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Solvent –free oxidation of dec-1-ene using gold/graphite catalyst using an *in situ* generated oxidant.

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Abstract

The oxidation of dec-1-ene is investigated under solvent-free conditions using gold nanoparticles supported on graphite and in a batch reactor in the presence of a radical initiator using oxygen from air as the terminal oxidant. The evolution of the products with reaction time shows that there is an initial induction period and during this time very little epoxide is formed and the products of allylic oxidation are dominant. Subsequently the epoxide becomes the major product prior to the diol being formed from hydrolysis due to the presence of by-product water formed from the selective oxidation reaction. It is considered that the allylic oxidation products are in part converted *in situ* into aldehydes which form peracids during the induction period; the peracid leads to epoxide formation as the major product as the conversion is increased. The effect of addition of a number of aldehydes is investigated, all leading to enhanced epoxide formation when added in small amounts. Molar enhancements of epoxide yield can approach twice the amount of aldehyde initially added. This behaviour is in contrast to earlier studies which utilise aldehydes in greater than stoichiometric amounts as sacrificial reactants. The importance of *in situ* aldehyde formation is also demonstrated by the addition of benzyl alcohol which under the reaction conditions rapidly gives benzaldehyde and enhanced epoxide formation. Possible mechanistic interpretations of the observations are discussed.

Introduction

Epoxidation of linear terminal alkenes remains a challenging reaction and particularly so if molecular oxygen from the air is to be used as the terminal oxidant. Alkenes can be readily oxidised using more reactive terminal oxidants such as ozone or hydrogen peroxide,¹ but these are expensive to use on a large scale. Hence there is real interest in identifying new catalytic approaches for the oxidation of linear terminal alkenes.

In this paper we are primarily concerned with the oxidation of dec-1-ene as a model linear terminal alkene and we use solvent-free conditions with air as the terminal oxidant. There have been a number of previous studies concerned with dec-1-ene oxidation, but these have used more expensive oxidants and/or stoichiometric oxidants.²⁻¹³ In previous studies we have investigated the oxidation of alkenes using supported gold nanoparticles particularly for the oxidation of cycloalkenes.¹⁴ We demonstrated that cyclooctene could be selectively epoxidised using air in conjunction with a peroxide initiator. We extended this to a range of cycloalkenes and showed that the ring size was important in controlling whether epoxidation or allylic oxidation was the dominant reaction pathway.¹⁵ We subsequently turned our attention to linear internal alkenes and examined the oxidation of hex-2-ene using supported gold catalysts with peroxide initiators.¹⁶ In addition, we found that when two oxidisable functional groups were present as in unsaturated alcohols such as hex-2-en-1-ol, the alcohol functional group was oxidised in preference to the alkene.¹⁷ Subsequently, and most importantly, we discovered that the alkenes in our studies had contained stabilisers to prevent oxidation; upon their removal we found that the peroxide initiator was not necessary for the oxidation of cyclic and internal linear alkenes.¹⁸ However, the peroxide initiators were still required for the epoxidation of terminal alkenes¹⁸ and hence, as noted earlier, the oxidation of terminal alkenes remains a major challenge in selective oxidation catalysis.

One interesting approach that has been exploited in the quest to improve oxidation reactions is the use of sacrificial additives; for example, aldehydes form peracids under these reaction conditions and the peracids act as very potent oxidants. For example, Mukaiyama *et al.*¹⁹ studied

a number of epoxidation reaction in the presence of an aldehyde as a sacrificial reductant and obtained the epoxide with 100% selectivity. These characteristics make the Mukaiyama method attractive for commercial applications, despite the fact that more than stoichiometric amounts of the co-reacting aldehyde are required to achieve this effect.

We were concerned that the enhancement of epoxidation of 1-decene that we had observed using gold nanoparticles supported on graphite and oxygen in the presence of a free radical initiator (AIBN) might be wholly or in part a consequence of aldehydes generated during the initiating process. In this paper we show that, during the oxidation of a linear terminal alkene in the absence of added aldehyde, there is a significant induction period, during which the products of allylic oxidation are formed. In the presence of the gold catalyst, the aldehydes that are formed act as *in situ* additives enhancing the yield of the epoxides. We also investigate the addition of sub-stoichiometric amounts of aldehydes to the oxidation of dec-1-ene and show that these small amounts are highly effective in increasing the epoxide yield. Increases approach twice the amount of aldehyde added.

