Surface Chemistry

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A Pathway for NH Addition to Styrene Promoted by Gold**

*Xingyi Deng, Thomas A. Baker, and Cynthia M. Friend**

Gold-based heterogeneous catalysts have surprising potential for low-temperature oxidation processes,[1–4] including alcohol oxidation,[5–8] direct synthesis of hydrogen peroxide,[9,10] CO oxidation,[11,12] and olefin epoxidation.[11,13] These systems have potential for a substantial positive impact on the environment and economy because of their high selectivity and also the low temperature at which they operate.[14] Hence, a substantial amount of effort has been directed to further improve the performance of heterogeneous gold catalysts and to understand the origin of their catalytic activity.[15–18]

Herein, we investigate the addition of NH to styrene using heterogeneous Au because of the potential importance of these three-membered N-containing rings in organic synthesis as a building block for biologically active molecules and for use in antitumor and antibiotic applications.[19–21] Previously, we demonstrated that the Au(111) surface promotes oxidation reactions that also occur on catalysts with high surface areas at higher pressure, once oxygen has been adsorbed onto the surface,[22] thereby establishing that Au(111) is a good model for understanding the molecular-level detail of heterogeneous Au-based oxidation catalysis. Hence, reactions that occur on Au(111) provide a guide for the type of reactions that may be induced by heterogeneous gold catalysts.

Nitrene addition to styrene is promoted by a gold surface, which indicates that such reactions should be possible with heterogeneous Au catalysts. To our knowledge, this is the first report of gold-catalyzed functionalization of an olefin with NH in a heterogeneous system, which may have advantages and mechanistic differences when compared to aziridination in solution,[23,24] or in other methods of activating ammonia for amination.[25]

Aziridines are structurally analogous to epoxides and may be formed by addition of a nitrene group to the olefin. Recently, we showed that oxidized Au(111) promotes styrene epoxidation.[22] This observation motivated us to explore the

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[*] X. Deng, T. A. Baker, Prof. C. M. Friend
Department of Chemistry and Chemical Biology
Harvard University
Cambridge, MA 02138 (USA)
Fax: (+1) 617-496-8410
E-mail: cfriend@deas.harvard.edu
Prof. C. M. Friend
Division of Engineering and Applied Sciences
Harvard University
Cambridge, MA 02138 (USA)

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analogous aziridination of styrene on Au(111). Indeed, aziridination of styrene does occur on Au(111) covered with NH_x. By precovering the surface with NH, we are able to study the elementary steps important in catalytic processes. This is a well-established approach for studying other reactions important in catalysis using the tools of surface science.[26–28]

Reactive NH_x ($x = 1,2$) species are formed from the reaction of NH_3 with chemisorbed oxygen on Au(111) (Figure 1). By selecting the appropriate conditions, we are able to remove all the oxygen through the evolution of water. In temperature-programmed reaction experiments, water is evolved at 210 K if NH_3 is exposed to O-covered Au(111) at 110 K; however, when dosed with an excess of ammonia and the surface maintained at 190 K, the oxygen is removed through water evolution (Figure 1 a,b). Notably, ammonia does not react on the clean Au(111) surface, but desorbs molecularly at 155 K (data not shown). The NH_x formed on the surface undergoes disproportionation upon heating (Figure 1). Molecular ammonia desorbs from the surface at 160 K. A second NH_3 peak at 210 K is ascribed to the reformation of NH_3 from disproportionation of NH_x species. Adsorbed nitrogen atoms are also formed, which ultimately lead to N_2 formation at 425 K. No H_2 is evolved; rather hydrogen is removed either as water during formation of NH_x or by reformation of NH_3. All these observations show that N–H bonds are activated by the reaction of ammonia with oxygen-covered Au(111), analogous to reactions reported previously on Ag and Cu surfaces,[29–31] and to recent reports for Au(111) oxidized using an oxygen plasma.[32]

