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Solvent and oxidant effects on the Au/TiO_2-catalyzed aerobic epoxidation of stilbene

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ABSTRACT

Molecular oxygen can be used as the main oxidant to selectively epoxidize *trans*-stilbene over Au/TiO_2 catalysts, in a free-radical process. However, the nature of the radical initiator has a critical influence on the reaction selectivity. *tert*-Butylhydroperoxide (TBHP, catalytic amount) leads to high yields of epoxide; on the other hand, hydrogen peroxide and di-*tert*-butylperoxide merely cause degradation of *trans*-stilbene. The choice of the solvent is also critical. Amongst the selected solvents, only alkyl-substituted cyclohexanes lead to high yields of epoxide, despite the poor dispersion of the catalytic powder. Other solvents, including the more polar ones and cyclohexane, are significantly less efficient, both in terms of total activity and epoxide production. The latter does not go beyond the yield expected from the potential stoichiometric reaction between TBHP and *trans*-stilbene (5%). On the basis of these results, an aerobic epoxidation mechanism is proposed in which molecular oxygen is activated by a substituted cyclohexyl radical produced by abstraction of a tertiary hydrogen atom from the solvent molecule by a *tert*-butylperoxy radical.

1. Introduction

Supported gold nanoparticles have been shown to catalyze alkene epoxidations in the liquid phase in the presence of catalytic amounts of *tert*-butylhydroperoxide (TBHP) [1]. The Au/TiO_2 reference catalyst from the World Gold Council in particular exhibits high selectivity for the aerobic epoxidation of stilbene [2]. However, the choice of the solvent was found critical to achieve high levels of epoxidation [3]. Indeed, while yields of epoxide reach 50% in methylcyclohexane, less than 1% of epoxide is formed in toluene or acetonitrile. But the solvent also affects the overall activity of the catalyst, which converts less than 10% of *trans*-stilbene in toluene and acetonitrile. It was proposed that the gold-catalyzed epoxidation proceeds in methylcyclohexane through a free-radical process initiated by TBHP and propagated by a radical formed directly from methylcyclohexane, which activates molecular oxygen (oxidation products of methylcyclohexane were indeed detected). It was also noticed that using hydrogen peroxide (excess) instead of TBHP yields exclusively degradation products. This suggested that hydroxyl radicals were non-selective and that the selective epoxidation reaction was induced by the *tert*-butoxy radical. The gold-catalyzed epoxidation of stilbene thus appears to be very sensitive to the type of solvent and peroxide used.

In this paper, we aim at determining a suitable class of solvent for this catalyzed reaction and to refine our understanding of the free-radical mechanism involved. We present a systematic study of the influence of the radical initiator and the solvent on the catalytic properties of the Au/TiO_2 reference catalyst for the *trans*-stilbene epoxidation reaction. For this purpose, we have selected peroxides which exclusively yield hydroxyl (H_2O_2) or *tert*-butoxy (di-*tert*-butylperoxide) radicals upon homolytic cleavage in order to assess the properties of the $OH^\bullet$ and $^t BuO^\bullet$ radicals in this reaction. On the other hand, we have selected solvents, which allow both to properly dissolve *trans*-stilbene at 80 °C and to cover the whole range of polarity.

2. Experimental

2.1. Materials

1.5% Au/TiO_2 (type A, lot no. Au–TiO_2 #02-06, sample no. 84) was purchased from the World Gold Council. It basically consists in 3.5 ± 0.9 nm gold particles dispersed on titania P25 (Degussa, 50 ± 15 $m^2\,g^{-1}$, 75 ± 5 wt% anatase + 25 ± 5 wt% rutile with mean particle diameters of 25 and 39 nm). It contains 1.5 ± 0.1 wt% gold, as determined by in-house inductively coupled plasma optical emission

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spectroscopy (ICP-OES Activa from HORIBAJobin Yvon). It was heated in air at 250 °C for 4 h before use.

