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Initiator-free hydrocarbon oxidation using supported gold nanoparticles

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Abstract

The oxidation of cyclic alkenes (cyclopentene, cyclohexene, cycloheptene and cyclooctene) has been carried out under green solvent-free conditions using ambient air as the oxidant gas using a carbon-supported gold catalyst. We show that radical initiators are only required for this reaction when the cyclic alkene contains a stabilizer molecule, such as 6-bis(*t*-butyl)-4-methylphenol (BHT) or 3-octadecyl-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propanoate (irganox 1076). We show that either removing the stabilizer chemically or sourcing the cycloalkane without the stabilizer the oxidation, both with and without radical initiator, is identical. This indicates that the only function of the radical initiator is to counteract the stabilizer. We have extended this work to show that stabilizer-free internal linear alkenes can be effectively epoxidised with air using the carbon-supported gold catalyst. However, unfortunately linear α -alkenes still require the addition of an initiator to achieve reaction. This work demonstrates that removal of a sacrificial reagent from a reaction is possible which adheres to the principles of green chemistry.

Hydrocarbon oxidation reactions are important in the synthesis of fine chemicals, conversions using oxygen from air represent the greenest method of carrying out these reactions.^{1,2} Oxygen is a diradical in the ground state which enables its ease of activation in a number of radical reactions, making it possible to employ molecular oxygen in a range of low temperature oxidations.^{3,4} However, at present many molecules and catalysts are unreactive with molecular oxygen and therefore more reactive oxidising agents containing a terminal oxidant are employed; often these involve non-green stoichiometric oxygen sources such as permanganate or chromates.⁵ Selective electrophilic addition of oxygen to an unactivated alkene to form an epoxide without the use of such undesirable reagents is one of the major challenges in oxidation chemistry. Propene is epoxidised industrially using H₂O₂ as the oxidant,^{6,7} the epoxidation of ethene using molecular oxygen is carried out industrially using a silver catalyst⁸⁻¹¹ but higher alkenes are generally oxidised using a radical initiator.¹² The two most common classes of initiators are organic peroxides and azo compounds.^{13,14}

Peroxides, such as tert-butyl hydroperoxide (TBHP) can play important roles in the oxidation of alkenes, both as a reaction initiator (in catalytic amounts) or as an oxidant (in stoichiometric amounts).¹ The use of peroxide as reaction initiator in catalytic amounts and the use of air as oxidant have been widely reported in the literature.¹ Previously, we have demonstrated that gold nanoparticles supported on graphite are active for the solvent-free oxidation of cyclic alkenes.¹⁵ However, a catalytic amount of an initiator (either H₂O₂ or TBHP (tert-butyl hydroperoxide)) was required to initiate these reactions; no conversion was observed in the absence of initiator, an effect which has been widely replicated in the literature including several recent publications.^{1,16-19} However, in our initial paper¹ we did indicate that conversion in the absence of a radical initiator was possible for cyclohexene when much higher pressures of molecular oxygen were used. A subsequent paper by Lambert and co-workers¹⁶ confirmed that such initiator-free reactions are indeed feasible. This has prompted us to study this effect in much greater detail. In this present study, we have investigated the oxidation of a range of cyclic alkenes, under solvent free conditions and have demonstrated that these alkenes can be oxidized in the absence of radical initiators if the stabilisers added by the suppliers are first removed or indeed if stabiliser free-alkenes are sourced.

Stabilisers such as 2,6-bis(t-butyl)-4-methylphenol (BHT) or 3-octadecyl-(3,5-di-t-butyl-4-hydroxyphenyl)-propanoate (Irganox 1076) are typically added to some commercial alkenes as stabilisers to prevent auto-oxidation. These stabilisers are added in small quantities and are