Experimental Methods

Materials

Graphite (Sigma Aldrich), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich), dec-1-ene (Alpha Aesar, containing no stabilisers) and AIBN (Molecula) were used as received. Dec-2-enal, dec-2-en-1-ol, dec-1-en-3-ol, heptanal, octanal, nonanal, octanoic acid, decane, benzyl alcohol, benzaldehyde, acetophenone and benzoic acid were all supplied by Sigma Aldrich.

Catalyst preparation

The catalyst (1 wt.% Au/graphite) used in this study was prepared *via* an incipient-wetness impregnation method.¹⁴ The carbon support (graphite, 2 g) was transferred to a small evaporating basin. An aqueous solution (0.1 M) of chloroauric acid (equivalent to 20 mg of Au) was diluted with distilled water to make a total gold solution of 2 mL. The gold solution was added dropwise to the graphite powder followed by air drying at various intervals (1.0 – 1.5 hours). After complete addition of the gold solution the catalyst was dried in static air (25 °C, 16 h; 110

°C, 16 h). The catalyst has been extensively characterised in our previous studies of the oxidation of cycloalkenes and the catalyst used in these studies is fully described previously.¹⁴ Characterisation of the catalysts has shown that the gold is present as Au(0) using X-ray photoelectron spectroscopy, and this is not affected by the reaction conditions and used catalysts after the oxidation of alkenes the gold is unchanged. Also previous experiments have shown that these oxidation reactions are fully heterogeneous and no leaching of gold is observed.¹⁴⁻¹⁸

Oxidation of dec-1-ene

The following standard reaction conditions were used. All reactions were performed in a stirred glass round bottomed flask (50 mL) fitted with a reflux condenser and heated in an oil bath. In a typical reaction, of dec-1-ene (10 mL (53 mmol)) was refluxed for 1 to 96 h under atmospheric air in the presence of AIBN (35 μ mol) and catalyst (0.1 g). The liquid products were analysed using a Varian gas chromatograph 3300 fitted with a Zebron ZB-Wax Plus column and a flame ionization detector. The injector and detector temperatures were maintained at 250 °C throughout analysis. During the chromatographic analysis the column was heated from 60 °C to 200 °C at a heating ramp rate of 10 °C/min and held at the final temperature for 26 min. A range of additives were added to the reaction mixture as required; most were added at the start of the reaction, but the addition of water and or acids was also carried out during the reaction and this is specified in the text.

Results and discussion

The oxidation of dec-1-ene was studied using 1wt%Au/graphite using AIBN as a radical initiator using oxygen from air as the terminal oxidant under solvent-free conditions in a stirred glass reactor (Table 1, entry 1). The product distribution is broad but after 24 h reaction the 1,2 epoxide is the major reaction product, together with a range of C₇ – C₁₀ oxygenated products, which, significantly, include dec-2-enal. Evolution of the product distribution with reaction time shows that initially the epoxide is not formed in significant amounts (Figure 1) but rather the products of allylic oxidation, namely: dec-1-en-3-ol, dec-1-en-3-one, dec-2-en-1-ol and dec-2-enal. After an initial induction period of *ca.* 12 -24 h the 1,2-epoxide is formed in increasing