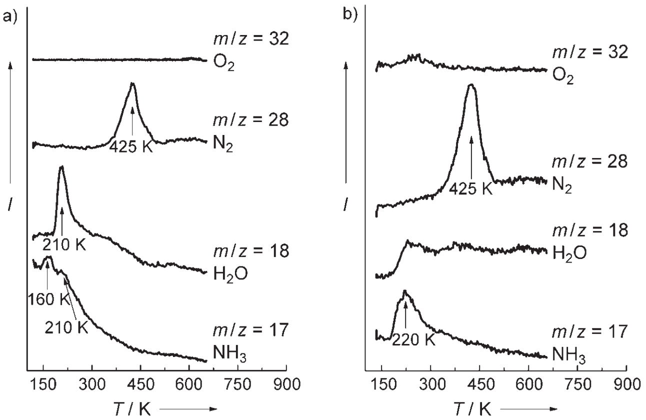


Figure 1. Temperature-programmed reaction spectra following the adsorption of NH_3 on O-covered Au(111) ($\theta_O = 0.2$ ML). When NH_3 is exposed to the O-covered surface at 110 K (a), all oxygen reacts with N–H bonds to form water on heating above 175 K. Exposure of NH_3 to the same surface at 190 K (b) leads to removal of all oxygen as water, so as to generate a surface which contains mainly adsorbed NH_x. The NH_x disproportionates to evolved gaseous NH_3 and adsorbed N upon heating to higher temperatures. The adsorbed nitrogen atoms combine to form N_2 at 425 K. The oxygen-covered surface was prepared by O_3 decomposition at 200 K. I = mass spectroscopy intensity.

All adsorbed oxygen is converted into water through the reaction with N–H bonds. Water is the only oxygen-containing species detected upon heating; NO, N_2O, and NO_2 are not detected (data not shown). Furthermore, there is no detectable formation of O_2, which would occur at around 550 K from oxygen-atom recombination if there were residual adsorbed oxygen present. The reactivity of the oxygen layer towards NH_3 and other species depends on the method used for oxidation.

To accumulate NH_x and remove OH and H_2O, as well as molecular NH_3 from the surface, we exposed the oxygen-covered Au(111) surface ($\theta_O = 0.2$ monolayer (ML)) to a larger dose of NH_3 at 190 K (a temperature that is high enough to prevent adsorption of molecular NH_3 and low enough to keep NH_x on the surface; Figure 1 b). After this treatment, NH_3 reformation from NH_x, was observed as a peak at 220 K and N_2 formation at 425 K. Water formed from the reaction of NH_3 with oxygen desorbs from the surface during the reaction and therefore there is no well-defined H_2O peak—only an increased water background was observed. This desorption is concomitant with ammonia desorption, possibly because of the displacement of water by ammonia from other surfaces. Since this method exclusively produces NH_x on the surface, it was used in all experiments described later.

Addition of NH to styrene was observed following the reaction of styrene on Au(111) covered with NH_x at 150 K (Figure 2). Specifically, a product with a parent ion at $m/z = 119$ and the most intense peak at $m/z = 118$ was evolved at 390 K and tentatively identified as 2-phenylaziridine. A small amount of H_2O was also produced in the reaction, possibly because of the presence of some residual oxygen on the surface following exposure to ammonia. Notably, no oxygen-

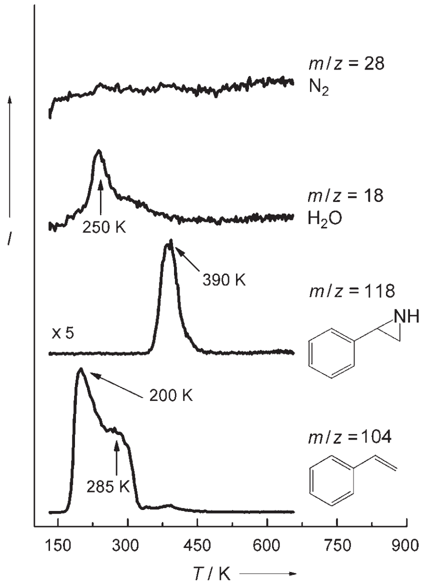


Figure 2. Temperature-programmed reaction spectra following the adsorption of styrene on NH_x-covered Au(111) at 150 K. The reaction yields 2-phenylaziridine (390 K), exclusively. Neither oxidation nor nitrilation products were observed. Some residual oxygen reacts with NH_x and forms H_2O at 250 K. No N_2 desorption was observed, which indicates a high overall activity since all the NH_x has been consumed in the reaction.

addition products (CO, CO_2, epoxide, or organic acids) were detected. Remaining styrene desorbed from the surface at 200 K (multilayers) and 285 K (monolayer). A residue containing carbon and nitrogen remained on the surface after reaction of styrene and NH_x. NO and CO_2 were produced after exposing the residue on the surface to ozone and subsequent heating. The fact that NO was produced from post-oxidation of the residue, but no N_2 was observed after reaction of styrene with NH_x, indicates that the nitrogen is bound to carbon in the residue.

