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Research Note

Influence of radical initiators in gold catalysis: Evidence supporting trapping of radicals derived from azobis(isobutyronitrile) by gold halides

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Abstract

Gold halides ($AuCl_3$, $HAuCl_4$, and AuCl) efficiently trap the radicals generated in the room-temperature photolysis of azobis(isobutyronitrile) (AIBN) to give an organogold $H[(CH_3)_2CCN]_2AuCl_2$ compound that has been characterized by spectroscopy. The characteristic features of the organogold are a quaternary carbon at 100 ppm on ^{13}C NMR and a HR-MS peak with a molecular formula of $C_8H_{13}N_2AuCl$. Catalytic data for cyclohexene aerobic oxidation confirms the beneficial influence of the presence of AIBN on the catalytic activity of Au/CeO_2.

Keywords: Gold catalysis; Radical trapping; Radical initiators; Organogold

1. Introduction

Catalysis by gold has emerged as one of the most active research fronts [1–3]. In contrast to platinum, palladium, and other noble metals, gold is catalytically inert until sufficiently small particles (in the nanometer range) are obtained. Aimed at increasing the activity of gold catalysts, heterogeneous and homogeneous catalysis have converged in the quest for small clusters or soluble monoatomic compounds. Gold halides have also been found to promote an array of reactions including cycloisomerizations, benzoannulations, and oxidations [4–8].

Gold nanoparticles have been found active and selective catalysts for the aerobic oxidation of alcohols [9] and aldehydes [10]. Recently, it has been reported that some aerobic oxidations can be largely promoted by adding small amounts of peroxides [11]. The influence of the presence of peroxides in gold catalysis is intriguing, and mechanistic proposals to rationalize this effect should take into account the ease of peroxide decomposition to give radicals. Herein, using gold halides as model gold compounds, we have performed a product study of the reaction of gold with azobis(isobutyronitrile) (AIBN) that eventually also leads to enhancement of the gold catalytic activity for alkene aerobic oxidation in the same way as peroxide does [12].

2. Experimental

Photolysis of AIBN in the absence and in the presence of gold halides was carried out in NMR tubes by dissolving the gold salts ($AuCl_3$, $HAuCl_4$, and AuCl, 3.2×10^{-2} M) in deuterated acetonitrile (0.5 ml) and subsequently adding the radical initiator (3.0×10^{-2} M). All of the solutions were purged with a nitrogen flow for 15 min and then irradiated using a water-refrigerated medium-pressure Hg lamp through quartz. ^1H and ^{13}C NMR were recorded using a Varian Gemini 3000 (300 MHz). High-resolution mass spectrometry was carried out using a VG Autospec.

3. Results and discussion

AIBN is a well-known radical initiator. On thermal or photochemical activation, AIBN decomposes to form 1-cyano-1-methylethyl radicals that can evolve in various pathways, such

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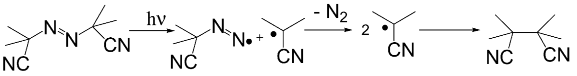
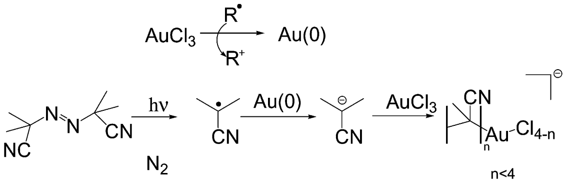


Scheme 1. Photochemical decomposition of AIBN to form 2,3-dicyano-2,3-dimethylbutane.



Scheme 2. Radical trapping by $AuCl_3$ with formation of an organogold compound.

as coupling reaction, hydrogen abstraction, electrophilic addition, disproportionation, and so on. The relative rate constants for the different available pathways depend on the medium and on the presence of radical traps. In our case, the limitated solubility of gold halides restricts the range of solvents that can be used. For this reason, herein acetonitrile was selected as solvent and AIBN decomposes photochemically at room temperature to give 2,3-dicyano-2,3-dimethylbutane (arising from the radical coupling) as the only product detectable by ^{1}H NMR (singlet at 1.52 ppm corresponding to the methyl groups). Scheme 1 indicates the most reasonable route to the dicyanobutane compound.

Photochemical decomposition was also performed under the same conditions in the presence of equimolar amounts of $AuCl_3$. In addition to the appearance of minor amounts of gold nanoparticles, the formation of organogold compounds was inferred. Gold reduction from Au(III) to Au(0) is known to occur in the presence of radicals that can act as electron donors, forming the corresponding carbocation and giving one electron to Au(III) [13]. Consequently, the progress of the photochemical reaction was followed by ^{1}H NMR spectroscopy, in which the disappearance of the singlet at 1.70 ppm corresponding to the AIBN methyl groups was accompanied by a concomitant increase in the singlet corresponding to the radical coupling product at 1.52 ppm and, more importantly, by the appearance of a new peak at 1.98 ppm. In addition, the relative molar proportions of all signals were obtained by integration of the peak area. The signal appearing at an unusually low field indicates that the methyl groups are bonded to a strong electron-withdrawing atom. We tentatively attributed this new peak to an organogold product arising from the radical trapping by the gold atom, as indicated in Scheme 2.

