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Catalysis Today 122 (2007) 284–291
CATALYSIS TODAY
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Insight into the free-radical chain mechanism of gold-catalyzed hydrocarbon oxidation reactions in the liquid phase

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Abstract

A free-radical mechanism has been evidenced in the liquid phase stereoselective epoxidation of *trans*-stilbene using methylcyclohexane (MCH) as solvent, limited amount of *tert*-butylhydroperoxide (TBHP), and supported gold catalysts. *Trans*-stilbene oxide is the major reaction product observed, with selectivities up to 88% when using the Au/TiO_2 reference catalyst from the World Gold Council. However the selectivity decreases significantly when using Au/C instead of oxide-supported gold catalysts or H_2O_2 instead of TBHP. HPLC and GC–MS analyses indicate that a fraction of MCH is oxidized during the epoxidation process. It seems that TBHP is the radical source while MCH is propagating the active radical. On the other hand, hydroxyl radicals are responsible for the degradation of the molecule. XPS studies show the presence of Au^0 (90%) and Au^+ (10%) on the Au/C catalyst and $Au^{\delta-}$ (90%) and Au^+ (10%) on the Au/TiO_2 catalyst. Both gold and, to a minor extent, titania seem to be involved in the reaction cycle.

Keywords: Gold catalysis; Epoxidation; Free-radical mechanism; *Trans*-stilbene

1. Introduction

Since the discovery of TS-1 in 1983, epoxidation of lower olefins has largely been carried out over these titanium-containing molecular sieves in the presence of hydrogen peroxide. The high activities and selectivities reported have been attributed to the isolation of Ti(IV) sites inside the hydrophobic pores of the silicalite, which allows selective adsorption of both the oxidant and the substrate, respectively [1]. Reaction seems to involve the transfer of an electrophilic oxygen from a alkylperoxometal species to the olefin. The use of TS-1 is however limited to olefins with ''kinetic diameter'' [2] typically below 5.5 Å. For example, it can be used for the epoxidation of 1-hexene while cyclohexene is essentially inert under similar conditions [2]. This has prompted researchers to design and use Ti(IV)-containing structures with larger pores, such as β-zeolite [3,4] and MCM-41 [5,6], together with *tert*-butylhydroperoxide (TBHP). However, if these structures are extremely efficient in the gas phase, their use in the liquid phase can be associated with Ti leaching, leading to undesired homogeneous catalysis [7–10].

On the other hand, carbon-supported gold nanoparticles have proven catalytically active in the liquid phase selective oxidations of alcohols [11–14] and aldehydes [15] using low pressure of oxygen (1–5 bar), while Au/TiO_2 has been shown to catalyze the total oxidation of dicarboxylic acids using air under more stringent conditions (190 °C/50 bar) [16]. Au/CeO_2 has been used for the solventless and selective aerobic oxidation of alcohols using air at atmospheric pressure [17]. Au/MCM-41 [18] and Au/ZSM-5 [19] have proven catalytically active for the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone using 10 bars of oxygen and 150 °C, while Au/C has shown limited activity in this reaction at 70 °C [20]. Styrene epoxidation has been studied using TBHP as the oxidant over Au/TiO_2 [21] and gold nanoparticles supported on Al_2O_3, Ga_2O_3, In_2O_3, Tl_2O_3 [22] and MgO, CaO, SrO, BaO [23] but poor yields were obtained. Styrene has also been epoxidized in the presence of excess TBHP over gold nanoparticles deposited on mesoporous alumina [24]. Finally, cyclohexene, cyclooctene, styrene, *cis*-stilbene, have been converted to the corresponding epoxides with relatively low

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doi:10.1016/j.cattod.2007.02.006

yields in the presence of catalytic amounts of TBHP and Au/C, in air at atmospheric pressure [25]. In this case, TBHP was described as an ‘‘initiator of a chain reaction sustained by oxygen’’. Earlier on, it has been shown that gold complexes could catalyze the epoxidation of cyclohexene in low yields, using molecular oxygen as oxidant [26].

We thought that combining the ability of gold to catalyze hydrocarbon autoxidations and the oxidizing properties of titania could lead to an interesting catalyst for the epoxidation of bulky olefins in the liquid phase. Here, we report on the selective oxidation of *trans*-stilbene (tS), as a model molecule for those substituted olefins, over the reference catalysts Au/TiO_2, Au/C and Au/Fe_2O_3 (all provided by the World Gold Council) [27] and one home-made titania-supported gold Au/TiO_2-PC500.

