http://dx.doi.org/10.5935/0103-5053.20150254

*J. Braz. Chem. Soc.*, Vol. 27, No. 2, 334-340, 2016.
Printed in Brazil - ©2016 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

**Article**

# AuNP@$TiO_2$ Catalyzed Peroxidation of Ethyl- and *n*-Propylbenzene: Exploring the Interaction Between Radical Species and the Nanoparticle Surface

***Charles-Oneil L. Crites,[a] José Carlos Netto-Ferreira,*,[a,b] Geniece L. Hallett-Tapley[c] and Juan Cesar Scaiano*,[a]***

*[a]Centre for Catalysis Research and Innovation, Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie, K1N 6N5 Ottawa, Canada*

*[b]Instituto Nacional de Metrologia, Qualidade e Tecnologia (INMETRO), Av. Nossa Senhora das Graças 50, 25520-020 Rio de Janeiro-RJ, Brazil*

*[c]Department of Chemistry, St. Francis Xavier University, P.O. Box 5000, B2G 2W5 Antigonish, Canada*

Ethyl- and *n*-propylbenzene peroxidation has been studied in the presence of supported gold nanoparticles on $TiO_2$ (AuNP@$TiO_2$). The decomposition products obtained from Fenton-induced cumene hydroperoxide decomposition, as well as the oxidation products of ethyl- and *n*-propylbenzene, implicate the participation of reactive oxygen species adsorbed on the AuNP surface. This surface intermediate is believed to be a fundamental participant in hydrogen abstraction reactions required to facilitate the formation of the observed carbonyl derived product.

**Keywords:** AuNP@$TiO_2$, peroxidation, reactive surface oxygen species, ethylbenzene, *n*-propylbenezene

## Introduction

The catalytic role of gold nanoparticles (AuNP) in the formation of radical species via Fenton decomposition of hydrogen peroxide by an electron transfer pathway has been thoroughly discussed.[1] Such catalytic pathways have been actively used to generate hydroxyl radical species employed in the degradation of trace amounts of phenol in aqueous solution.[2] In addition to facile separation, supported AuNP offer the added advantage of a more controlled hydrogen peroxide decomposition, useful in the oxidation of alcohols to the corresponding aldehyde products.[3,4]

Ongoing efforts have been focused on elucidating the specific role of AuNP catalysts in peroxidation reactions, as well as on the identification of radical species interacting with the AuNP surface. In 2007, Garcia and co-workers[5] suggested the formation and interaction of carbon centered radicals with the surface of supported AuNP during the study of alkene epoxidation. Furthermore, Bar-Ziv *et al.*[6] estimated a rate constant of $3.5 \times 10^8$ (mol $L^{-1})^{-1}$ $s^{-1}$ for the interaction between alkyl peroxyl radicals and metallic AuNP.

The role of the support during such peroxidation reactions must also be considered. In previous work, we proposed a mechanism that suggested the interaction of reactive species at the AuNP surface play a crucial role in the decomposition of cumyl hydroperoxide.[7] This decomposition pathway ultimately resulted in the formation of an alkoxy radical and the subsequent formation of cumyl alcohol as the final product.[4] The proposed mechanism involved a hybrid of a Fenton reagent degradation in solution, accompanied by cumene peroxidation and alcohol formation at the AuNP surface.

In this contribution, ethyl- and *n*-propylbenzene peroxidation is examined using cumene hydroperoxide as the initiator and AuNP@$TiO_2$ as the catalyst. By simultaneous monitoring the consumption of cumene hydroperoxide and product formation it is possible to more closely examine the role of supported AuNP in the peroxidation pathways.