Fig. 1 shows the relevant region of the ^{1}H NMR spectra, illustrating the main features observed when AIBN irradiation is carried out in the presence of $AuCl_3$. Similar ^{1}H NMR spectra, with minor ratio variations between the radical coupling product and the organogold compound, were recorded when AIBN was photolyzed in the presence of $HAuCl_4$ or AuCl, indicating that the same compounds are being formed. After 2 h of irradiation, the ratio between the organogold compound and the radical coupling product (determined by integration of the ^{1}H NMR peaks) was 70/30 for $AuCl_3$ and 60/40 for AuCl. This ratio remained almost constant during the course of the reaction. When AuCl was used as a quencher, the gold likely underwent a disproportionation process in which Au(I) ions led to Au(III) and Au(0) species, occurring concomitantly with radical trapping.

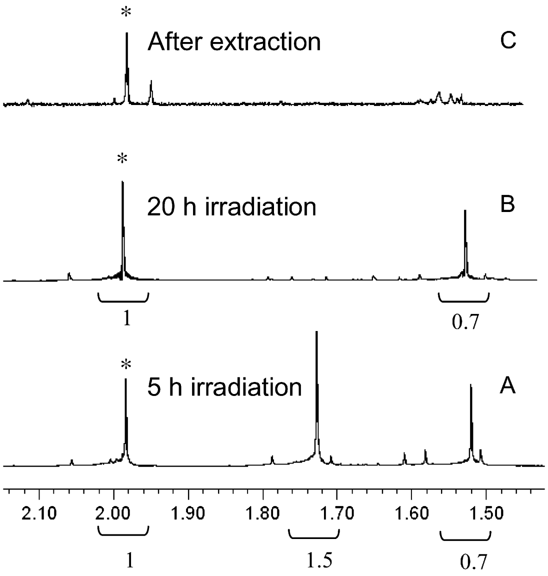


Fig. 1. ^{1}H NMR spectra of a solution of AIBN and $AuCl_3$ (equivalent amounts) in CD_3CN recorded 5 (A) and 20 h (B) after irradiation. ^{1}H NMR spectrum (C) corresponds to the mixture (B) after CD_3CN removal and partitioning between D_2O and $CDCl_3$. The peak attributable to the organogold compound has been marked with an asterisk and the relative proportions are indicated below the chemical shift scale.

^{13}C NMR spectra of the reaction mixture after complete disappearance of AIBN in the absence and in the presence of gold halides also show analogous differences to those seen in the ^{1}H NMR spectra. Thus, in CD_3CN the radical coupling product exhibited a peak at 22 ppm, corresponding to the methyl groups. The quaternary carbon of the radical coupling product was not observed, and the nitrile carbon of this product appeared to be merged with the CN carbon of the solvent. When AIBN was photolyzed in the presence of gold halides, in addition to the peak corresponding to the coupling product, a new down-field peak at 32 ppm was also recorded. The corresponding distortionless enhanced polarization transfer (DEPT) spectrum confirmed that this new peak corresponds to a methyl group that we assigned to the geminal methyl groups of the organogold compound, in agreement with our previous ^{1}H NMR observations.

No evidence of a quaternary carbon connected to gold was obtained. We assumed that this failure was due to the inefficient relaxation of this quaternary carbon. We confirmed this hypothesis by rerecording the ^{13}C NMR spectrum with the pulse delay time increased to 2 s, demonstrating a new signal at 100 ppm attributable to a quaternary carbon bonded to a positive gold atom. DEPT confirmed that this peak at 100 ppm corresponded to a quaternary carbon. Fig. 2 shows representative ^{13}C NMR spectra of the AIBN photolyzed in the presence of $AuCl_3$, including the corresponding DEPT spectra.