2. Experimental

2.1. Synthesis of the materials

The 1.5% Au/TiO_2 (type A, lots no. Au–TiO_2 #02-05 and #02-06, sample nos. 53 and 84), 1% Au/C (type D, sample no. 24) and 5% Au/Fe_2O_3 (type C, lot no. Au–Fe_2O_3 #02-04, sample no. 56) reference catalysts were purchased from the World Gold Council (WGC). Their preparation and characterization have already been described elsewhere [28,29]. Basically:

- Au/TiO_2 is prepared at AIST (Japan) following a deposition–precipitation protocol developed by Haruta and coworkers [30–34], from titania P25 (Degussa, $50 \pm 15\ m^2\ g^{-1}$, 75 ± 5 wt% anatase + 25 ± 5 wt% rutile with mean particle diameters of 25 and 39 nm, respectively, as determined by XRD) and $HAuCl_4{\cdot}3H_2O$. The powder catalyst contains 1.4 ± 0.1 wt% of gold, as determined by inductively coupled plasma (ICP) chemical analysis. The average particle diameter of gold in the fresh catalyst is 3.7 ± 1.5 nm, as analyzed by transmission electron microscopy.
- Au/Fe_2O_3 is prepared by co-precipitation at AIST (Japan). It contains 4.4 wt% gold with average particle diameter 4.0 ± 0.9 nm.
- Au/C is prepared at Milano University (Italy) by Rossi and coworkers [13] using deposition of gold sols on high surface area carbon (X40S, $1200\ m^2\ g^{-1}$). Gold content is 1.0 wt% with average particle diameter 10.5 nm (TEM) / 6.7 nm (XRD).

The Au/TiO_2-PC500 catalyst was prepared in-house from titania PC500 powder (Millenium Chemicals, $340\ m^2\ g^{-1}$, 83.4 wt% TiO_2, 100% anatase, 0.34 wt% SO_3) and $HAuCl_4{\cdot}3H_2O$ (Strem Chemicals, 99.99%). A deposition–precipitation method was used, which slightly differs from the original one developed by Haruta et al., in that it contains no heat treatment, just like in [35]. In this method, the pH (3) of a $HAuCl_4{\cdot}3H_2O$ solution in water (5×10^{-3} M) is adjusted to 9, by adding a NaOH 0.2 M solution. The resulting solution is added drop by drop to a stirred suspension of the support material (1 g) in water (50 mL). The pH of the resulting mixture is again adjusted to 9 before it is left to stir at 20 °C for 18 h. The powder is recovered by filtration, washed with 1 L deionized water to ensure complete removal of chlorine ions ($AgNO_3$ test) and weakly adsorbed species. This allows to minimize the Cl content in our final material (<100 ppm). The powder is then dried at 80 °C in vacuum for 20 h and stored in air at 20–22 °C, which apparently results in reduction of gold. No heat treatment is applied prior to catalytic tests. It contains 1.6 wt% gold with average particle diameter (in the fresh catalyst) 5.8 ± 2.9 nm (TEM) and pure anatase TiO_2 with average crystallite size 8 nm (XRD). Its characterization is being published [36].

For blank experiments, TiO_2 P25 was purchased from Degussa and 1%Pt/C from Aldrich.

2.2. Characterization

The gold contents of the catalysts were determined by in-house chemical analysis (ICP or ICP-MS).

X-ray diffraction (XRD) powder patterns were recorded between 3° and 80° (2θ) on a Bruker (Siemens) D 5005 diffractometer using Cu Kα_2 radiation with steps of 0.02° and 10 s (or 1 s) per step.

Transmission electron microscopy (TEM) was performed on a JEOL JEM 2010-F operating at 200 kV and equipped with a Pentafet-Link ISIS energy dispersive X-ray (EDX) spectrometer from Oxford Instruments allowing local elemental analysis with a spatial resolution of ~1 nm.

X-ray photoelectron spectroscopy (XPS) experiments were carried out in a VG Scientific ESCALAB 200R spectrometer including a hemispherical analyzer and working at a pressure lower than 10^{-9} mbar. XPS measurements were performed using the Al Kα line of the dual anode and a pass energy of 50 eV. The instrument was calibrated with a silver sample (Ag $3d_{5/2}$ at 368.3 eV). The peaks were referenced to the C–(C,H) components of the C 1s band at 284.6 eV.

2.3. Catalytic testing and product analysis

The catalytic tests were carried out in magnetically stirred (900 rpm) glass batch reactors containing substrate (tS, 1 mmol), gold based catalyst (Au: 10 μmol), solvent (20 mL) and oxidant (TBHP, 0.05–4 mmol), which were held in air at atmospheric pressure for 24 h. The temperature used was approximately 20 °C below the boiling point of the solvent, that is 60 °C for acetonitrile and cyclohexane and 80 °C for toluene and methylcyclohexane. They used the following chemicals: *tert*-butylhydroperoxide (TBHP, 70% in H_2O, Alfa Aesar), *trans*-stilbene (tS, 97%, Alfa Aesar), methylcyclohexane (MCH, 99%, Sigma–Aldrich) or acetonitrile (ACN, 99.9%, Carlo Erba Reagents) or toluene (TOL, 99.9%, Merck) or cyclohexane (CH, 99.7%, Riedel-de Haën).