often not listed in the product information. Our initial studies investigated the epoxidation of *cis*-cyclooctene in the absence of a radical initiator (TBHP) when the stabiliser had been removed (see experimental for full details of the method). The catalysts used in this study were prepared by sol-immobilisation as previous studies have shown that this methodology affords the most active catalysts.²⁰ 1%Au/graphite (1%Au/G) was used as catalyst and we have previously reported extensive characterisation of these catalysts; the metal particle size distribution was found to be in the range of 1-12 nm with an average particle size of 4.7 nm and a median size of 4 nm.^{21, 22} Reactions carried out in the absence of catalyst, with and without stabiliser, are summarised in the supplementary information (table S1), table 1 summarises the performance of the catalyst for *cis*-cycloalkene oxidation, before and after the stabiliser removal treatment, using air as the O₂ source and 1%Au/G as catalyst. The results show that, before treatment *cis*-cyclooctene, which contains irganox 1076 as a stabiliser, exhibits 5.6% conversion with around 83% selectivity towards the epoxide when tert-butyl hydroperoxide (TBHP) is used as a radical initiator, the mechanism of the product formation in these oxidation reactions has been discussed previously.²³ In contrast, in the absence of radical initiator (TBHP), no *cis*-cyclooctene conversion was observed. This is consistent with previous studies which confirm that a catalytic amount of initiator is necessary for this oxidation.^{1, 10, 21} The experiment was repeated after removal of the stabiliser, under the same reaction conditions as were used without the treatment and the conversion with and without TBHP is shown in Table 1. It is interesting to note that 5.6% conversion, with 86% epoxide selectivity is achieved in the absence of radical initiator. Furthermore, the addition of TBHP to the (treated) stabiliser free *cis*-cyclooctene did not lead to any enhancement of the conversion or epoxide selectivity indicating that the radical initiator does not enhance the conversion but instead simply counteracts the effects of the stabiliser by reacting with it.

In view of these promising results, we tested two samples of cyclohexene, firstly cyclohexene (as received) which contained 0.01% BHT as stabilizer, and secondly a sample that was stabiliser-free. Table 1 also shows that, in the case of the cyclohexene that contained the stabilizer, 8% conversion was achieved when a small amount of TBHP was added as a radical initiator. However, no cyclohexene oxidation was observed in the absence of radical initiator. In contrast, the cyclohexene which was inhibitor-free gave very similar activity and selectivity in the absence or presence of TBHP. In a further set of experiments, cyclopentene and cycloheptene were used as the substrate (Table 1). Again, we found that if the cycloalkene contained stabiliser, no reaction was observed in the absence of a radical initiator

but with a small amount of radical initiator the oxidation occurs. In contrast, the inhibitor-free cycloalkene can be oxidised with almost the same activity and selectivity either in presence or in absence of radical initiator. We have also investigated α -alkenes under stabiliser-free conditions; the results are shown in Table S2. For 1-octene and 1-hexene the addition of the radical initiator was required to achieve conversion even when these substrates were stabiliser-free. However, in the case of *cis*-2-hexene and *cis*-3-hexene, for which the alkene bond has a more similar environment to the cyclic alkenes reported above, almost the same conversion was achieved either in the presence or the in absence of the radical initiator.

Using these optimised conditions, time-on-line studies were carried out for cyclohexene and *cis*-cyclooctene either containing stabiliser or stabiliser-free. When the cycloalkene contained stabiliser, a small amount of radical initiator (TBHP) was added. The results, shown in Figure 1, clearly indicate that, by removing the stabiliser, the activity is identical to that when stabiliser and initiator are present at all times tested.

Finally, to determine the detrimental effect of the stabiliser (BHT) on the conversion of cyclopentene and cyclohexene, we doped small quantities of BHT into stabiliser-free cycloalkenes. The effects of this doping are shown in Figure 2, it is clear that the addition of even a small amount (10^{-6} M) of the stabiliser has a detrimental effect on the conversion and a concentration of 3×10^{-5} M is sufficient to completely quench the oxidation reaction for either alkene (Fig 2a). This concentration of stabiliser was subsequently used to demonstrate the effect of the amount of TBHP on the conversion of stabilised cycloalkenes and these results are shown in Figure 2b. For cyclopentene, if TBHP is added in equimolar quantities to the stabiliser there is no conversion, in fact in terms of TBHP over 10 times the concentration of that of the stabiliser is required to show any improvement on the negligible conversion that is observed. The reaction was carried out with up to 33 times the concentration of TBHP relative to the stabiliser which still only led to less than 50% of the stabiliser-free conversion. For cyclohexene as soon as any initiator was added there was an increase in conversion, however we again did not observe the same conversion as was achieved in the stabiliser free alkene despite the large excess of initiator relative to the stabiliser. In summary, this work emphasises the level of attention that needs to be applied the source and exact content of substrates when they are to be used for catalytic studies.