We unequivocally established that the product formed at 390 K contains nitrogen by using $^{15}NH_3$ as our starting reagent (Figure 3). The parent ion shifts from $m/z = 119$ to 120 when the reaction of styrene on the surface covered with $^{15}NH_x$ was performed. Notably, a shift of the m/z signal by $+1$ is also observed for all the observed mass fragments which contain nitrogen; for example, the most intense fragmentation [$M-1$] shifts from $m/z = 118$ to 119.

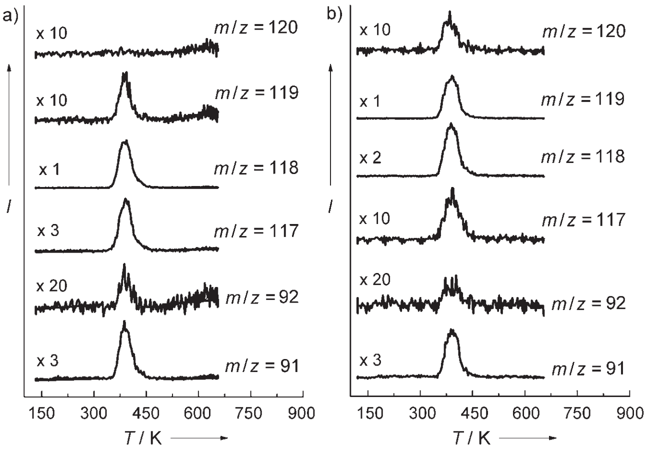
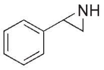
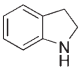
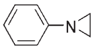
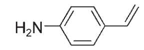


Figure 3. Mass spectrometer fragmentations of 2-phenylaziridine from the reaction of styrene on a Au(111) surface covered with a) $^{14}NH_x$ or b) $^{15}NH_x$. The shift of $+1$ for the parent ion (m/z 119 to 120), as well as the most intense peak (m/z 118 to 119) when using $^{15}NH_3$, is a strong indication that the product contains nitrogen.

The stoichiometry (C_8H_9N) of the product was determined from the parent ion signal ($m/z = 119$) in conjunction with the shifts in the signals found in the experiments using $^{15}NH_3$. The intensities of the major fragmentation ions of the product from the experiment using our mass spectrometer were compared with the literature values of selected ion intensities of isomers with C_8H_9N stoichiometry (Table 1). The use of literature values to eliminate possible products based on the yields of the fragment ions is validated by the good agreement with the measured intensities of the fragment ions of indoline.

We assign the product formed in the reaction as 2-phenylaziridine based on analysis of its fragmentation pattern (Table 1). The fragments of the product we observed do not match any of those C_8H_9N isomers cited by the National Institute of Standards and Technology (NIST). In addition, the presence of the $m/z = 91$ fragment and the absence of a mass shift for this fragment when $^{15}NH_3$ was used as the source of nitrogen is compelling evidence that the product has a benzyl group ($C_6H_5CH_2$-), which is consistent with the 2-phenylaziridine structure. Furthermore, this result rules out *N*-phenyl aziridines and the imine, $C_6H_5C(CH_3){=}NH$ as the product because the strong $m/z = 91$ signal contains nitrogen in this isomer. Although the mass spectrum for 2-phenylaziridine is not available from the NIST database for direct comparison, our observations all strongly point to it being the product. The other imine $C_6H_5CH_2C(H){=}NH$ cannot be completely ruled out.

Table 1: Mass spectrometer fragmentation patterns of 2-phenylaziridine from the reaction of styrene on a Au(111) surface covered with NH_x and also reactions of isomers with C_8H_9N stoichiometry.

m/z	2-Phenylaziridine 	Indoline[a] 	*N*-Phenylaziridine[b] 	4-Aminostyrene[b] 
91	40	45 (30)	(100)	(24)
92	3	5 (3)	(10)	(5)
117	36	45 (29)	(0)	(15)
118	100	100 (100)	(9)	(58)
119	6	50 (63)	(40)	(100)
120	0	4 (6)	(4)	(8)

[a]These data rule out the possibility of the product being indoline, *N*-phenylaziridine, or 4-aminostyrene. [b] The numbers in the parentheses were obtained from the NIST database.