The reaction products were identified and quantified by HPLC (Perkin-Elmer Series 200 lc pump, autosampler and UV–vis detector set at 250 nm, reverse phase C-18 column Brownlee, ValueLineSpheri-5 C18, 220 mm × 4.6 mm, acetonitrile/water as eluent at 1 cm^3 min^{-1}). Some reaction mixtures were also analyzed by GC–MS (Hewlett Packard 6890/5973 system; electron impact ionization at 70 eV, He carrier gas, 30 m × 0.25 mm VF5-MS, 100% dimethylpolysiloxane capillary column).

Check experiments and HPLC calibration were carried out using *trans*-stilbene oxide (epoxide, 99%, Acros Organics), benzaldehyde (>98%, Acros Organics), deoxybenzoin (>97%, Alfa Aesar), hydrobenzoin (99%, Alfa Aesar), benzil (>99%, Acros Organics), *cis*-stilbene (96%, Sigma–Aldrich), *cis*-stilbene oxide (97%, Sigma–Aldrich), 2,6-di-*tert*-butyl-4-methylphenol (>99%, Sigma–Aldrich) and hydrogen peroxide (29–32% in H_2O, Alfa Aesar).

Conversion (%) is defined as [[(initial concentration of tS) − (final concentration of tS)]/(initial concentration of tS) × 100]; yield of epoxide (%) is defined as [(final concentration of epoxide)/(initial concentration of tS) × 100]; selectivity to epoxide (%) is defined as [(final concentration of epoxide)/[(initial concentration of tS) − (final concentration of tS)] × 100].

3. Results

3.1. *trans*-stilbene oxidation in excess TBHP (4 mol equiv.)

3.1.1. Solvent effects

We found that, in the presence of 400 mol% TBHP and Au/C, methylcyclohexane as solvent provides better yields of *trans*-stilbene oxide than cyclohexane and acetonitrile (Fig. 1). Au/TiO_2 also leads to higher yields of epoxide in MCH as compared to CH. These higher yields come from higher selectivities at higher conversions, which is quite remarkable, especially since the tests in MCH were carried out at a higher temperature than those performed in ACN and CH (see Section 2.3). It appears therefore that, unlike titanium silicalite-catalyzed alkene epoxidations which take place in high polarity solvents [37], gold systems exhibit higher yields and selectivities towards epoxide in low polarity solvents. This contrasts for example with cyclohexene epoxidation over Ti-MCM-41/TBHP, for which acetonitrile was proposed as the optimum solvent [37]. In the following section, MCH will thus be used as the solvent in order to compare the catalytic properties of the gold materials.

3.1.2. Catalytic behaviors

By comparing the four gold catalysts (Fig. 2), we realize that the conversions observed vary in a short range from 81 to 95% (in 24 h) with Au/TiO_2 > Au/Fe_2O_3 > Au/TiO_2-PC500 > Au/C. Selectivities vary from 53 to 77% with Au/TiO_2 > Au/TiO_2-PC500 ~ Au/Fe_2O_3 > Au/C. It is interesting that the order of activity could be explained by a traditional gold particle size effect, the catalysts with the smallest particle size being the most active. The particle size effects usually observed in the gas phase are however more critical [34] and the selectivities should be higher on larger particles, which is not the case. This shows that this liquid phase catalytic reaction is governed by something more than the gold particle size effect.

Furthermore, the critical support effects encountered in gold-catalyzed oxidations in the gas phase [38] are not so marked under these conditions of epoxidation. Indeed, while Au/C is pretty much inactive for CO oxidation, it displays interesting catalytic properties in reaction with *trans*-stilbene and 400 mol% TBHP (81% conversion, 53% selectivity in 24 h). This liquid phase reaction is nevertheless influenced by the nature of the support: Au/TiO_2 is more active and especially more selective (a higher selectivity is achieved at higher conversion) than Au/C, which illustrates the superiority of titania as a support for epoxidation and could suggest its involvement in the reaction. Indeed, while 19% of tS is converted (in 24 h) in the absence of a catalyst with 52% selectivity to the corresponding epoxide, adding TiO_2-P25 increases the tS conversion to 31% with similar selectivity (56%) and TiO_2-PC500 brings the conversion to 48% with lower selectivity (42%). This is probably due to the presence of sulfonated (i.e. acidic) surface functions on high surface area TiO_2-PC500.

However, a check experiment demonstrates that Pt/C is more active and selective than Au/C and nearly as selective as Au/TiO_2, indicating that, under these conditions, the advantage of using gold in this reaction is not obvious.