amounts in preference to the allylic products. At much longer reaction times the epoxide selectivity declines in preference to the formation of the 1, 2-diol. This latter observation can be understood in terms of hydrolysis of the 1,2-epoxide as water is co-formed with the oxidation products. As the reaction progresses in the stirred reactor the concentration of water increases with increasing conversion and so the sequential reaction of the 1,2-epoxide to the diol prevails. During the initial reaction it is clear that the products of allylic oxidation listed above are dominant. It is known that alkene epoxidation can be markedly enhanced by the addition of aldehydes in excess of stoichiometric amounts.¹⁹⁻²² Aldehydes form peracids under these reaction conditions which promote the formation of the epoxide. In our experiments we consider that the dec-2-enal can form a peracid that leads to the formation of the epoxides. However, we wanted to investigate the possibility that the allylic alcohol products could also play a role during the induction period. We²³ as well as Corma and co-workers²⁴⁻²⁶ have previously shown that primary alcohols can be selectively oxidised to aldehydes using supported gold nanoparticles, under solvent-free conditions and in the absence of base, and hence this may be a possible reaction pathway. To investigate this we added a number of potential reactants (*ca.* 1 mmol) to determine their effect on the product distribution at 24 h reaction time (Table 1). The addition of decane and octanoic acid (Table 1, entries 2, 3) had no effect on the dec-1-ene conversion or the product distribution; neither of these additives would be expected to enhance the formation of peracids. Dec-1-en-3-ol appears to have no effect on the conversion of 1-decene but does surprisingly enhance the epoxide selectivity somewhat, though less so than aldehydes (see below); if oxidised under the reaction conditions the secondary allylic alcohol would form a ketone, which would be expected to be inert. Indeed, adding acetophenone has a negligible effect on the course of reaction (Supplementary Information, Fig. S1). In contrast, the addition of dec-2-en-1-ol leads to an enhancement in dec-1-ene conversion and the yield of the 1,2-epoxide (Table 1, entry 5) and the selectivity to the epoxide is also enhanced. In this case we consider that the enol is oxidised to the enal which subsequently forms a peracid on reaction with molecular oxygen. We have previously shown that enols can be oxidised under these reaction conditions to form enals.¹⁷ When aldehydes are added at the start (Table 1, entries 6-9) the increase in conversion and the enhancement in the yield of the epoxide is more marked; indeed, the increase in epoxide yield appears to exceed the quantity of aldehyde added. Hence we conclude that the induction period we observe is due to the following factors. First there is a low background reaction of allylic oxidation that may occur in the homogeneous

liquid phase under the influence of the radical initiator rather than involve the catalyst surface. We consider that the allylic aldehyde, produced from the initial oxidation of dec-1-ene via 2-decenyl hydroperoxide, reacts to form the peracid directly, whereas the terminal alcohol is oxidised by the gold surface to form the aldehyde which in turn forms peracid. These processes occur during the slow, initial phase of the reaction and generate the intermediate peracid which then goes on to convert dec-1-ene into the 1,2-epoxide in the main part of the reaction. Hence, the induction period allows the formation *in situ* of molecules that promote the formation of the epoxide. It should be emphasised that the alcohols and aldehydes involved in our experiments are present at levels much lower than those used as sacrificial reductants in previous studies where aldehydes have been added to induce epoxide formation in high selectivity at high conversion when high concentrations of the sacrificial reagent are required to observe this effect.¹⁹⁻²² This observation has prompted us to investigate further the addition of sub-stoichiometric amounts of aldehydes and alcohols, since this has clearly not been considered in previous studies.

Initially we studied the effect of adding small amounts of 2-decenal to the reaction mixture (Table 2, entries 1-4). It is clear that the addition of decenal induces the formation of additional epoxide in amounts significantly greater on a molar basis than the amount of 2-decenal introduced. Next we investigated the addition of octanal (1.1 mmol) to the reaction mixture. It is clear (Table 1, entry 8) that this amount of octanal leads to the formation of an additional 1.9 mmol of the epoxide confirming that the effect of the additive is a general phenomenon; this amplification effect has not been observed previously in alkene epoxidation because aldehydes have usually been added in much greater than stoichiometric amounts.¹⁹⁻²² The effect of the addition of octanal on the product distribution with reaction time over a period of 96 h is shown in Figure 2. The epoxide yield is initially enhanced by about 1 mmol but as the reaction proceeds the enhancement increases with time to ca. 2 mmol after 48 h. There is a roughly parallel increase in the quantity of C₇ – C₉ carboxylic acids; the stoichiometric reaction of 1 mol of aldehyde RCHO, converted into the peracid RCO-OOH, should lead to 1 mol of 1,2-epoxydecane and 1 mol of RCO₂H. In the later stages, the epoxide yield reaches a maximum and then declines, with concomitant formation of the diol, presumably by epoxide hydrolysis as water accumulates and the acidity of the reaction mixture increases. . Initially the difference in the C₇-C₉ acids can be considered to be due to the addition of octanal which will form octanoic