## Experimental

### Materials

Ethylbenzene (99%), *n*-propylbenzene, cumene hydroperoxide (80%, the majority of the balance being

---

*e-mail: josecarlos@photo.chem.uottawa.ca, scaiano@photo.chem.uottawa.ca
This manuscript is dedicated to Frank Herbert Quina.

cumene) (CHP), cumyl alcohol (98%; 2-phenyl-2-propanol), acetophenone (98%), propiophenone and 1-phenyl-1-propanol (99%) were purchased from Sigma Aldrich (Canada) and used as received. $TiO_2$ (P25) was a gift from Evonik Degussa (Canada). AUROlite™ 1% AuNP@$TiO_2$ was purchased from Strem Chemicals (USA) and was ground using a mortar and pestle prior to use. Optima grade heptane and 2-propanol were purchased from Fisher Chemicals (Canada) and used as received. *sec*-Phenethyl alcohol (98%) was bought from Acros Organic (Canada) and was purified prior to use.[4]

### Methods

The average size of AuNP@$TiO_2$ (2.3 nm) was determined using a JEM-2100F FETEM transmission electron microscope (TEM) from Jeol Ltd.

Analysis of the reaction mixtures (cumyl alcohol, acetophenone, cumene hydroperoxide, *sec*-phenethyl alcohol and ethylbenzene hydroperoxide) was performed using an Agilent 1100 high performance liquid chromatography (HPLC) with a 99:1 heptane/isopropanol eluent mixture and a normal phase Rx-silica column.

In flow experiments a Matheson flow meter was employed.

### Peroxidation of *n*-propylbenzene under air saturated conditions

In a 50 mL, two-neck round bottom flask, catalyst (100 mg) and cumene hydroperoxide (140 mmol) were added to 10 mL of *n*-propylbenzene and the reaction was heated to 40 or 80 °C. An aliquot was taken from the reaction mixture every hour, centrifuged and subsequently analyzed by HPLC. Control reactions were carried out using the support itself and in the absence of catalyst.

### Peroxidation of ethylbenzene under air saturated conditions

In a 50 mL, two-neck round bottom flask, catalyst (100 mg) and cumene hydroperoxide (140 mmol) were added to 10 mL of ethylbenzene and the reaction was heated to 40 or 80 °C. An aliquot was taken from the reaction mixture every hour, centrifuged and subsequently analyzed by HPLC. Control reactions were carried out using the support itself and in the absence of catalyst.

## Results

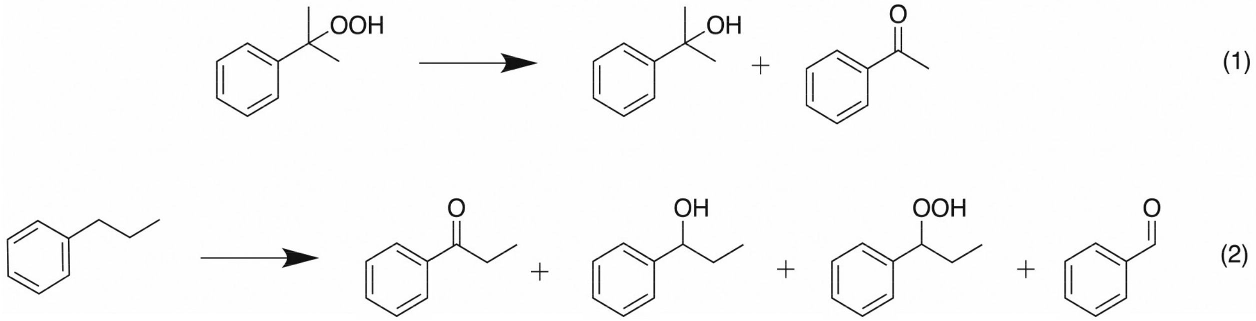
### Peroxidation of *n*-propylbenzene

Peroxidation of *n*-propylbenzene was carried out using CHP as initiator. Control experiments ($TiO_2$ only and CHP initiator only) showed no evidence of *n*-propylbenzene peroxidation. By using these reagents, it is possible to monitor the initiation of the reaction by measuring the disappearance of CHP (Scheme 1, equation 1) and the reaction progression by monitoring the formation of oxidation products from *n*-propylbenezene [(*n*-propylbenzene hydroperoxide, 1-phenyl-1-propanol, benzaldehyde and propiophenone (Scheme 1, equation 2)].