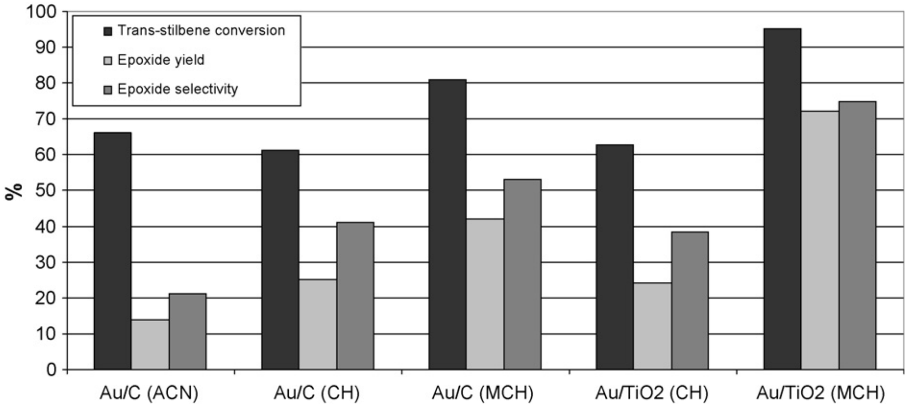


Fig. 1. Solvent effects in the catalytic epoxidation of *trans*-stilbene (1 mmol), in the presence of TBHP (4 mmol), supported catalyst (Au: 10 μmol), solvent (20 mL), 60 °C (ACN, CH) or 80 °C (MCH), 24 h.

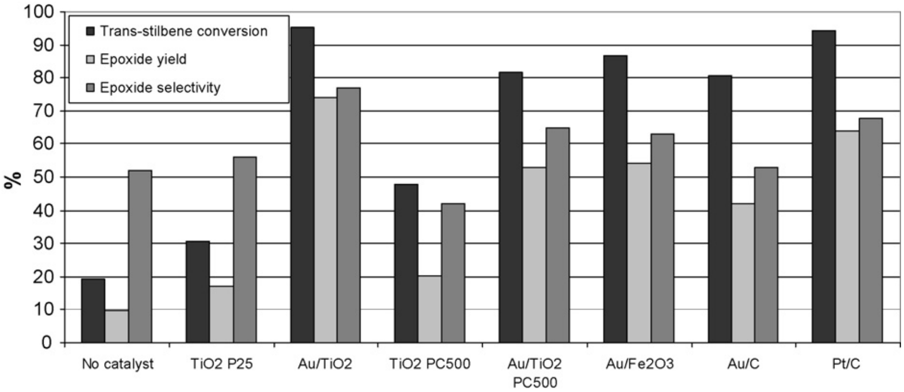


Fig. 2. Catalytic behaviors of gold-based materials (Au: 10 μmol) in the epoxidation of *trans*-stilbene (1 mmol) in MCH (20 mL), using TBHP (4 mmol), 80 °C, 24 h.

3.2. Identification and reactivity of potential by-products

In an attempt to identify by-products and determine possible intermediates in the Au/TiO_2-catalyzed oxidation of tS in the presence of excess TBHP, we found that, at no time of the reaction, more than 2% of tS is converted to HPLC-detectable products other than *trans*-stilbene oxide. The *trans*-epoxide is indeed formed as the primary product with yields increasing from 3% after 20 min reaction up to 74% after 24 h (which results from high conversion, 95%, and relatively high selectivity, 77%). No *cis*-epoxide is observed, indicating a true stereoselective transformation. Deoxybenzoin is detected with yields increasing steadily from 0.1% (40 min) to 1.4% (24 h), most probably resulting from over-oxidation, as will be described below. Benzil is detected throughout the reaction with yields of 0.4–0.7%. Benzaldehyde is detected as a trace product (<0.1%) both with HPLC and GC–MS and ~20% of converted tS remains unaccounted for.

We believe that this fraction is probably transformed into total oxidation products such as CO_2, but that only a part of it results from over-oxidation of *trans*-stilbene oxide. Indeed, when 1 mmol of the epoxide is let to react under the same conditions (MCH, TBHP 4 mmol, Au/TiO_2), only 5% is converted after 24 h, including 1% to deoxybenzoin (Fig. 3). Under the same conditions, 1 mmol benzaldehyde is fully converted within 30 min to deoxybenzoin (3–4%) and HPLC-undetectable products, illustrating the high oxidizability, i.e. susceptibility to autoxidation, of this compound [39], and 1 mmol hydrobenzoin is fully converted over 30 min to benzil, benzoin and benzaldehyde. Benzoin and benzaldehyde will be fully transformed in the next 22 h, while benzil will be only partially converted, to HPLC-undetectable products. When 1 mmol deoxybenzoin is let to react under the same conditions, 47%