The following solvents were purchased from Sigma–Aldrich and used without further purification: *n*-heptane (99%), methylcyclohexane (MCH, 99%), 1,3 dimethylcyclohexane (99%), 1,4 dimethylcyclohexane (99%), piperidine (99.5+%), 1-methylpiperidine (98%), benzylalcohol (99%), acetophenone (99%), propionitrile (99%), dimethylsulfoxide (DMSO, 99.6%). Cyclohexane (99.7%, Rieden de Haën), toluene (99.8%, SDS), dimethylformamide (DMF, 99.8%, Acros) and acetonitrile (99.9%, Carlo Erba Reagents) were also used without further purification.

tert-Butylhydroperoxide (70% TBHP in H_2O, Alfa Aesar), di-*tert*-butylperoxide (98% DTBP, Sigma–Aldrich) and hydrogen peroxide (29–32% H_2O_2 in H_2O, Alfa Aesar) were used as initiators. *trans*-Stilbene (tS, 96%) was purchased from Sigma–Aldrich.

2.2. Catalytic evaluation (Scheme 1) and product analysis

The catalytic tests were carried out in magnetically stirred (900 rpm) glass batch reactors held at 80 °C for 24 h in air at atmospheric pressure. The reaction mixtures consist of substrate (tS, 186 mg/1 mmol), solvent (20 mL), catalyst (27 ± 2 mg/2.1 ± 0.2 μmol Au) and co-oxidant (0.05 mmol).

The reaction products were identified and quantified by HPLC (PerkinElmer Series 200 lc pump, autosampler and UV–vis detector set at 250 nm, reverse phase C-18 column Brownlee, ValueLine-Spheri-5 C18, 220 mm × 4.6 mm, acetonitrile/water as eluent at 1 $cm^3\ min^{-1}$). The 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). Some reaction mixtures were also analyzed by UV–vis spectroscopy (Lambda 35 PerkinElmer UV/vis spectrometer, absorbance mode, 200–1100 nm, slit width 1 nm, scan speed 120 nm/min, data interval 3 nm, using quartz Suprasil cells with a light path of 10 mm).

trans-Stilbene conversion (C%) is defined as [(initial concentration of tS) – (final concentration of tS)]/(initial concentration of tS) × 100. The yield of epoxide (Y%) is defined as (final concentration of epoxide)/(initial concentration of tS) × 100. Selectivity (S%) is defined as the (epoxide yield)/(tS conversion) ratio (×100). They are all determined by HPLC-product analysis.

3. Results and discussion

3.1. Influence of the nature of the peroxide

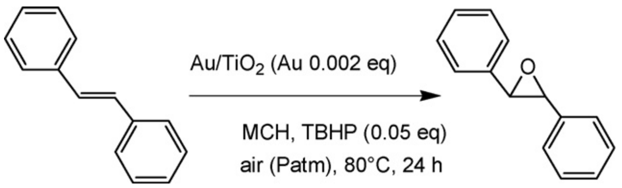
This study has been carried out using methylcyclohexane as solvent. Although the presence of catalytic amounts of TBHP leads to significant production of epoxide, neither di-*tert*-butylperoxide (^{t}BuO–OBu^t), nor hydrogen peroxide (HO–OH) is suitable for epoxidation (Table 1). Both peroxides essentially degrade about 20% of *trans*-stilbene most probably into total oxidation products. This shows that both *tert*-butoxy and hydroxyl radicals, produced from homolytic cleavage of the above-mentioned peroxides, are non-selective when used separately. Actually, when used together (entry 4), the catalytic results are hardly improved: stilbene conversion remains at 20% and the epoxide yield does not even reach 2%. This indicates that the epoxide forming reaction involves more than a synergistic effect between *tert*-butoxy and hydroxyl radicals. It rather relies on the formation of *tert*-butylperoxy radicals, which results from hydrogen abstraction from TBHP by ^{t}BuO$^\bullet$, as shown in Scheme 2 (initiation) [4]. The rate of hydrogen abstraction from TBHP by *tert*-butoxy radicals is indeed several orders of magnitude faster than the rate of H abstraction from hydrocarbons and especially cycloalkanes [5]. Increasing the concentration of ^{t}BuO$^\bullet$ radicals, by adding extra DTBP (entry 5), does not improve conversion or yield; it rather negatively affects selectivity. The presence of extra OH$^\bullet$ radicals (entry 6) decreases the selectivity even further, possibly due to direct reaction with *trans*-stilbene which leads to degradation products. This is consistent with the active radical being a peroxy species, as peroxy radicals are generally more selective [6] and less reactive [7] than alkoxy radicals. Direct, unselective attack onto *trans*-stilbene could thus be prevented.