We have shown that selective cyclic alkene oxidation can be achieved under green, solvent-free conditions without the addition of a radical initiator. We have demonstrated that the only

function of the radical initiator is to oxidise the stabilisers present in the cyclic alkenes and the removal of a sacrificial reactant from the process adheres to the principles of green chemistry.

Experimental Section

Preparation of catalyst by using Sol-immobilisation

1% Au was prepared by the sol-immobilisation method as follows: an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey, 12.25 g in 1000 mL) was prepared. Polyvinyl alcohol (PVA) (1 wt% solution, Aldrich, $M_w=10000$, 80% hydrolysed, $\text{PVA}/\text{Au} = 1.2$ (by wt)) was added to the solution and stirred with $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ for 15 min. 0.1M of NaBH_4 (> 96% Aldrich, NaBH_4/Au (mol/mol=5)) was freshly prepared and then added to form a dark brown sol. The mixture was stirred for 30 min and adjusted to $\text{pH} = 1$ by the drop wise addition of sulphuric acid. Support (1.98 g) was added to mixture. The slurry was then stirred for 1h and, following this, the catalyst was recovered by filtration, washed with 2L distilled water and dried (110°C , 16 h). The characterisation of this catalyst has been extensively reported previously [10] the metal particle size distribution was found to be in the range of 4-7 nm.

Treatment method

Typically, aqueous potassium hydroxide (20 ml, 3M) was added to cycloalkene (20 ml) under vigorous stirring for 10 min at room temperature. The two layers were separated and aqueous potassium hydroxide (20 ml, 3M) was added to the cycloalkene layer under vigorous stirring. The cycloalkene layer was separated and then washed thoroughly with distilled water (20 ml) two times under vigorous stirring for 10 min at room temperature. The cycloalkene layer was separated and then dried.

Oxidation of alkenes: Standard reaction conditions

Information on the alkenes source and stabiliser content is detailed in table S3. Oxidation of alkenes using oxygen from air was carried out in a glass reactor consisting of a 50 ml round-bottomed flask fitted with a reflux condenser. Typically a supported gold catalyst (0.12 g) was suspended in the alkene (10 ml) at the required temperature followed by the addition of a

small amount of radical initiator TBHP (when used). The reaction mixture was stirred for the requisite time at atmospheric pressure.

A sample of the reaction was analysed after the reaction was completed. The analysis was conducted using gas chromatography (GC) (Varian Star CP-3800) with a CP-Wax 52 column and a flame ionization detector (FID). For each reported data point, the GC analysis was run twice. Overall error, based on repeat reactions was calculated to be 1.97%.

Table 1: Comparison of the oxidation activity of cyclic alkenes using a 1%Au/Graphite catalyst Reaction conditions: Substrate (5 ml), Au/G (0.06 g), glass reactor, TBHP (0.032 x 10⁻³ mol where present), 24h and atmospheric pressure. ^bstabiliser removed by treatment

Substrate	T (°C)	Stabiliser	TBHP	Conversion (%)	Selectivity (%)			
					Epoxide	Alcohol	Ketone	Dimers ^d
Cyclooctene	80	Present	Yes	5.6	83.7	10	5	-
Cyclooctene	80	Present	No	0	-	-	-	-
Cyclooctene	80	Removed ^b	Yes	5.3	86.8	7	5	-
Cyclooctene	80	Removed ^b	No	5.6	86.7	7	5	-
Cycloheptene	60	Present	Yes	9.1	18.4	41.8	39.7	-
Cycloheptene	60	Present	No	0	-	-	-	-
Cycloheptene	60	None ^c	Yes	10.1	18.2	43.5	38.4	-
Cycloheptene	60	None ^c	No	9.4	18.4	43.3	38.3	-
Cyclohexene	50	Present	Yes	8.2	6.4	41.4	50.5	-
Cyclohexene	50	Present	No	0	-	-	-	-
Cyclohexene	50	none ^c	Yes	8.9	6.3	46.0	47.0	-
Cyclohexene	50	none ^c	No	8.7	6.3	41	44	-
Cyclopentene	26	Present	Yes	4	12.7	37.6	23.7	19
Cyclopentene	26	Present	No	0	-	-	-	-
Cyclopentene	26	none ^c	Yes	4.4	12.4	43.6	23.9	13.5
Cyclopentene	26	none ^c	No	4.4	12.5	36.2	22.4	22

^bstabiliser removed by treatment method reported in the supplementary information.

