl. Catal. A: Gen.* **2006**, *302*, 1−4. (b) Thompson, D. T. *Top. Catal.* **2006**, *38*, 231−240. (c) Bond, G. C.; Thompson, D. T. *Catal. Rev. Sci. Eng.* **1999**, *41*, 319−388.

(2) (a) Chen, M. S.; Goodman, D. W. *Catal. Today* **2006**, *111*, 22−33. (b) Kung, M. C.; Costello, C. K.; Kung, H. H. *Catalysis* **2004**, *17*, 152−165.

(3) Hutchings, G. J.; Haruta, M. *Appl. Catal. A: Gen.* **2005**, *291*, 2−5 and other articles in this issue.

(4) Janssens, T. V. W.; Carlsson, A.; Puig-Molina, A.; Clausen, B. S. *J. Catal.* **2006**, *240*, 108−113.

(5) (a) Miller, J. T.; Kropf, A. J.; Zha, Y.; Regalbuto, J. R.; Delannoy, L.; Louis, C.; Bus, E.; van Bokhoven, J. A. *J. Catal.* **2006**, *240*, 222−234. (b) Weiher, N.; Bus, E.; Delannoy, L.; Louis, C.; Ramaker, D. E.; Miller, J. T.; van Bokhoven, J. A. *J. Catal.* **2006**, *240*, 100−107.

(6) Overbury, S. H.; Schwartz, V.; Mullins, D. R.; Yan, W.; Dai, S. *J. Catal.* **2006**, *241*, 56−65.

(7) Casaletto, M. P.; Longo, A.; Venezia, A. M.; Martorana, A.; Prestianni, A. *Appl. Catal. A: Gen.* **2006**, *302*, 309−316.

(8) Lazar, M.; Angelici, R. J. *J. Am. Chem. Soc.* **2006**, *128*, 10613−10620.

(9) (a) Robertson, M. J.; Angelici, R. J. *Langmuir* **1994**, *10*, 1488−1492. (b) Shih, K.-C.; Angelici, R. J. *Langmuir* **1995**, *11*, 2539−2546. (c) Ontko, A. C.; Angelici, R. J. *Langmuir* **1998**, *14*, 1684−1691. (d) Ontko, A. C.; Angelici, R. J. *Langmuir* **1998**, *14*, 3071−3078.

(10) Michelin, R. A.; Pombeiro, A. J. L; Guedes da silva, M. F. *Coord. Chem. Rev.* **2001**, *218*, 75.

(11) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335−341.

(12) (a) Chen, M.; Cai, Y.; Yan, Z.; Goodman, D. W. *J. Am. Chem. Soc.* **2006**, *128*, 6341−6346. (b) Gottfried, J. M.; Schmidt, K. J.; Schroeder, S. L. M.; Christmann, K. *Surf. Sci.* **2003**, *536*, 206−224.

(13) Lemire, C.; Meyer, R.; Shaikhutdinov, Sh. K.; Freund, H.-J. *Surf. Sci.* **2004**, *552*, 27−34.

(14) Entelis, S. G.; Nesterov, O. V. *Russ. Chem. Rev.* **1966**, *35*, 917.

(15) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W.-D.; Häkkinen, H.; Barnett, R. N.; Landman, U. *J. Phys. Chem. A* **1999**, *103*, 9573−9578.

(16) Shi, F.; Deng, Y. *J. Catal.* **2002**, *211*, 548−551.

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