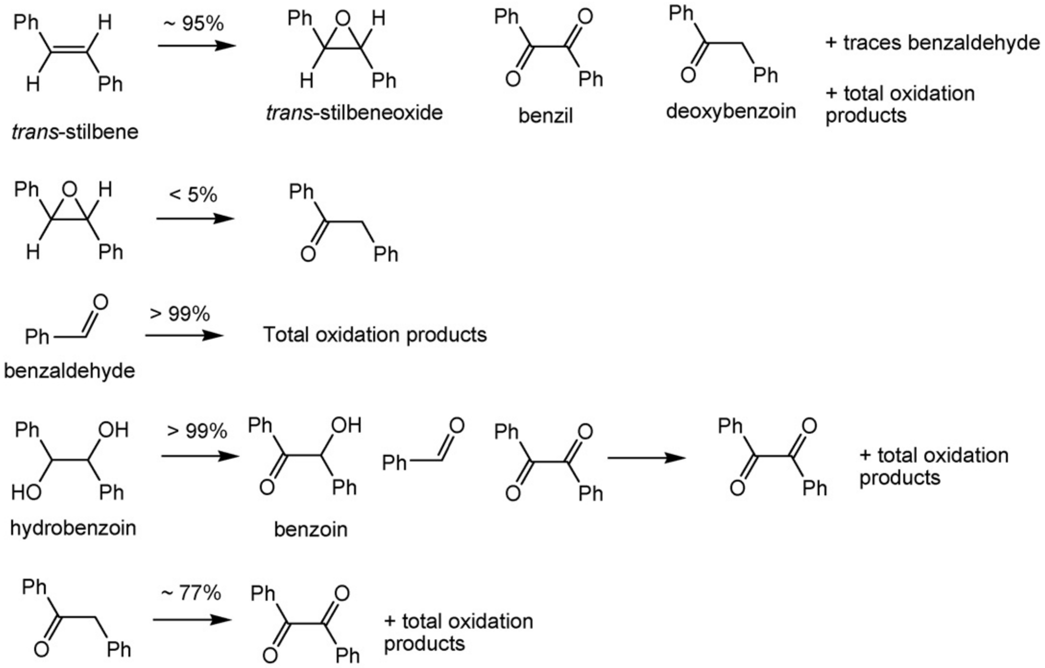


Fig. 3. Reactivity of potential by-products of *trans*-stilbene epoxidation under the following conditions: substrate (1 mmol), TBHP (4 mmol), Au/TiO_2 (Au: 10 μmol), MCH (20 mL), 80 °C, 24 h.

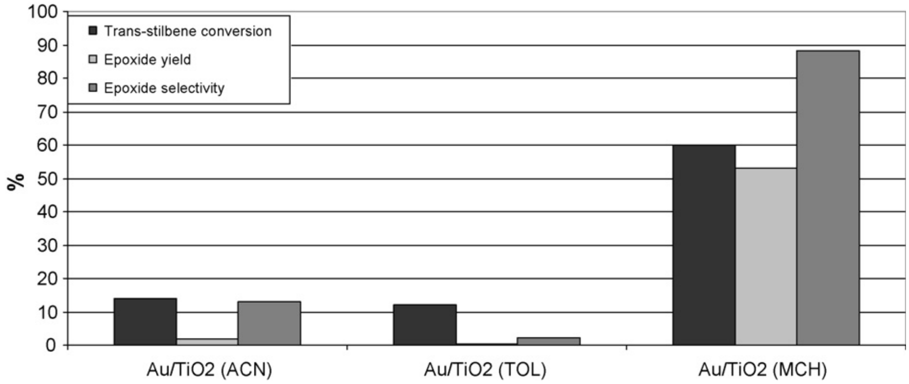


Fig. 4. Solvent effects in the catalytic epoxidation of *trans*-stilbene (1 mmol), in the presence of TBHP (0.05 mmol), Au/TiO_2 (Au: 10 μmol), solvent (20 mL), 60 °C (ACN) or 80 °C (TOL, MCH), 24 h.

is converted after 8 h and 77% is converted after 24 h to benzil (with 53 and 23% selectivity, respectively) and HPLC-undetectable products. It is therefore conceivable that hydrobenzoin, benzaldehyde and deoxybenzoin could be intermediates for parallel reactions leading to full oxidation products but no obvious intermediate for epoxidation can be proposed at this point.

3.3. *trans-stilbene oxidation in limited TBHP (0.05 mol equiv.)*

3.3.1. *Solvent effects*

We find that, in the presence of 5 mol% TBHP and Au/TiO_2, methylcyclohexane as solvent provides better catalytic activity and selectivity towards *trans*-stilbene oxide than toluene and acetonitrile (Fig. 4). Again, the selectivity obtained at higher temperature and conversion in MCH is higher than that obtained in ACN. In this case though, the positive solvent effect seems more pronounced than in the presence of excess TBHP and Au/C; the reactions in toluene and acetonitrile yield indeed less than 5% epoxide while a reaction in methylcyclohexane will give 53% epoxide.