^cstabiliser-free alkenes purchased (Aldrich). ddimers observed are 3-(cyclopent-2-en-1-yloxy)cyclopent-1-ene Cyclopentanone, 3-[(2-cyclopenten-1-yl)oxy] as identified by GC-MS and NMR. ^eAll selectivities are based on calculated mols of products.

Table 2: Comparison of oxidation activity for α -alkenes (stabilizer-free), in the presence/absence of TBHP and in the presence of 1%Au/Graphite catalyst.

α -Alkene		Conversion %	
		With TBHP	Without TBHP
(stabiliser free)			
1-octene	70	2.9	0
1-hexene	40	1.2	0
cis-2-hexene	40	1.2	0.9
cis-3-hexene	40	9.6	11.4

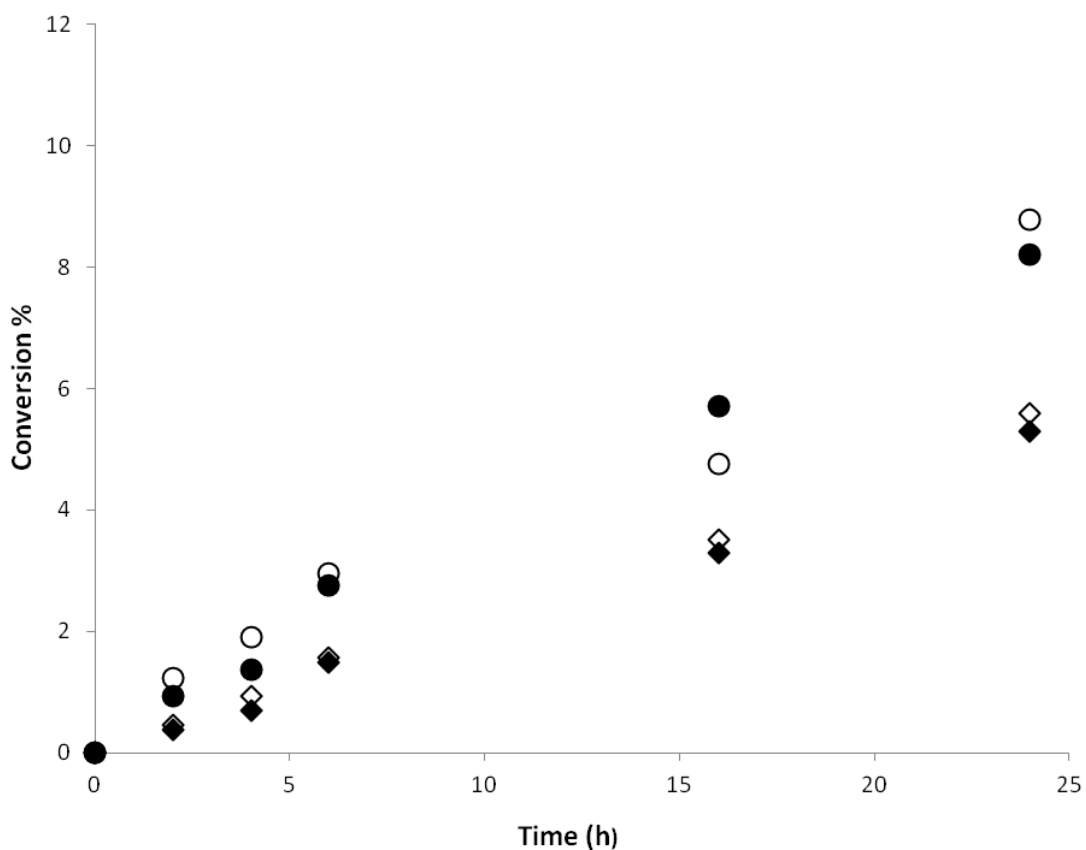


Figure 1: Effect of reaction time for the conversion of cis-cyclooctene at 80 °C and cyclohexene at 50 °C. Reaction conditions: 5 ml of alkene, 0.06g Au/G, glass reactor, TBHP (0.032×10^{-3} mol) and atmospheric pressure. Cyclohexene containing stabiliser with TBHP (●), stabiliser-free cyclohexene without TBHP (○), cis-cyclooctene containing stabiliser with TBHP (◆) and cis-cyclooctene after the removal of stabiliser without TBHP (◇).

