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## Epoxidation of stilbene using supported gold nanoparticles: cumyl peroxyl radical activation at the gold nanoparticle surface<sup>†</sup>

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The catalytic epoxidation of *cis*-stilbene using cumene as a solvent in the presence of supported gold nanoparticles (AuNP) yields a mixture of *cis* and *trans*-stilbene oxides. EPR and product distribution studies support a new mechanistic proposal where oxygen centred radicals activate the AuNP surface and form active surface oxygen species responsible for the epoxidation products.

Epoxidation plays a very important role in organic chemistry due to the high reactivity and extended versatility of the epoxide moiety. Typical peracids, notably meta-chloroperbenzoic acid (m-CPBA), can be used as epoxidation agents and are widely employed at the laboratory scale. Epoxidation using hydroperoxides, such as the Sharpless epoxidation, involves a concerted mechanism in which homogenous Ti complexes are employed as catalysts.<sup>1</sup> Heterogeneous catalysts based on mesoporous materials, used in conjunction with several hydroperoxides as oxygen donors, have been frequently employed in epoxidation reactions.<sup>2-5</sup> More recently, supported AuNP on a variety of materials, including TiO<sub>2</sub>,<sup>6</sup> have received attention as possible alternate catalysts for alkene epoxidation. A typical epoxidation reaction involves an aerated or oxygenated solution containing a free radical initiator, such as an azo compound,<sup>7</sup> or, more frequently, a hydroperoxide.<sup>8,9</sup> A tertbutyl hydroperoxide (TBHP) initiator is typically placed in the presence of a solvent that can be easily oxidized (e.g., cumene or methylcyclohexane)<sup>10</sup> and an alkene, the epoxidation substrate. Comparison of experimental results from different laboratories is complicated due to the large variability of reaction conditions, initiators, catalysts and substrates that have been employed.

<sup>a</sup> Department of Chemistry and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada. This work focuses on the reaction between AuNP-generated radicals and alkenes to promote epoxidation in a system where epoxidation occurs concurrently with solvent oxidation that follows the autooxidation pathway proposed by Ingold<sup>11</sup> in the 1960s.

Previous work investigating the role of supported AuNP as catalysts in epoxidation reactions has suggested that their involvement is limited to the formation of the peroxyl radicals as part of a normal free-radical chain reaction.<sup>12</sup> The epoxidation of stilbene by AuNP in a solvent that can be easily oxidized (*e.g.*, cumene or methylcyclohexane) can be considered a secondary process accompanying oxidation,<sup>13</sup> and, therefore, an understanding of the primary solvent peroxidation process, solvent is needed. Previous work from our group<sup>14</sup> aimed at understanding the role of supported AuNP@TiO<sub>2</sub> in cumene peroxidation revealed cumyl alcohol, and not cumene hydroperoxide (CHP), as the major product.<sup>14</sup> This work is aimed at examining the epoxidation reaction of *cis*-stilbene when using supported AuNP@TiO<sub>2</sub> as a catalyst. The role of this catalyst and the TBHP initiator in the peroxidation process have been examined in some detail.<sup>14</sup>

Table 1 presents the results obtained when using AuNP@TiO<sub>2</sub> as the catalyst for the epoxidation reaction of *cis*-stilbene with cumene as the solvent undergoing peroxidation at 80 °C. Specific experimental conditions can be found in the ESI.† Briefly the reaction involved 10 mL of cumene (7.1 M), 94 µl of *cis*-stilbene (0.5 mmol), 7.8 µl (0.05 mmol) of *tert*-butyl hydroperoxide and *tert*-butylbenzene as internal standard.

Table 1 shows that no *trans*- or *cis*-stilbene oxide was obtained in the absence of the catalyst, or when  $TiO_2$  alone

Table 1Percent conversion of cis-stilbene and % yield of trans-(TSO) and cis-stilbene oxide (CSO) after 24 $h^a$					
Catalyst	Conversion (%)	Yield (TSO) (%)	Yield (CSO) (%)		
Au/TiO <sub>2</sub>	18.7	16.3	2.6		
TiO <sub>2</sub>	48.0	0	0		
No catalyst	0	0	0		

<sup>a</sup> Reaction performed at 80 °C for 24 hours using cumene as solvent.

