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Gold-catalyzed aerobic epoxidation of *trans*-stilbene in methylcyclohexane. Part II: Identification and quantification of a key reaction intermediate

Kevin Guillois, Stéphane Mangematin, Alain Tuel, Valérie Caps*

Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON, UMR 5256 CNRS - University of Lyon), 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

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ABSTRACT

The gold-catalyzed aerobic oxidations of alkenes are thought to rely on the in situ synthesis of hydroperoxide species, which have however never been clearly identified. Here, we show direct experimental evidence for the presence of 1-methylcyclohexyl hydroperoxide in the aerobic co-oxidation of stilbene and methylcyclohexane catalyzed by the $Au/SiO_{2\text{-}R972}$ optimized catalyst prepared in Part I. Determination of its response in gas chromatography, by triphenylphosphine titration followed by ^{31}P NMR, allows to easily follow its concentration throughout the co-oxidation process and to clearly highlight the simultaneous existence of the methylcyclohexane autoxidation pathway and the stilbene epoxidation pathway.

1. Introduction

The oxidative transformation of alkane and alkene into useful oxygenated intermediates, such as alcohols and epoxides, is a key-step in the synthesis of fine chemicals. It has recently appeared that supported gold nanoparticles could catalyze both the epoxidation of larger alkenes (e.g. styrene), using *tert*-butyl hydroperoxide (TBHP) as the oxidant [1–6], and the oxidation of alkanes, such as cyclohexane [7–12], under oxygen pressure. In fact, the gold-catalyzed oxidation of alkenes can proceed in the presence of only a catalytic amount of TBHP (5 mol%) when performed in air at atmospheric pressure [13–16]. This aerobic reaction is thought to be initially triggered by TBHP [17] and subsequently sustained by molecular oxygen from the air [18,19], via formation of a hydroperoxide intermediate from the substrate molecule [20].

For alkenes such as stilbene, having no hydrogen atom in alpha position of the carbon–carbon double bond, the direct formation of hydroperoxide from the substrate is not likely. The gold-catalyzed aerobic epoxidation of stilbene can however still proceed, but only when using substituted cycloalkane solvents [21,22]. In this case (for this protected olefin), epoxidation is proposed to occur via a mechanism involving the methylcyclohexane (MCH) solvent and more specifically the *in situ* formation of a peroxyl radical from addition of molecular oxygen onto a methylcyclohexyl radical [23]. The peroxyl species can then add onto the C═C bond, which is favored by the high rate constant, or abstract a hydrogen atom from the tertiary alkane molecule, due to the favorable 155:1 MCH-to-stilbene molar ratio, to produce 1-methylcyclohexyl hydroperoxide. The first step results in an adduct that rearranges into an epoxide and a 1-methylcyclohexoxyl radical. Both steps lead to methylcyclohexan-1-ol to close the reaction cycle. Yet, so far, the occurrence of the hydroperoxide intermediate in these gold-catalyzed aerobic oxidations of alkenes in the liquid phase, whether from the substrate or the solvent, has merely been postulated on the basis of the reaction products distribution. No direct evidence of its presence has been published to date.

In Part I, we reported the synthesis of an optimized gold catalyst for the methylcyclohexane-mediated aerobic epoxidation of stilbene reaction, composed of 3 nm gold particles dispersed on a hydrophobic silica support [24]. This new $Au/SiO_{2\text{-}R972}$ catalyst, which exhibits the same intrinsic activity as that of the state-of-the-art [25] and benefits from a more convenient and practical synthesis, leads to complete conversion within 72 h (using a typical 155:1:0.002 MCH/tS/Au molar ratio), with 79% selectivity towards *trans*-stilbene oxide [24].