acid (1.1 mmol) but as the reaction proceeds the amount of these acid products is enhanced markedly. The yield of acids is, however, always less than that of epoxide until epoxide hydrolysis to the 1,2-diol supervenes. Indeed, after 96 hours the quantity of acids and the 1,2-diol are equal (ca. 8 mmol), with very little of the epoxide remaining. The simple idea of aldehyde conversion into peracid, followed by O-transfer to 1-decene, yielding equimolar amounts of epoxide and carboxylic acid cannot represent the whole mechanistic story.

The effect of the addition of benzaldehyde on the oxidation of dec-1-ene (Fig. 3) was not as marked as the addition of aliphatic aldehydes, although the effect is still observed to be greater than stoichiometric when small amounts are added (Table 2, compare entries 1, 5). To demonstrate the effects are not specific to dec-1-ene we have also carried out similar experiments with hex-1-ene (See supplementary information, Table S1). The addition of acetophenone has no effect on the reaction as the formation of a peracid is not feasible (See supplementary information, Figure S1). At longer reaction times the formation of the diol becomes more pronounced and so the amount of the epoxide is diminished. At higher levels of benzaldehyde (Table 2, compare entries 1, 6, 7) smaller amounts of the epoxide are formed relative to the amount of benzaldehyde added.

The addition of benzyl alcohol (Fig. 4) also is effective in promoting the formation of the epoxide. Again the effect is greater than stoichiometric but the formation of the diol is much more marked than that observed with the addition of benzaldehyde. In view of this we studied the effect of adding benzoic acid (Fig. 5) and although there was no effect, as expected, on the amount of epoxide formed at short reaction times, at longer reaction times the formation of the diol was enhanced markedly. In the selective oxidation of dec-1-ene water is inevitably formed along with the epoxide or other selective oxidation products, as well as from dehydration of hydroperoxides and oxidative dehydrogenation of alcohols. In the solvent-free conditions we are employing this aids the hydrolysis of the epoxide to the ring-opened diol. This reaction is acid catalysed; in the standard reaction the formation of by-product C₇-C₉ acids provides the catalyst. However, the addition of benzoic acid at the start of the reaction greatly enhances this effect. To explore this further we investigated the effect of adding water at 48h and 72h reaction time (Fig. 6) and it is clear that this facilitates the formation of the diol. The addition of both benzoic acid and water (Fig.7) serve to compound this effect markedly.

In summary, we have established the following features of the enhanced epoxidation of 1-alkenes when exposed to oxygen in the presence of gold nanoparticles supported on graphite in the presence of a low level of a radical initiator:

1. Sub-stoichiometric amounts of added aldehydes increase conversion of 1-decene and increase the amount of the 1,2-epoxide produced.
2. The types of aldehyde exhibiting the effect embrace simple alkanals, α , β -unsaturated aldehydes and aromatic aldehydes; primary alcohols that can be oxidised to aldehydes under the reaction conditions are also effective.
3. Particularly at low levels of added aldehyde, the increased amount of epoxide formed is greater on a mol for mol basis than the quantity of aldehyde introduced but does not appear to exceed a 2-fold amplification.
4. The enhancement in epoxide yield is accompanied by a somewhat smaller increase in the generation of carboxylic acids in product mixtures until the point where epoxide hydrolysis starts to take effect.