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Table 2CHP and cumyl alcohol obtained in the epoxidation reaction ofcis-stilbene in cumene using AuNP@TiO2 as catalyst

Catalyst	CHP (mM)	Cumyl alcohol (mM	M
Au/TiO <sub>2</sub>	89	549	
TiO <sub>2</sub> <sup>a</sup>	0	0	
No catalyst	420	24	
<sup><i>a</i></sup> Phenol was obta	ined as the only product		

was used. Significant *cis*-stilbene conversion (48%) was observed in the presence of  $TiO_2$  and has been attributed to mineralization products, supported by similar results obtained by Caps *et al.*<sup>10</sup> for *trans*-stilbene in the presence of  $TiO_2$ . However, when AuNP@TiO<sub>2</sub> was employed as catalyst, a mixture of *cis*- and *trans*stilbene oxide is obtained. Similar results were observed by Hughes *et al.*<sup>8</sup> when using supported AuNP@graphite.

The formation of both cis- and trans-stilbene oxide in the presence of supported AuNP catalysts suggests the involvement of a stepwise mechanism in which the formation of an intermediate capable of easy bond rotation is required prior to completion of the epoxidation process. Table 2 presents the amounts of CHP and cumyl alcohol formed during the epoxidation of *cis*-stilbene in the presence of AuNP@TiO<sub>2</sub>, TiO<sub>2</sub> or in the absence of any catalyst using cumene as solvent showing that in the absence of catalyst, CHP predominates. Qualitatively comparing the information in Tables 1 and 2 can provide valuable information as the possible pathway for AuNP-mediated epoxidation. In the absence of catalyst, no epoxidation products were observed and CHP is the major product. The involvement of free cumyl peroxyl radicals in the direct epoxidation of *cis*-stilbene seems unlikely, as the catalyst is definitely required. When AuNP@TiO2 was employed as the epoxidation catalyst both isomers of stilbene oxide were obtained, in conjunction with the predominant formation of cumyl alcohol. As suggested by our previous work, the AuNP surface-induced decomposition of CHP is one of two pathways responsible for the formation of highly reactive cumyl alkoxyl radicals leading to the formation of cumyl alcohol.14 In addition, the surface induced decomposition of the cumyl peroxyl radicals results in the formation of a reactive oxygen species on the surface of the AuNP that could be responsible for the products observed in this system.

EPR spin trap experiments employing 3,4-dihydro-2,3-dimethyl-2*H*-pyrrole-1-oxide (DMPO) were performed in order to identify better the nature of the radicals present in the epoxidation reaction mixture. The radical/trap adduct depends on the nature of the radical involved and exhibits characteristic EPR spectral features. We were not able to observe any EPR signal in the absence of catalyst or in the presence of the TiO<sub>2</sub> support, most likely because the amount of radical present is far below the detection limit of our system (Fig. S2 and S3, ESI†). In the presence of AuNP@TiO<sub>2</sub>, the EPR spectrum (Fig. 1) clearly illustrates the presence of an oxygen centred radical/DMPO adduct, as determined by comparison with literature precedents.<sup>15,16</sup> The experimental results obtained by EPR spectroscopy suggest that the major radical species present in solution is oxygen centered, but unfortunately the data is characteristically ambiguous as to whether an alkoxyl or peroxyl radical has been trapped.<sup>17</sup>



Fig. 1 Representative EPR spectrum for the oxyl radical/DMPO adduct obtained in the AuNP@TiO<sub>2</sub> catalyzed peroxidation of cumene. The coupling constants are  $a_{\rm H} = 9.8$  G and  $a_{\rm N} = 14.9$  G.