In this context, the ability of AuNP@$TiO_2$ to participate simultaneously in two different reaction pathways can be examined. Figure 1 shows the decomposition profile of 140 mmol CHP into cumyl alcohol and acetophenone catalyzed by AuNP@$TiO_2$ and in the presence of *n*-propylbenzene.

The results in Figure 2 clearly indicate the formation of propiophenone in the catalyzed peroxidation of *n*-propylbenzene, but cumyl alcohol is the dominant product formed as a result of CHP decomposition. Notably, initiator (CHP) degradation reached a plateau after approximately 2 h of reaction and after this time its decomposition becomes much slower.

The results presented in Figure 2 are indicative of propiophenone as the major product formed by way of *n*-propylbenzene peroxidation. In addition, both alcohol and aldehyde products were detected, in agreement with past observations by Kawanami and co-workers.[8] The formation of benzaldehyde is likely generated as a result



**Scheme 1.** Products obtained in the decomposition of CHP (reaction 1) and *n*-propylbenzene peroxidation (reaction 2).

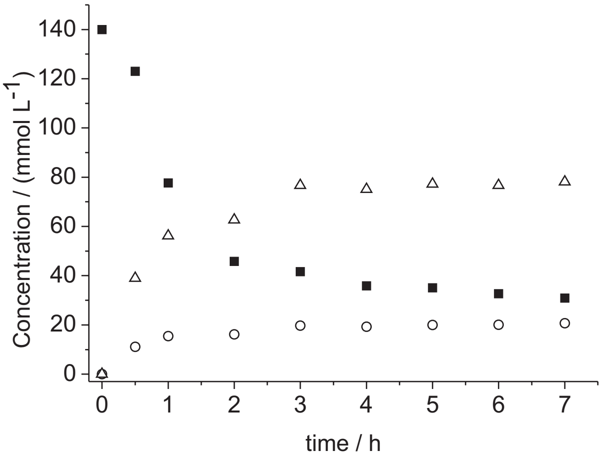


**Figure 1.** Decomposition of CHP and formation of related products catalyzed by AuNP@TiO$_2$: acetophenone (○); CHP (■); cumyl alcohol (△); at 80 °C, using 140 mmol of CHP as initiator and in the presence of *n*-propylbenzene.

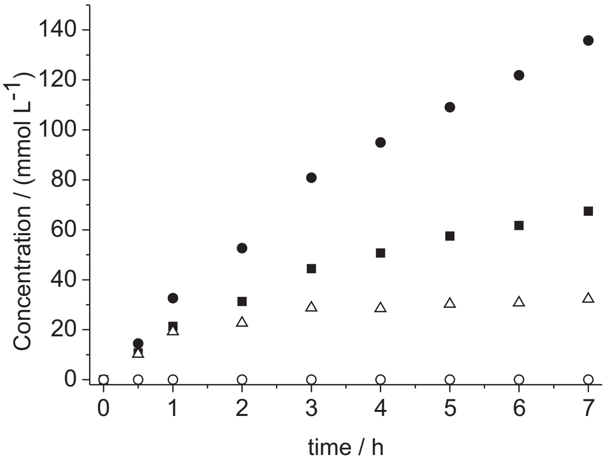


**Figure 2**. Product formation in the peroxidation of *n*-propylbenzene: propiophenone (●); 1-phenyl-1-propanol (■); benzaldehyde (△); *n*-propylbenzene hydroperoxide (○); at 80 °C using 140 mmol of CHP as initiator.

of *n*-propylbenzene alkoxyl radical β-scission, whereas 1-phenyl-1-propanol can be formed through a hydrogen transfer to the *n*-propylbenzene alkoxyl radical. When comparing the results obtained in Figures 1 and 2, the steady generation of propiophenone and 1-phenyl-1-propanol long after completion of the ca. 2 h CHP degradation process suggests that the role of AuNP is simply not limited to Fenton chemistry.