3.3.2. *Catalytic behaviors*

Under these optimized conditions (MCH, 0.05 mol equiv. TBHP, 80 °C, 24 h), the differences in the catalytic behaviors of the gold reference materials are more pronounced (Fig. 5) than in the reaction with excess TBHP (Section 3.1). Nevertheless, the order for activity/selectivity remains the same with Au/TiO_2 > Au/Fe_2O_3 > Au/C. Moreover, Pt/C is now completely inactive under these conditions, showing a real effect of gold in this reaction. It is noted that 14% tS is converted in the absence of a solid catalyst but no epoxide is yielded. Adding TiO_2-PC500 increases tS conversion to 44% but again without forming any epoxide. On the other hand, TiO_2-P25 yields 5% epoxide, resulting from a low conversion and relatively high selectivity (63%). Over Au/TiO_2, the yield of epoxide reaches 53%, which means that 0.53 mmol tS have been converted to *trans*-stilbene oxide, with only 0.05 mmol TBHP present. This clearly shows that another oxygen source has been used during the process. In other words, TBHP is used catalytically, possibly as a radical initiator as already mentioned [25], and molecular oxygen from the air would be activated by the radical formed.

4. Discussion

Before a reaction mechanism can be proposed for the catalytic epoxidation of *trans*-stilbene in methylcyclohexane with catalytic amount of TBHP, it remains to:

- Clearly evidence the presence and the involvement of free-radicals in this optimized version of the reaction.

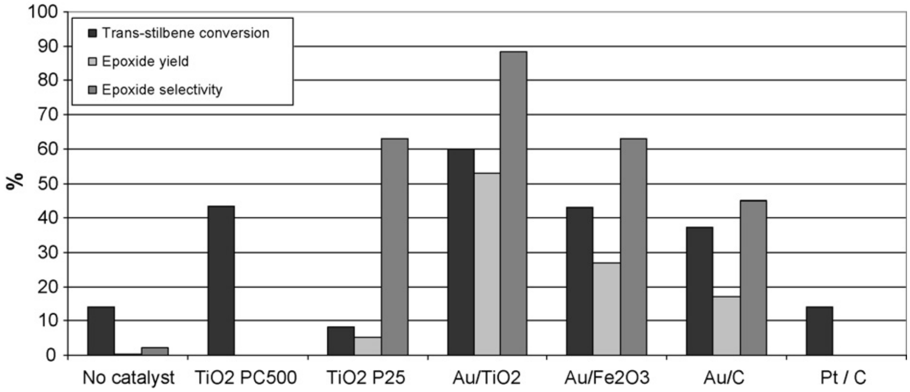


Fig. 5. Catalytic behaviors of gold-based materials (Au: 10 μmol) in the epoxidation of *trans*-stilbene (1 mmol) in MCH (20 mL), using TBHP (0.05 mmol), 80 °C, 24 h.

- Identify these active radicals and their ways of production.
- Identify the way for oxygen activation.
- Identify the way of attack by the activated oxygen species onto the substrate.
- Determine the involvement of the solid catalyst in all these steps.

4.1. *Evidence for a free-radical mechanism*

A characteristic of radical chain reactions is that their rates are strongly dependent on the concentration of the chain initiator [40]. This is indeed what we observe: when 5 mol% TBHP is used instead of 400 mol% TBHP, the initial reaction rate is dramatically decreased (Fig. 6). Furthermore, removing the radical source from the reaction medium (i.e. performing the reaction in the absence of TBHP) leads to less than 1% epoxide formation in 24 h. On the other hand, adding a radical scavenger to the optimized reaction should inhibit epoxide production. Indeed, when 2,6-di-*tert*-butyl-4-methylphenol (10 mol%) is added to MCH, tS, TBHP (5 mol%), Au/TiO_2, less than 5% *trans*-stilbene oxide is yielded in 24 h. These diagnostic tests [40] clearly evidence the presence of free-radical species within the reaction medium and their involvement in the production of *trans*-stilbene oxide.

The fact that 0.53 mmol *trans*-stilbene oxide are produced over Au/TiO_2 with only 0.05 mmol TBHP also shows that molecular oxygen from the air is involved in the process. This is confirmed by an experiment carried out under argon, in which less than 5% *trans*-stilbene oxide is yielded. Oxygen seems indeed to be activated via free-radical species.