Table 1
Influence on the type of peroxide used (catalytic amount) on the Au/TiO_2-catalyzed epoxidation of *trans*-stilbene

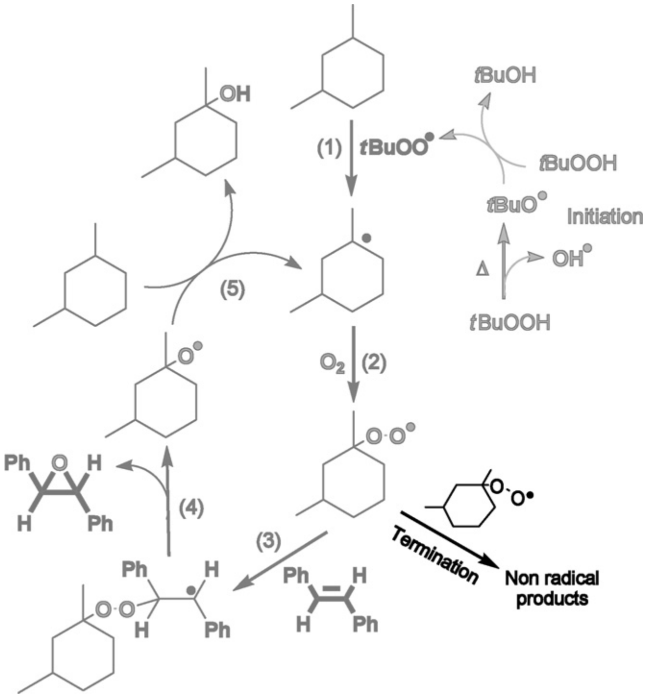
Entry	Peroxide	Catalytic properties		
		C%	Y%	S%
1	TBHP	42	27	64
2	DTBP	20	0.5	3
3	H_2O_2	24	0.5	2
4	DTBP + H_2O_2[a]	20	1.8	9
5	TBHP + DTBP[a]	39	22	58
6	TBHP + H_2O_2[a]	39	20	52

Reactions conditions: tS (1 mmol), methylcyclohexane (20 mL), Au/TiO_2 (27 ± 2 mg/2.1 ± 0.2 μmol Au) and peroxide (0.05 mmol), air/atmospheric pressure/80 °C/24 h.

[a] 0.05 mmol of each peroxide.



Scheme 1. Reaction conditions for the Au/TiO_2-catalyzed epoxidation of *trans*-stilbene.



Scheme 2. Proposed mechanism for the Au/TiO_2-catalyzed aerobic epoxidation of *trans*-stilbene in 1,3-dimethylcyclohexane.

Table 2
Solvent properties and effects on the Au/TiO_2-catalyzed epoxidation of *trans*-stilbene

Entry	Solvents	$\varepsilon/\varepsilon_0$ (25 °C) [8]	O_2 solubility (mol%)	O_2 content (mmol)	Catalytic properties		
					C%	Y%	S%
1	*n*-Heptane	1.9	0.204 [9]	0.056	13	2.4	19
2	Cyclohexane	2.0	0.125 [9]	0.046	1.6	1.0	61
3	Methylcyclohexane	2.1 [10]	0.160 [9]	0.050	42	27	64
4	1,3-Dimethylcyclohexane				67	43	63
5	1,4-Dimethylcyclohexane				63	41	65
6	Toluene	2.4	0.094 [11]	0.035	3.2	2.0	61
7	1-Methylpiperidine				0.2	<0.1	–
8	Piperidine	5.8			3.1	<0.1	–
9	Benzylalcohol	12.7			2.1	0.2	9.5
10	Acetophenone	17.4			5.6	1.7	31
11	Propionitrile	28.3			9.4	4.7	50
12	Dimethylformamide	37.0			3.7	0.4	10
13	Acetonitrile	37.5	0.041 [12]	0.031	3.8	2.5	67
14	Dimethylsulfoxide	46.7			6.7	<0.1	–

Reactions conditions: tS (1 mmol), solvent (20 mL), Au/TiO_2 (27 ± 2 mg/2.1 ± 0.2 μmol Au) and TBHP (0.05 mmol), air/atmospheric pressure/80 °C/24 h.