### Peroxidation of ethylbenzene

The peroxidation of ethylbenzene was investigated in a similar manner; the major product obtained in this reaction was acetophenone (AcPh). However, quantification of acetophenone formation is problematic as it can be formed both via Fenton decomposition of CHP and ethylbenzene (EB) peroxidation. Thus, one needs to differentiate between these two potential pathways for AcPh formation. Such a distinction can be easily made using simple calculations employing equations 3 and 4:

$$[\text{CHP decomposition}] = [\text{cumyl alcohol}] + [\text{AcPh CHP}] \qquad (3)$$

$$[\text{AcPh total}] = [\text{AcPh CHP}] + [\text{AcPh EB}] \qquad (4)$$

where equation 3 simply states that the concentration of CHP decomposition is directly related to the detected concentration of cumyl alcohol and acetophenone products (AcPh CHP). Likewise, equation 4 illustrates that the total concentration of acetophenone is composed of both acetophenone generation pathways: CHP (AcPh CHP) and ethylbenzene peroxidation (AcPh EB). Rearrangement of the two equations provides a simple calculation (equation 5) that will allow for an approximation of acetophenone concentration obtained, individually, from each route.

$$[\text{AcPh EB}] = [\text{AcPh total}] - ([\text{CHP decomposition}] - [\text{cumyl alcohol}]) \qquad (5)$$

The results in Figure 3 show that in the presence of ethylbenzene CHP is completely decomposed within the first 30 min of reaction. This can be directly translated into [cumyl alcohol]. From these two values (the amount of cumyl alcohol and the amount of CHP), one can calculate the amount of acetophenone obtained from the decomposition of CHP by using equation 3 presented above.

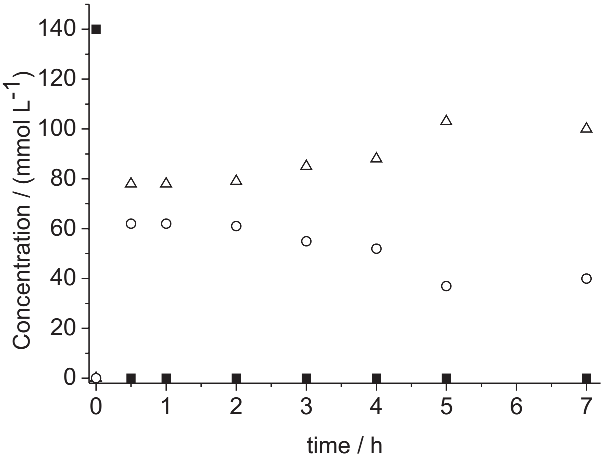


**Figure 3.** Decomposition of 140 mmol of CHP over 6 h at 80 °C using commercial AuNP@TiO$_2$ as catalyst, in the presence of ethylbenzene: CHP (■); cumyl alcohol (△); calculated amount of acetophenone formed from the decomposition of CHP (○).

It is worth noting the difference in CHP decomposition when in the presence of either *n*-propylbenzene (Figure 1, 85% conversion after 2 h) or ethylbenzene (Figure 3, 100%

conversion after 30 min). The effect of substrate on the decomposition of CHP could be a differing peroxyl radical affinity for the AuNP surface for either *n*-propylbenzene or ethylbenzene. In the case of the *n*-propylbenzene peroxyl radical, this reduced affinity would lead to a decreased ability of the nanoparticle to participate in the Fenton process.

Figure 4 illustrates the direct products formed through ethylbenzene peroxidation: acetophenone, ethylbenzene hydroperoxide and *sec*-phenethyl alcohol. From equations 3-5, the amount of acetophenone obtained from the peroxidation of ethylbenzene can be calculated. Figure 4 shows that a considerable product formation is observed within the first hour, regardless of the rapid and complete CHP degradation after the first 30 min, again suggesting that the role of the AuNP is not limited to Fenton chemistry.