The critical solvent effects (acetonitrile and toluene yielding less than 5% *trans*-stilbene oxide while MCH yields more than 50% epoxide, Section 3.3.1) show that oxygen activation is tightly related to the nature of the solvent. Furthermore, identification by GC–MS of minor amounts of methylcyclohexyl hydroperoxide (compound A, Scheme 1) and methylcyclohexan-1-ol (compound C, Scheme 1) amongst the reaction products shows that a fraction of the solvent has been oxidized. This allows to think that the solvent molecule could directly take part in the reaction mechanism, as the active (i.e. propagating) radical. It is possible indeed that a methylcyclohexyl radical is produced under these conditions via abstraction of the tertiary hydrogen atom of methylcyclohexane while the C–H bond energies in ACN and TOL are higher. This abstraction can be carried out by *tert*-butoxy radicals resulting from homolytic cleavage of TBHP; the involvement of methyl radicals coming from β-scission of *tert*-butoxy radicals is unlikely since the rate of β-scission decreases with decreasing polarity (dielectric constant) of the solvent while the yield of epoxide increases under similar conditions [41].

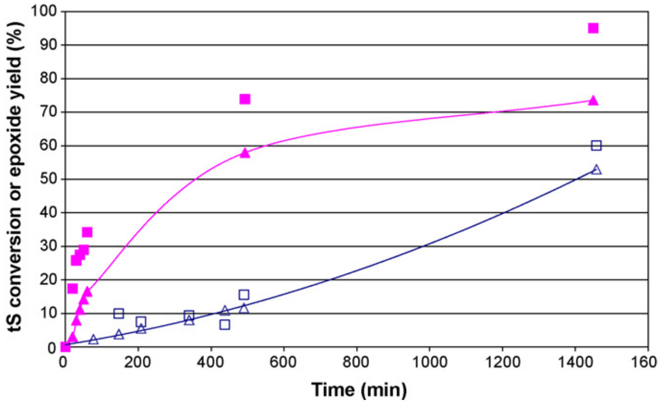
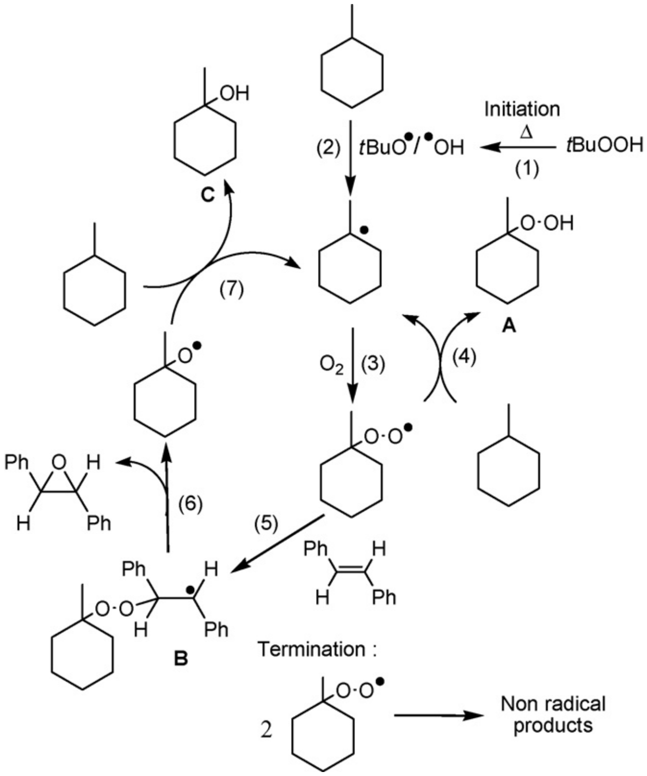


Fig. 6. *trans*-stilbene conversion (squares) and epoxide yield (triangles) as functions of time using tS (1 mmol), MCH (20 mL), 80 °C in the presence of 5 mol% TBHP (open symbols) or 400 mol% TBHP (full symbols).

All this suggests that the epoxidation of *trans*-stilbene involves a cooxidation of MCH and tS. In the proposed mechanism (Scheme 1), the initiation step consists in thermolysis of TBHP (1) and production of the methylcyclohexyl radical (2). The propagation step (3) consists in production of the methylcyclohexyl peroxy radical. It can then add to tS (5) or, to a lesser extent [42], carry out hydrogen abstraction from methylcyclohexane (4) to regenerate the methylcyclohexyl radical and form methylcyclohexyl hydroperoxide (compound A). Addition to (as compared to hydrogen abstraction from) tS is favored since tS has no allylic hydrogen that could be abstracted [43]. Species B is consistent with the results obtained in the Au/C-catalyzed oxidation of *cis*-stilbene, which yields exclusively *trans*-stilbene oxide. This implies the presence of an intermediate which allows rotation around the C–C bond. Addition can be followed by unimolecular decomposition (6) to form the epoxide and a methylcyclohexoxy radical. This species will then abstract the tertiary hydrogen



Scheme 1. Proposed mechanism for the epoxidation of *trans*-stilbene in methylcyclohexane, in the presence of TBHP (5 mol%) and a gold-based catalyst.

from MCH (7) to produce methylcyclohexan-1-ol (compound C) and regenerate the methylcyclohexyl radical. Termination probably occurs via recombination of the peroxo radicals [44,45].