We suggest that the formation of 2-phenylaziridine is the result of the transfer of NH to styrene on Au(111) by analogy with the corresponding epoxidation reaction on this surface.[22] Spectroscopic studies are underway to identify the NH_x species present on the surface during reaction. We will show in a subsequent report that styrene nitrilation (forming benzo- and benzyl nitrile) occurred only when nitrogen atoms were pre-adsorbed on Au(111).[33] This observation indicates that the presence of NH_x (NH and/or NH_2), not nitrogen atoms, is necessary for aziridination.

Our results indicate that 2-phenylaziridine is formed from the Au-promoted reaction of styrene and NH_x. In this reaction, oxygen is used to activate the NH_3 and to form NH_x species on the surface. By adjusting the preparation conditions, oxygen is consumed by the NH_3 and forms H_2O, which desorbs, and NH_x remains exclusively on the Au(111) surface.

The aziridination of organic molecules is generally a complex process usually promoted by a homogeneous catalyst.[24] Our study clearly shows the promise of the aziridination of a C=C bond by using a heterogeneous gold system, which may provide a convenient and more efficient route. The key features are the N–H bonds so as to form the desired nitrene and a C=C bond. Notably, the temperature needed for this process is low, which is significant for the selective synthesis of molecules important in the pharmaceutical industry. Nevertheless, there are still unanswered questions including the identification of the product by other means to completely rule out other products like imines, the generality of the process for more complex nitrenes and olefins, the degree of selectivity, whether these reactions can be carried out stereoselectively, and whether this process can be carried out catalytically. Although this study was carried out using a single crystal and under ultrahigh-vacuum conditions, it is reasonable that this pathway would also apply for high-pressure conditions using supported nanoscopic Au clusters, especially since the related oxidation reactions on gold occur under both low- and high-pressure conditions.

Experimental Section

All experiments were performed in a stainless-steel ultrahigh-vacuum chamber with a base pressure of $<1\times10^{-10}$ Torr, as described previously.[34] The chamber was equipped with a quadrupole mass spectrometer (UTI model 100C) which was used for temperature-programmed reaction spectroscopy (TPRS), an Auger electron spectrometer (AES), and low-energy electron diffraction optics (LEED).

The Au(111) surface was prepared by cycles of sputtering of Ar$^+$ ions (1000 eV, 1.3 μA) at 300 K, followed by annealing at 900 K for 5 min, and then at 700 K for 30 min. This procedure was repeated until no impurities were detected using AES.

Ozone was produced by electrical discharge and was trapped in silica gel (3–8 mesh, Fisher Scientific Co.) at −78 °C using a mixture of dry ice and ethanol. The Au(111) surface at 200 K was exposed to O$_3$, with a pressure rise of 1×10^{-8} Torr over 20 s, which resulted in an approximate 0.2 ML. The resulting oxygen atom coverage was determined by comparing the integrated area of the O$_2$-desorption peak relative to a saturation coverage (ca. 1 ML) which had been determined previously.[35,36] Following the deposition of oxygen, the surface was exposed to NH$_3$ (Matheson, anhydrous grade) or ^{15}NH$_3$ (Cambridge Isotope Laboratories, 98 %). The NH$_3$ was deposited at 190 K for 2 min with a pressure rise of 1×10^{-10} Torr. Finally, styrene (Alfa Aesar, 99.5 %) was deposited at 150 K for 30 s with a pressure rise of 1×10^{-10} Torr and was used after cycles of freeze-pump-thaw purification, with the purity checked by mass spectrometry.

All temperature-programmed reaction spectra (TPRS) were taken by a computer-controlled UTI 100c mass spectrometer, as described in detail previously.[37] The crystal was biased at −100 V during the collection of temperature-programmed reaction data, so as to avoid an electron-induced reaction from the mass-spectrometer filament. The temperature was measured with a K-type (Chromega/Alomega) thermocouple and radiative heating was used to achieve the temperature ramp to 650 K. The heating rate for TPRS was relatively linear, in the range 150–600 K with an average of about 6 K s^{-1}.

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