Given the different nature of the radical coupling product and the presumed organogold compound arising from radical

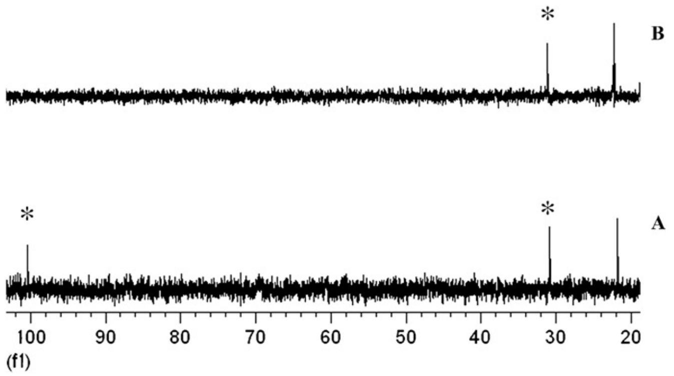
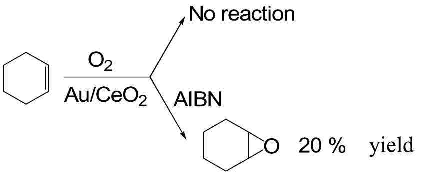


Fig. 2. ^{13}C-NMR (A) and DEPT (B) spectra of a solution of AIBN and $AuCl_3$ in CD_3CN recorded 20 h after irradiation. The peaks attributed to the organogold compound have been marked with asterisks.

trapping, after photolysis and acetonitrile removal, these could be separated simply by partitioning the reaction mixture between D_2O and $CDCl_3$, whereby the organogold compound should become dissolved in the aqueous phase. Room temperature decomposition of this organogold compound in water was observed over the time, thus precluding a ^{13}C NMR measurement in this solvent. However, the persistence of the organogold compound in water was sufficiently long to enable recording of a ^{1}H NMR spectrum in which the peak characteristic of the radical coupling product was absent (Fig. 1C).

High resolution MS of the organogold compound gave a peak at 369.062 Da, corresponding to a molecular formula of $C_8H_{13}N_2AuCl$ (exact mass, 369.043 daltons) compatible with an ion such as $[(CH_3)_2CCN]_2AuClH^+$ arising from an organogold compound as indicated in Scheme 2. This ionic $H[(CH_3)_2CCN]_2AuCl_2$ organogold(III) compound was compatible with all of the available NMR spectroscopic data (including unusual down-field chemical shifts due to the strong influence of positive gold atom) and also with MS (after loss of a chloride from the molecular ion). This anionic organogold compound would arise from the trapping of the 1-cyano-1-methylethyl radical by the gold atom. Concerning the characterization by mass spectrometry of an organogold compound containing two (instead of one) organic substituents, previous theoretical calculations [14] have suggested that the relative reaction rate of radical trapping by metal ions increases gradually from $AuCl_3$ upon substitution with organic ligands. In other words, according to the quantum chemical calculation, the addition of a second radical should be faster than the trapping of the first radical. Also presumably, this ionic compound would be soluble in water and would undergo chloride substitution by OH^- in water, thus explaining its instability in aqueous phase. Radical trapping by transition metal atoms and ions, such as Cu(I) and palladium, is not unprecedented [15], and our finding indicates an analogous behavior for gold. In contrast to water, $[(CH_3)_2CCN]_2AuCl_2^-$ is stable in CD_3CN even after prolonged heating at 70 °C.



Scheme 3. Aerobic oxidation of cyclohexene by ceria supported gold nanoparticles in the presence and in the absence of AIBN.

To show that our observations of radical trapping by gold has a relationship with catalysis, we performed a continuous-flow catalytic reaction (0.3 ml/min) using a fix catalytic bed (1 g) of ceria-supported gold nanoparticles (Au/CeO_2 with 1.3 wt% of gold) to promote the aerobic oxidation of cyclohexene at 60 °C. As expected in view of earlier studies, only traces of oxidation products were observed under these conditions. However, adding AIBN in small quantities (1%) to the feed produced a significant increase in cyclohexene conversion (Scheme 3). The product distribution included the corresponding cyclohexene epoxide (20%), together with 2-cyclohexenol (15%) and some other minor products. Blank experiments performed with Au and without AIBN and with AIBN without Au showed negligible conversion under our working conditions. The influence of radical initiators observed in the present study is in line with an earlier report of the influence of peroxides in the gold-supported catalytic oxidation of cyclohexene [11].

Thus, based on the reactivity of gold chlorides with AIBN and the related catalytic tests showing the influence of peroxide [11] on the gold-catalyzed aerobic oxidation, we conclude that radical initiators most likely can promote the catalytic activity of gold in hydrocarbon aerobic oxidation by the intermediacy of organogold species arising from radical trapping by gold nanoparticles. The presence of positive gold atoms in gold nanoparticles has been clearly established [12], and these positive gold atoms will act similarly to Au(III) or Au(I) chlorides, forming R–Au organogold species on the surface of the gold catalyst. These organogold compounds can promote aerobic oxidation without the need for additional amounts of radical initiator through a reversible capping/decapping of gold atoms in radical–chain mechanisms. Our findings can serve to develop more efficient gold catalysts based on organogold species rather than in purely inorganic gold catalysts.

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