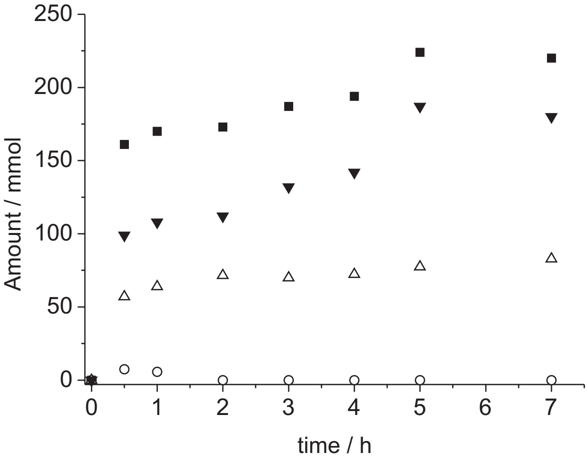


**Figure 4.** Products formed from the AuNP@$TiO_2$-catalyzed peroxidation of ethylbenzene using 140 mmol $L^{-1}$ of CHP as initiator at 80 °C: total acetophenone (▼); acetophenone formed via ethylbenzene peroxidation (○); *sec*-phenethyl alcohol (△); and ethylbenzene hydroperoxide (■).

## Discussion

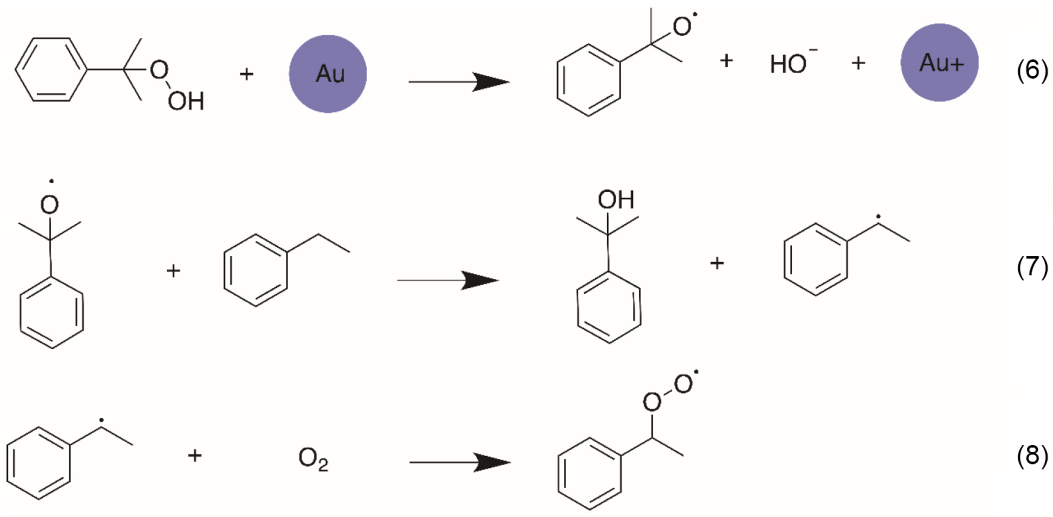
The results obtained in this study strongly suggest the presence of a multiple pathway mechanism in the supported AuNP mediated peroxidation of *n*-propylbenzene and ethylbenzene. In order to more closely understand the mechanism and explain the observed product distribution, it is necessary to identify and explain the possible reaction pathways at play and relate them to the chemistry that can take place in solution as well as on the nanoparticle surface. Previous work from our group[7] has indicated that similar AuNP catalyzed peroxidations rely heavily on both solution and surface chemistry components.