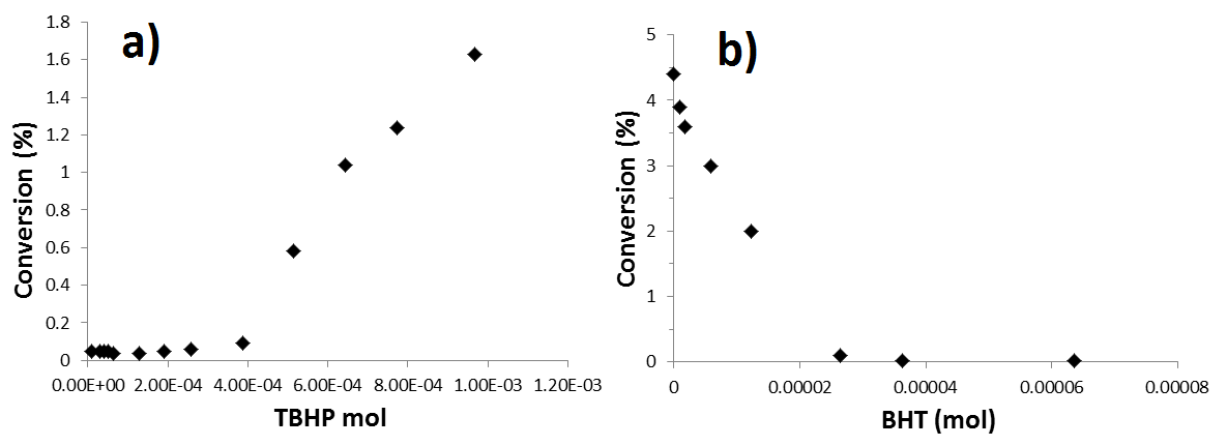
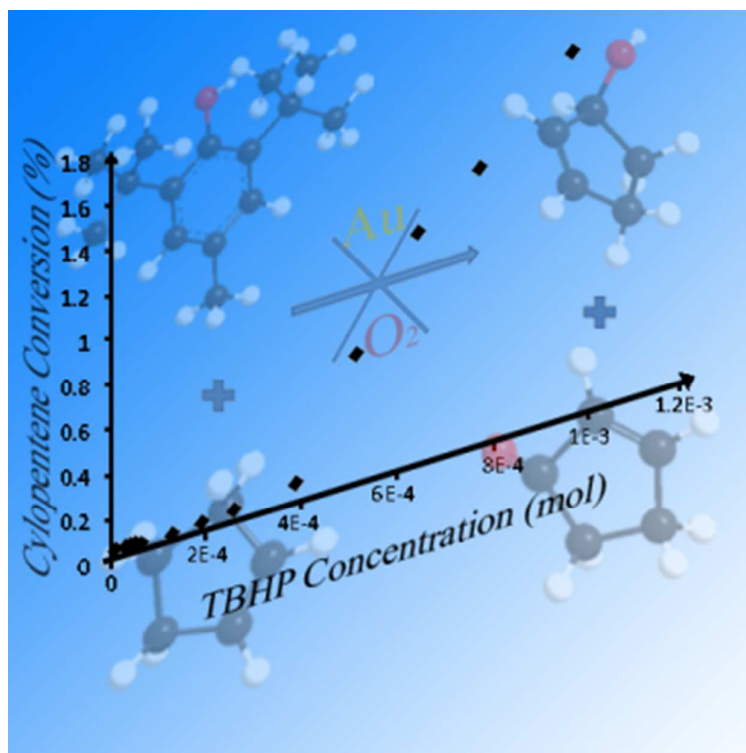


Figure 2: a) The addition of radical initiator to cyclopentene containing BHT (3×10^{-5} M) and b) the addition of BHT to stabiliser free cyclopentene. Reaction conditions: substrate (10 ml), catalyst (0.12g), glass reactor, atmospheric pressure.

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In the catalytic oxidation of cycloalkenes and linear internal alkenes using oxygen radical initiators are not required if the stabilisers are removed prior to reaction.