3.2. Solvent effects

Table 2 shows the catalytic properties of the Au/TiO_2 catalyst for the epoxidation of *trans*-stilbene in each solvent as well as the dielectric constants of the solvents used. The dielectric constant (or relative permittivity) is a relative measure of the solvent polarity. Some data on oxygen solubility are also included, when available. It is clear from Table 2 that, amongst all the solvents investigated, only mono- and di-substituted cyclohexanes allow to achieve significant yields of epoxide and high selectivity. The solvent efficiency (in terms of epoxide production, then stilbene conversion) is as follows: 1-methylpiperidine < piperidine < dimethylsulfoxide < benzylalcohol < dimethylformamide < cyclohexane < acetophenone < toluene < *n*-heptane < acetonitrile < propionitrile ≪ methylcyclohexane < 1,4-dimethylcyclohexane < 1,3-dimethylcyclohexane. It does not seem to follow any trend in terms of solvent dielectric constant, which suggests that the solvent effect on the Au/TiO_2-catalyzed epoxidation of *trans*-stilbene is more than a polar effect. The first six solvents in the series produce less than 1% epoxide (Table 2, entries 7, 8, 14, 9, 12, 2); the following 5 (Table 2, entries 10, 6, 1, 13, 11), less than 5%, which is the upper limit of the stoichiometric reaction between *trans*-stilbene (1 eq) and *tert*-butylhydroperoxide (0.05 eq). Thus, in none of these 11 reaction media (Table 2, entries 1, 2, 6–14), is there any evidence for the involvement of molecular oxygen in the epoxidation mechanism. TBHP could well be used as the principal oxidant. In the following, these 11 solvents will be referred to as "inefficient".

It is interesting that acetonitrile, which is commonly used for epoxidation of lower alkenes by the titanium silicalite/TBHP system [13], appears amongst the best of these 11 solvents (together with propionitrile) and produces low but non-negligible yields of epoxide with the highest selectivity observed amongst the inefficient solvents (Table 2, entry 13). Furthermore, in both nitrile solvents (and only in those), is benzaldehyde produced from *trans*-stilbene as a significant by-product (~1.5%). This shows that total oxidation pathways are minimal (quasi-inexistant for reaction in acetonitrile), which is consistent with the presence of a non-radical mechanism. Polar solvents are anyway expected to hinder radical oxidations as the solubility (hence the actual concentration) of oxygen in these media is lower, as compared with non-polar solvents (Table 2).

In propionitrile, the purple catalytic powder turns white after a few minutes of reaction, which might indicate leaching of gold from the catalyst surface, although the reaction mixture remains colorless. UV–vis analysis of the liquid reaction medium (not shown) gives a broad absorption band between 220 and 350 nm, typical of organic compounds, that is not particularly informative. However, a UV–vis spectrum (Fig. 1) of a propionitrile solution (containing no organics) that has been in contact with the reference catalyst at 80 °C for 20 min exhibits a pattern, with two distinct absorbance maxima at 232 and 240 nm, that can be attributed to the $[Au^{I}(CN)_2]^-$ anion [14,15]. It is thus possible that oxidative addition [14] of propionitrile on surface gold atoms makes gold gradually leach out from the titania surface [16]. Inorganic cyanides are indeed extensively used in metallurgical processes for leaching gold from ores [17,18]. Actually all gold (1.5 μmol) can be leached out from the reference catalyst (21 mg) in 16 min in propionitrile (14 mL), even in the absence of other reagents such as TBHP for example. On the other hand, no leaching of gold was observed under reaction conditions in acetonitrile. The additional formation of epoxide (4.7% vs. 2.5%) observed in propionitrile (Table 2, entry 11) could thus be due to a homogeneous catalytic process involving $Au^{I}(CN)_2$ anions.