4.2. Reaction with hydroxyl radicals

Direct addition of hydroxyl radicals to tS cannot be fully excluded [46,47], especially in excess TBHP. Addition of *tert*-butoxy radicals would be slower [48,49], since ^{t}BuO$^\bullet$ are more active for hydrogen abstraction [50,51]. It is interesting that using H_2O_2 (4 mmol) instead of TBHP leads, over Au/C, to 30% tS conversion *without formation of any epoxide*. This indicates that the conversion of *trans*-stilbene due to attack by the hydroxyl radical will lead exclusively to degradation products, which could explain the lower selectivities obtained in excess TBHP. Moreover, since 14% *trans*-stilbene is transformed while only 0.3% epoxide is produced in the absence of a catalyst (5 mol% TBHP), we believe that this attack of tS by OH$^\bullet$ is non-catalytic and guided only by the electrophilicity of the hydroxyl radical [52].

4.3. Possible role of gold and titania in the suggested mechanism for gold-catalyzed trans-stilbene epoxidation

The introduction of TiO_2-P25 brings selectivity to the reaction but lowers the conversion (8%). This suggests that titania traps these non-selective hydroxyl radicals and allows ^{t}BuO$^\bullet$ to react with MCH, enabling the epoxide-forming reaction to proceed. The presence of gold on titania P25 further increases both conversion and selectivity. It seems that gold acts in synergy with the titania support and possibly catalyzes hydrogen abstraction from MCH by ^{t}BuO$^\bullet$ (2) and/or formation of the peroxy radical (3). The involvement of gold in the propagation sequence is most likely since the yield of epoxide produced after the catalyst has spent 6 h in the reaction medium before being removed remains at about 18%, instead of going up to 33% (24 h, Au/C, 0.4 mmol TBHP). It is also interesting that the produced epoxide is always in the *trans* form, whether from *trans*- or *cis*-stilbene, suggesting that *selective* unimolecular decomposition (6) has occurred. This is consistent with adsorption onto a solid surface, which creates sterical constraints, thereby decreasing both symmetry and accessibility of the molecule and forcing the reaction to proceed in a specific way. Furthermore, less than 0.04 ppm gold was detected (ICP-MS) in the reaction medium after removal of the catalyst, showing that less than 0.04% of supported gold have leached into the organic phase. On the other hand, 50 ppm of free gold was found inactive for the production of epoxide from *trans*-stilbene, indicating that this reaction is truly heterogeneous.

XPS studies show two contributions for the Au $4f_{7/2}$ peak on the Au/TiO_2 and Au/C catalysts, both before and after reaction: the main contribution (∼90%) is at a binding energy of 83.0 ± 0.1 eV for Au/TiO_2 and at a binding energy of 84.1 ± 0.1 eV for Au/C, corresponding to $Au^{\delta-}$ and Au^0, respectively. The presence of $Au^{\delta-}$ in titania-supported gold catalysts has already been explained by a charge transfer from the support to the gold particle [38]. The minor contribution (∼10%) is at a binding energy of 85.5 ± 0.1 eV both for Au/TiO_2 and Au/C, before and after reaction, indicating the presence of Au^+, probably at the gold/support interface. It is interesting that this contribution is insignificantly increased after reaction, suggesting that gold has suffered negligible oxidation during the reaction. It is not clear which oxidation state of gold is actually active in this reaction. However, if we assume that active gold is involved in interactions with electrophilic peroxy radicals, we could suggest that $Au^{\delta-}$ is more active than Au^0 and Au^+, which would be consistent with the observation that Au/C is less active and selective than Au/TiO_2. Further work is in progress to clarify that point.

5. Conclusion

In summary, we have shown that *trans*-stilbene can be epoxidized stereoselectively at atmospheric pressure and mild temperature in the presence of a supported gold catalyst and a catalytic amount of TBHP. High yields of epoxide are achieved in methylcyclohexane using Au/TiO_2 as the catalyst. TBHP is used as the radical initiator and oxygen from the air as the primary oxidant. The active (i.e. propagating) radical is one produced from the solvent, indicating a cooxidation of MCH and tS. Both gold and titania seem to take part in this free-radical reaction mechanism sustained by molecular oxygen, possibly by trapping the unselective hydroxyl radicals, catalyzing the active radical formation and stabilizing the intermediate resulting from the addition of the methylcyclohexyl peroxy radical onto *trans*-stilbene.

Acknowledgments

The authors wish to thank the French Ministry of Education and Research for P. Lignier's PhD grant, Dr. A.M. Sorokin for fruitful discussions, S. Mangematin and L. Massin from the scientific and technical services of IRCELYON for valuable support.

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