In Part II, we now use this optimized catalyst to bring direct experimental evidence for the formation of 1-methylcyclohexyl hydroperoxide (MCOOH) in the $Au/SiO_{2\text{-}R972}$-catalyzed aerobic co-oxidation of methylcyclohexane and *trans*-stilbene. This key reaction intermediate, which was postulated to have a very central implication in the reaction mechanism, is here clearly identified by GC–MS in SIM (selective ion monitoring) mode. The concentration

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* Corresponding author. Present address: KAUST Catalysis Center (KCC), 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia. Tel.: +966 2 808 0304.

E-mail address: valerie.caps@kaust.edu.sa (V. Caps).

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of the hydroperoxide in the 96 h-reaction mixture is measured using PPh_3 titration followed by ^{31}P NMR, which subsequently allows us to determine its response factor in gas chromatography and to follow the evolution of its concentration throughout the reaction. This profile reveals that, unlike in typical radical autoxidations, MCOOH accumulates during the co-oxidation process, suggesting that the gold-catalyzed decomposition of hydroperoxide is indeed the limiting step of the process.

2. Experimental

The synthesis of $Au/SiO_{2\text{-R972}}$ by direct reduction of $AuPPh_3Cl$ in the presence of the silica support is extensively described and discussed in Part I [24]. It was inspired by [26]. In brief, $AuPPh_3Cl$ is first synthesized from reduction of $HAuCl_4$ by dimethylsulfide (C_2H_6S, 99%, Sigma Aldrich), followed by ligand exchange with triphenylphosphine (PPh_3, Sigma Aldrich) [27]. 5 g of Aerosil® R972 hydrophobic fumed silica (Evonik Industries, $110\,m^2\,g^{-1}$) is then added to a solution of $AuPPh_3Cl$ in ethanol ($220\,mL/2.3 \times 10^{-3}\,mol\,L^{-1}$), stirred for 1 h at 22 °C and for 13 more hours after addition of 10 equiv. $NaBH_4$ (20 mL of a freshly prepared $0.3\,mol\,L^{-1}$ solution in ethanol). The dark brown powder is isolated by centrifugation, washed twice with 200 mL water/ethanol (60/40), then with 150 mL hexane, and dried at 90 °C for 16 h. It is heated at 200 °C for 2 h under vacuum, yielding 0.73 wt.% $Au/SiO_{2\text{-R972}}$ (ICP) with 2.9 ± 1.2 nm Au particles (TEM), corresponding to a dispersion of gold atoms of 43% (assuming a typical cubocathedron geometry of the gold particle).

Catalytic evaluation is carried out in round-bottom flask in the presence of *trans*-stilbene (substrate, 0.5 mmol, 96%, Aldrich), Au/SiO_2 (54 mg, 2 μmol Au), methylcyclohexane (solvent, 20 mL/155 mmol, 99.5% Aldrich) and TBHP (initiator, 50 μmol, 7 μL of a 70% TBHP in water Alfa Aesar solution), stirred together at 300 rpm and held at 80 °C for 96 h in air at atmospheric pressure. The reaction mixture is sampled periodically.