The size and shape dependent electronic properties of small AuNP have a significant influence on its ability to directly activate  $O_2$  in oxidation reactions.<sup>18</sup> Nanoparticles smaller than 2 nm can exhibit this type of behaviour close to ambient temperature and, thus, can lead to epoxidation of substrates, such as styrene.<sup>19</sup> Previous work from our group has demonstrated that peroxyl radicals can be decomposed on the AuNP surface leading to the formation of surface-oxygen species,<sup>14</sup> while EPR spin trap experiments in the current contribution are consistent with the participation of free radicals. Combined, our results lead to the proposal that the oxygen-active species formed on the catalyst support have a direct involvement in the epoxidation process.

In the proposed mechanism, shown in Fig. 2, the first two steps involve our previously proposed activation of the cumyl peroxyl radical on the supported AuNP surface leading to the formation of a reactive surface-oxygen species. This process is accompanied by the formation of a cumyloxyl radical (homolysis) and subsequent H-abstraction to form the observed cumyl alcohol product. The epoxidation then occurs *via* reaction between the alkene and surface oxygen species.

Since both products, *i.e.*, *cis*- and *trans*-stilbene oxide, are obtained, the proposed mechanism must account for a transition state for the reaction on the nanoparticle surface allowing significant rotational freedom given the stereochemical outcome of the reaction. The final step of Fig. 2 depicts the formation of epoxide by way of a reactive oxygen species residing on the nanoparticle surface. It is important to note that though the detailed nature of the interaction between the



**Fig. 2** Proposed steps for the epoxidation of *cis*-stilbene involving reactive oxygen species formed on the AuNP surface.



Fig. 3 Possible pathways for the direct reaction a AuNP-oxygen radical adduct and *cis*-stilbene.

stilbene and AuNP surface is not completely understood, coordination of stilbene to the nanoparticle surface could account for the moderate epoxidation yields observed (see Table 1); that is, essentially all the surface bound active oxygen leads to epoxidation.

The exact nature of the intermediates involved in this reaction is open to speculation. Based on the previous work of Bruice and Castellino,<sup>20</sup> a mechanism involving both the direct attack of a nanoparticle-bound radical species on *cis*-stilbene or a mechanism involving an electron transfer process can be proposed, as shown in Fig. 3.

Pathway a in Fig. 3 describes the direct radical addition of the reactive oxygen species present on the AuNP surface to cisstilbene and the subsequent formation of the corresponding epoxide; the attachment to the surface may prevent full randomization of the intermediate and thus some retention of the cis conformation. In contrast, pathway b illustrates an electron transfer process from cis-stilbene to the AuNP, leading to the formation of an anionic gold species and the stilbene radicalcation; its easy isomerization could lead to both isomers, with the trans configuration clearly dominating due to the absence of any sterical constraints. These two species could then undergo a recombination reaction on the surface, forming the depicted radical intermediate, much the same as in path a, but with a different stereochemical history. This is followed by ring closure to the isomeric epoxide products, with transstilbene oxide likely dominating due to increased free rotation about the central C-C bond in the initial cis-stilbene radical cation intermediate.8 Evidence of an electron transfer from a molecule to the AuNP with formation of the corresponding radical cation was recently proposed for the isomerization of azobenzene.<sup>21</sup> Finally, the last step in both pathways leads to the formation of a mixture of cis- and trans-stilbene oxides.

In conclusion, the mechanism for the AuNP-catalyzed epoxidation of stilbene is proposed to involve the formation of a reactive oxygen species by way of AuNP surface induced decomposition of a peroxyl radical intermediate. These results are supported by product studies that demonstrate the formation of both *cis*- and *trans*-stilbene oxide. EPR spin-trap experiments were also used to substantiate the formation of an oxygencentered radical in the reaction mixture. The presence of an oxygen-centered radical, coupled with the observed product distribution of *cis/trans*-stilbene oxide and lack of epoxidation in the absence of the supported AuNP catalyst suggests the involvement of the AuNP surface on product formation by way of a cumyl peroxyl radical surface decomposition and argues against the direct involvement of a free peroxyl radical in the attack and epoxidation of *cis*-stilbene. An alternative mechanism has also been proposed and is suggested to involve an electron transfer from the *cis*-stilbene to the oxygen bound AuNP adduct, ultimately resulting in ring closure that can also account for the observed epoxide stereochemistry.

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