The results obtained from the peroxidation of *n*-propylbenzene and ethylbenzene in the presence of CHP and AuNP@$TiO_2$ illustrate a complete decomposition of the CHP initiator after 2 and 0.5 h, respectively. However, even after complete initiator consumption, formation of the expected peroxidation products steadily continues (Figures 2 and 4). Clearly, since peroxidation product formation continues long after the CHP initiator has disappeared, the participation of the AuNP surface in the peroxidation mechanism involves more than the simple Fenton chemistry required to induce CHP decomposition. The AuNP can be envisioned as participating in the peroxidation mechanism in one of two manners. The first possibility lies solely in the aforementioned participation of the AuNP surface in the Fenton decomposition of CHP, a route that has been long established.[7] The second possible pathway for AuNP involvement entails the affinity of *n*-propylbenzene or ethylbenzene peroxyl radical species for the AuNP surface and the propensity of this interaction to facilitate the decomposition of this peroxyl radical species into the corresponding carbonyl (benzaldehyde or acetophenone) and alcohol (1-phenyl-1-propanol or *sec*-phenethyl alcohol) products, for *n*-propylbenzene and ethylbenzene, respectively. The difference between these products distribution depends entirely on the fate of the peroxyl radical species.

Using the example of ethylbenzene to illustrate, the initial peroxyl radical generation is proposed to occur via AuNP-mediated decomposition of CHP, as shown in Scheme 2. In brief, Fenton chemistry could decompose CHP to a cumyl alkoxyl radical (equation 6). The subsequent reaction of these species with ethylbenzene should form ethylbenzene radicals by hydrogen abstraction (equation 7). Finally, the ethylbenzyl radical could then react with oxygen to form the suggested ethylbenzene peroxyl radical species (equation 8). Even though the support itself is not able to decompose cumene hydroperoxide into radical species, a possible contribution from the support to this decomposition reaction can come from its interaction with AuNP through a process in which the $TiO_2$ matrix can transfer electrons to the nanoparticle and *vice versa*.

Following CHP degradation and subsequent formation of ethylbenzene peroxyl radicals, interaction of the newly formed radical species with the AuNP surface would be unlikely to occur. More likely, as shown in Scheme 3, would be the reaction between the ethylbenzene peroxyl radical and a molecule of ethylbenzene to form, by hydrogen abstraction, ethylbenzene hydroperoxide (equation 9). This newly formed hydroperoxide could then undergo the well known AuNP-catalyzed Fenton chemistry to form the final alkoxyl radical (equation 10), the origin of the observed acetophenone formation. In other words, the new hydroperoxide can also behave as an initiator.

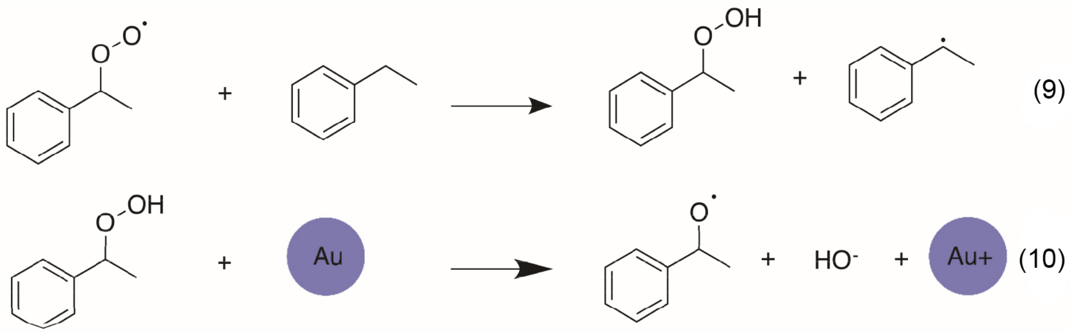
In the second possible AuNP-mediated pathway, the ethylbenzene peroxyl radical is decomposed into