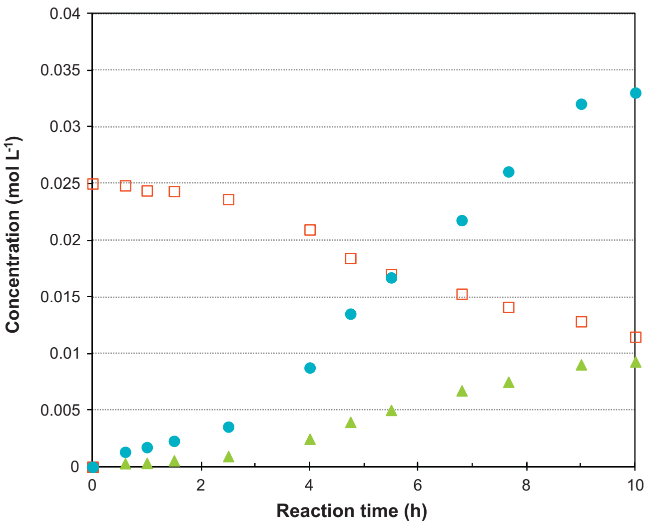
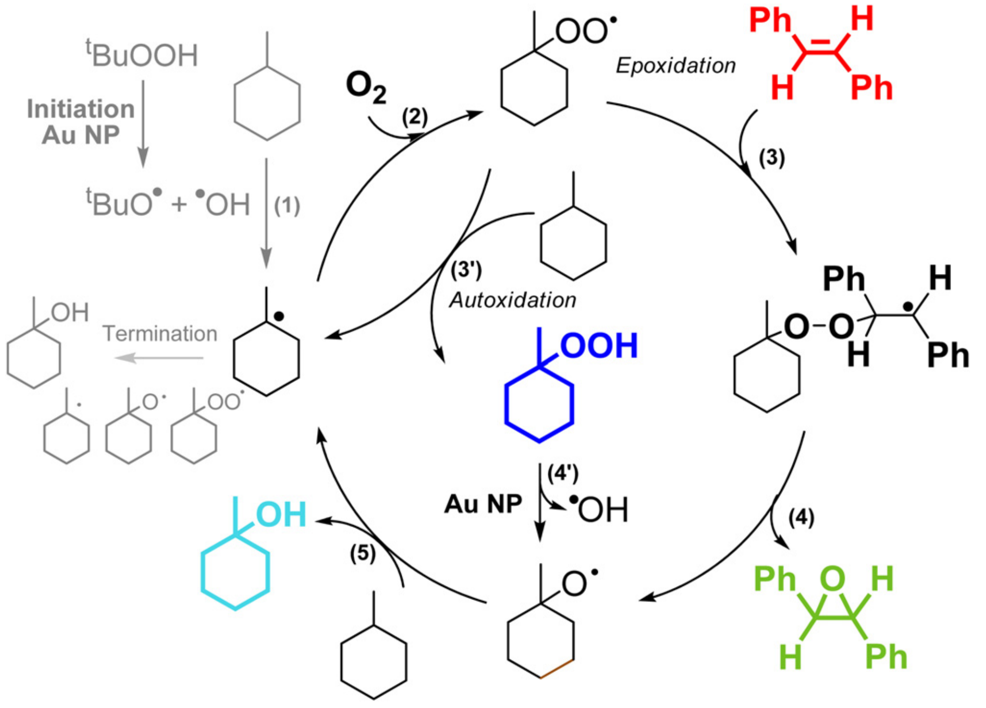


Fig. 1. Concentration profiles of *trans*-stilbene (□), *trans*-stilbene oxide (▲) and methylcyclohexan-1-ol (●) in the initial times of the methylcyclohexane/*trans*-stilbene aerobic co-oxidation catalyzed by $Au/SiO_{2\text{-R972}}$.

Samples of the reaction mixtures are analyzed by Gas Chromatography (Shimadzu GC-2014), using an Equity TMS 30 m × 0.25 mm × 0.25 μm column programmed from 40 °C to 180 °C, an injector and FID detector set at 280 °C and 200 °C respectively, and He as carrier gas ($26.6\,mL\,min^{-1}$). External calibration is carried out by injecting standard solutions of the following chemicals in acetonitrile: *trans*-stilbene (96%, Aldrich), *trans*-stilbene oxide (99%, Acros), benzil (99%, Acros), deoxybenzoin (97%, Alfa Aesar), benzaldehyde (98% Acros) and methylcyclohexan-1-ol (96% Aldrich). The quantification of *trans*-stilbene, benzaldehyde, *trans*-stilbene oxide is counter-checked by injecting the mixtures in High Performance Liquid Chromatography (Perkin-Elmer HPLC



Scheme 1. Postulated mechanism for the gold-catalyzed aerobic co-oxidation of methylcyclohexane and *trans*-stilbene, involving an autoxidation and an epoxidation pathway.