Heterocyclic amines are the most inappropriate solvents for this reaction (Table 2, entries 7 and 8). The reaction media turn orange in both cases although the catalyst color has apparently not changed. In general, cyclic compounds do not seem suitable except if they are substituted. None of the hydrocarbons containing heteroatoms (N, O, S) leads to significant yields of epoxide (Table 2, entries 9, 10, 12 and 14). Stronger interactions between the solvent and the catalytic powder might be responsible for limited catalytic

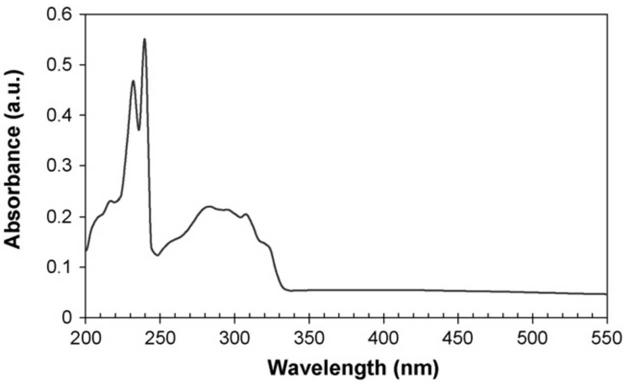


Fig. 1. UV–vis spectrum of the supernatant of a Au/TiO_2/propionitrile mixture left to react at 80 °C for 20 min (ref.: propionitrile).

activity. In DMF, for example, the catalyst turns blue, indicating some changes at the catalyst surface, which could result from a chelation of gold particles with the strongly donating solvent molecules. DMSO is also likely to strongly interact with gold particles, as sulfur is known to exhibit high affinity for gold. However, no change of the catalyst color has been observed in this case.

Despite the poorer dispersion of the Au/TiO_2 powder within the non-polar reaction media, some hydrocarbons, derived from methylcyclohexane, are efficient solvents for gold-catalyzed stilbene epoxidation (Table 2, entries 3–5). On the other hand, neither cyclohexane nor *n*-heptane is an efficient solvent, despite the higher oxygen solubility reported in the latter (Table 2, entries 1 and 2). Epoxide yields thus appear to closely depend on the molecular structure of the solvent, and, more specifically, on the presence of tertiary alkyl groups. Furthermore, epoxide formation is accompanied in all cases by partial oxidation of the solvent molecule, precisely at (one of) the tertiary C–H bond(s). 1-Methylcyclohexanol, 1,3-dimethylcyclohexanol and 1,4-methylcyclohexanol have indeed been detected by GC–MS. Secondary oxidation products are also present but in minor amounts. Concerning the reaction in methylcyclohexane (Table 2, entry 3), more 1-methylcyclohexanol (and more epoxide) are observed (GC–MS and HPLC respectively) when TBHP instead of H_2O_2 (Table 1, entry 3) is used as the initiator, despite the higher concentration of $OH^\bullet$ radicals in the latter case. This shows that the epoxidation process and the oxidation of the solvent are interconnected. Indeed, although direct oxidation of methylcyclohexane with hydroxyl radicals is possible, more 1-methylcyclohexanol is formed through the production of *trans*-stilbene oxide. Furthermore, in these non-polar solvents, the epoxide yields achieved (27–43%) are significantly beyond that expected from a stoichiometric reaction between *trans*-stilbene and TBHP (5%). It thus suggests that oxygen from the air is used as the principal oxidant. Formation of the epoxide then relies on the activation of molecular oxygen, which we believe is carried out by a substituted cyclohexyl radical (Scheme 2) produced by abstraction of (one of) the tertiary hydrogen atom(s) from the solvent molecule by the *tert*-butylperoxy radical.

It is interesting that the epoxide yields obtained in dimethylcyclohexanes are 50% higher than that obtained in methylcyclohexane. This is consistent with the increased H abstraction rate observed on di-substituted cyclohexanes vs. mono-substituted cyclohexane [19]. The distance between the two methyl groups in the solvent molecule do not seem to affect the epoxidation efficiency of the catalyst/oxygen activation efficiency of the substituted cyclohexyl radical, as both 1,3- and 1,4-dimethylcyclohexanes give similar results in terms of conversion and selectivity (Table 2, entries 4 and 5).