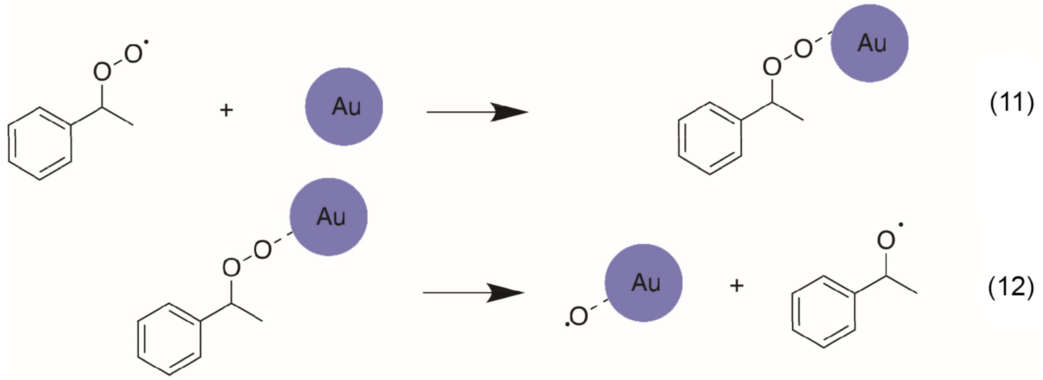
**Scheme 2.** Formation of the ethylbenzene peroxyl radical via the initial Fenton-induced decomposition of CHP and subsequent hydrogen abstraction and reaction with oxygen by the 1-phenyl-1-ethyl radical.

ethylbenzene alkoxyl radical via the interaction with the AuNP surface. This is analogous to the formation of cumyl alkoxyl radical from cumyl peroxyl radicals presented in our previous work.[7] Scheme 4 illustrates the reactions involved in this type of surface chemistry. The ethylbenzene peroxyl radical would interact with AuNP forming a surface bound oxygen adduct (equation 11) that could then be decomposed into the corresponding alkoxyl radical (equation 12). As a consequence of this decomposition, reactive surface oxygen species are generated and remain adsorbed on the AuNP surface.

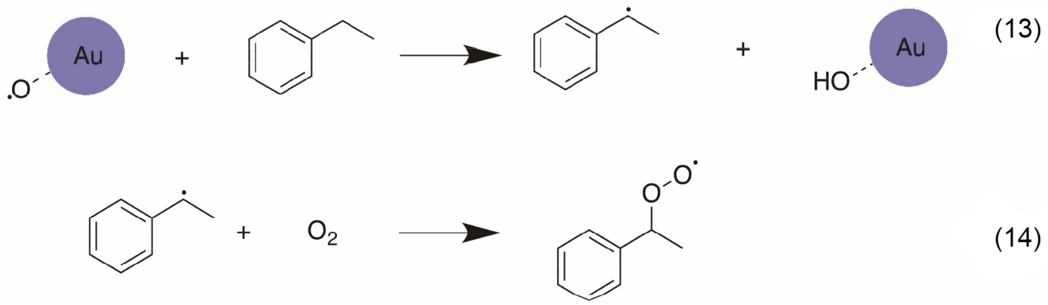
The proposed pathways rely heavily on the successful surface induced decomposition of CHP. After the initial CHP degradation, the formation of acetophenone can feasibly occur by two separate routes. The first pathway involves an alkoxyl radical generated in solution (Scheme 3, equation 10)



**Scheme 3.** Formation of the ethylbenzene alkoxyl radical via Fenton decomposition of ethylbenzene hydroperoxide.



**Scheme 4.** Formation of the ethylbenzene alkoxyl radical via the AuNP-induced decomposition of ethylbenzene peroxyl radical.



**Scheme 5.** Role of the AuNP surface in the formation of ethylbenzene peroxyl radical.

and the second relies on the interaction of the ethylbenzene peroxyl radical with the AuNP surface (Scheme 4, equation 11). The likelihood of acetophenone formation by reaction with a solution based alkoxyl radical is small since the concentration of radicals present in solution is low at any given time. The more probable option is the interaction of the ethylbenzene peroxyl radical with the nanoparticle surface via an alcohol oxidation type pathway[9] or even the involvement of the reactive surface oxygen species.