Hydrogen atoms from primary and secondary alkyl functions, whether from linear or cyclic alkanes, are generally less reactive towards abstraction [19–21] due to the higher energies of these C–H bonds [22]. Nonetheless, benzyl alcohol and benzaldehyde have been observed as products of toluene oxidation (HPLC, GC–MS), which can be attributed to destabilization of the primary C–H bond [22] by the phenyl ring. Fragments attributed to benzoyl carbinol are also detected (GC–MS), which indicates (minor) oxidation of acetophenone. This suggests that some primary alkyl radicals might be formed under our catalytic conditions. Similarly, secondary alcohol and ketone products have been observed from cyclohexane (cyclohexanol and cyclohexanone), methyl-substituted cyclohexanes (2-methylcyclohexanol, 2-methylcyclohexanone, 3-methylcyclohexanol, 3-methylcyclohexanone, 4-methylcyclohexanol and 4-methylcyclohexanone; 2,4-dimethylcyclohexanol, 2,4-dimethylcyclohexanone, 3,5-dimethylcyclohexanol and 3,5-dimethylcyclohexanone; 2,5-dimethylcyclohexanol and 2,5-dimethylcyclohexanone) and heptane (2-heptanol, 2-heptanone, 3-heptanol, 3-heptanone). Secondary alkyl radicals might thus also be formed under our conditions despite the high pre-exponential factors/activation energies measured for abstraction of secondary hydrogens by *tert*-butylperoxy radicals from cyclohexane/methylcyclohexane [23]. It is possible that the energy barriers are lowered in the presence of the gold catalyst. In any case, neither the primary nor the secondary alkyl radicals formed “propagate” the proposed mechanism (Scheme 2), as the epoxide yields obtained within these solvents are lower than the already described stoichiometric limit (5%). Although no attempt has been made to experimentally determine which step(s) of the propagation sequence is (are) actually hindered, addition of primary and secondary alkyl radicals to the oxygen molecule has been reported to be about one order of magnitude slower than addition of tertiary alkyl radicals [20]. Moreover, rate constants for chain termination are higher for primary and secondary alkylperoxy radicals than for tertiary alkylperoxy radicals [21]. On the other hand, based on steric considerations [24], a slower addition of primary/secondary (vs. tertiary) alkylperoxy radicals to *trans*-stilbene is unlikely [25]. Thus, we suggest that, in solvents that exclusively produce primary or secondary alkyl radicals, step 2 (Scheme 2) is hindered while the termination step is enhanced, thereby resulting in limited epoxide yields. On the other hand, in solvents bearing tertiary hydrogen atoms, epoxidation of *trans*-stilbene (Scheme 2, step 3 + 4) results in hydroxylation of the solvent molecule at the tertiary carbon atom (Scheme 2, step 5).

It is noted that the Au/TiO_2 reference catalyst exhibits low activity for the aerobic oxidation of benzylalcohol. A fraction only of benzylalcohol (less than 1%) is oxidized to benzaldehyde (HPLC). Indeed, the benzylalcohol molecule seems to require much more stringent oxidative conditions in order to be transformed over titania-supported gold catalysts [26]. It is also interesting that, in the presence of aldehyde, the epoxide yield remains very low. This indicates that cooxidation of olefin and aldehyde, which often increases the epoxidation rate, is unlikely under these conditions [27–31].

4. Conclusion

We have shown that the Au/TiO_2-catalyzed aerobic epoxidation of *trans*-stilbene is very specific to both the nature of the radical initiator used and the molecular structure of the solvent. In particular, high activity/selectivity relies on the ability of the initiator to form peroxy radicals (initiation step) and is related to the presence of tertiary hydrogen atoms in the solvent molecule. Secondary oxidation products (from the solvents) can also be formed under these conditions, despite the lower reactivity of secondary C–H bonds. One of the implications of this work is that direct oxidation of cyclohexane to industrially useful cyclohexanol and cyclohexanone could be achieved at low temperature over gold catalysts upon fine tuning of the catalytic material.

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