Scheme 5 describes possible AuNP-catalyzed routes for acetophenone formation. The reactive oxygen species adsorbed on the AuNP surface could then abstract a hydrogen from another molecule of ethylbenzene leading to the formation of an ethylbenzene alkyl radical (equation 13) to continue propagating the catalytic cycle and forming the ethylbenzene peroxyl radical through reaction with $O_2$ (equation 14).

The nature of the radical species on the nanoparticle surface is open to speculation. Nevertheless, the involvement of a surface radical species is clearly needed in order to form acetophenone after the initial 30 min. Formation of active oxygen species has been previously proposed in other publications, such as in the work by Gu and co-workers[10] on the peroxidation of ethylbenzene by gold nanowires.

Thus, the AuNP plays two critical roles in the catalyzed peroxidation of ethylbenzene. Initially, the AuNP are responsible for the decomposition of CHP via Fenton chemistry. Following complete decomposition of the CHP initiator, AuNP surface participate in the peroxidation mechanism by way of a reactive surface oxygen species. The mechanistic pathways of *n*-propylbenzene peroxidation can be envisioned as occurring in the same manner, simply using *n*-propylbenzene as the starting substrate. In this case, the interpretation of acetophenone formation is straightforward, as it can only derive from the CHP initiator.

## Conclusions

The catalyzed oxidation of *n*-propylbenzene and ethylbenzene by AuNP@$TiO_2$ was performed using CHP as the initiator. Simultaneous monitoring of the CHP decomposition and the alkylbenzene oxidation allowed for the proposal of two different mechanistic pathways involving the direct participation of the AuNP catalyst. A Fenton-type mechanism occurs until the CHP initiator has been completely consumed. This step is then followed by a surface-type mechanism in which reactive oxygen species generated on the AuNP surface continue to propagate the catalytic cycle.

## Supplementary Information

Supplementary Information (representative HPLC chromatograph and details on the methods to determine the calibration factor for *n*-propylbenzene and ethylbenzene hydroperoxide) is available free of charge at http://jbcs.sbq.org.br as PDF file.

## Acknowledgements

We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada for support of this research. J. C. N-F. thanks the University of Ottawa for a visiting professor fellowship.

## References

1. Navalon, S.; Martin, R.; Alvaro, M.; Garcia, H.; *Angew. Chem., Int. Ed.* **2010**, *49*, 8403.
2. Navalon, S.; Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H.; *ChemSusChem* **2011**, *4*, 1712.
3. Kiyonaga, T.; Jin, Q.; Kobayashi, H.; Tada, H.; *ChemPhysChem* **2009**, *10*, 2935.
4. Hallett-Tapley, G. L.; Silvero, M. J.; González-Béjar, M.; Grenier, M.; Netto-Ferreira, J. C.; Scaiano, J. C.; *J. Phys. Chem. C* **2011**, *21*, 10784.
5. Álvaro, M.; Aprile, C.; Corma, A.; Ferrer, B.; García, H.; *J. Catal.* **2007**, *245*, 249.
6. Bar-Ziv, R.; Zilbermann, I.; Zidki, T.; Cohen, H.; Meyerstein, D.; *J. Phys. Chem. C* **2009**, *113*, 3281.

7. Crites, C.-O. L.; Hallett-Tapley, G. L.; Frenette, M.; González-Béjar, M.; Netto-Ferreira, J. C.; Scaiano, J. C.; *ACS Catal.* **2013**, *3*, 2062.
8. Dapurkar, S. E.; Shervani, Z.; Yokoyama, T.; Ikushima, Y.; Kawanami, H.; *Catal. Lett.* **2009**, *130*, 42.
9. Conte, M.; Miyamura, H.; Kobayashi, S.; Chechik, V.; *J. Am. Chem . Soc.* **2009**, *131*, 7189.
10. Hu, L.; Cao, X.; Yang, J.; Li, M.; Hong, H.; Xu, Q.; Ge, J.; Wang, L.; Lu, J.; Chen, L.; Gu, H.; *Chem. Commun.* **2010**, 1303.

*Submitted: July 25, 2015*