Based on these experimental findings we can now start to explain the evolution of the products with time in reactions with no added aldehyde. Initially during the induction period very little epoxide is formed and the major products are those from radical induced allylic oxidation. These could be being formed in the homogeneous liquid phase but the catalyst surface could be involved. Subsequently, the aldehyde is oxidised to peracid and the primary alcohol, dec-2-enol, after oxidation *in situ* catalysed by the gold to the aldehyde, also generates peracid. Such peracids are then able to transfer an oxygen atom to the alkene in a non-radical process, involving a cyclic transition state, resulting in epoxide formation and the generation of an equimolar amount of the carboxylic acid, in this case dec-2-enoic acid. Consequently, when aldehydes are added to reaction mixtures at the start of the oxidation, the formation of epoxide becomes the dominant reaction pathway and the conversion of dec-1-ene increases. This is represented in scheme 1 which is consistent with other studies concerning alkene oxidation.²⁷ This picture, however, does not explain our repeated observation that the enhancement of the epoxide yield exceeds the quantity of aldehyde added.

In previous studies²⁸ of the epoxidation of cis-cyclo-octene using a supported gold catalyst on graphite in conjunction with a free radical initiator, we have proposed that intermediate O-centred allyloxy radicals derived from the alkene, *via* the corresponding hydroperoxide perhaps on the gold surface, attach themselves to one of the sp^2 carbons of another alkene molecule. The resultant intermediate radical then fragments to afford a molecule of epoxide, together with an allylic cyclo-oct-2-enyl radical, which restarts the catalytic cycle. A similar mechanism can be written for the epoxidation of the less reactive dec-1-ene and this may be responsible for the slow production of epoxide at the start of the present reactions. When aldehydes are present, we consider that radical abstraction of a hydrogen atom produces an acyl radical ($R-CO\cdot$) which reacts with oxygen to produce the acylperoxy ($R-CO-O-O\cdot$) radical. In competition with H-abstraction to give the peracid, itself a stoichiometric epoxidising species, $R-CO-O-O\cdot$ acts as the epoxidising species by attachment to the terminal carbon of 1-decene followed by fragmentation to produce an epoxide and a carboxy radical, $R-CO-O\cdot$. The subsequent behaviour of the carboxy radical will depend on the structure of the group R. For simple alkanals, $R = R'CH_2$, fragmentation to produce an alkyl radical $RCH_2\cdot$ and carbon dioxide is likely to be the fastest process ($k \approx 10^9 \text{ s}^{-1}$); subsequently, the reaction sequence $RCH_2\cdot + O_2 \rightarrow RCH_2-O-O\cdot \rightarrow RCH_2-O-OH \rightarrow RCHO$ is feasible and a further epoxidation sequence can begin. This might explain how it is possible to exceed 1:1 stoichiometry in the enhancement of the epoxide yield by such aldehydes. This sequence of processes will involve reactions occurring at the gold surface together with reactions in the homogeneous liquid phase.

When R is aromatic or an alkenyl group as in benzaldehyde and 2-decenal, the carboxy radical resulting from the radical epoxidation is likely to lose CO_2 more slowly ($k \approx 10^6 \text{ s}^{-1}$) than when R = alkyl. This will be likely to permit H-abstraction to compete, generating the acid, although loss of CO_2 would not, in any case, open up a route to a new aldehyde. On this basis, the epoxide enhancement ought to be restricted to an amount equimolar with the added aldehyde. Another pathway must be available. An intriguing speculation is that carboxy radicals attack a further alkene molecule, a reaction well known in the initiation of free radical polymerisation, but the intermediate radical then fragments (rather than attack a further alkene) and produces another molecule of epoxide and $R-CO\cdot$, the radical originally formed from the added aldehyde. Such a process would account for the higher than stoichiometric effect of these aldehydes on the epoxide yield and the carboxylic acid deficit. It could be regarded as a true catalytic process,

although turnover numbers are unlikely to be very high because of the many competing pathways (including termination) available to the intermediates. We emphasise that this route, involving fragmentation of β -acyloxyalkyl radicals to generate epoxides is highly speculative and will require considerable further investigation to determine the role played by the gold catalyst surface. .

At higher dec-1-ene conversion as the concentration of by-product water increases together with by-product acids the acid catalysed hydrolysis of the epoxide becomes the dominant pathway. Hence to maintain high selectivity to the epoxide as the desired product it is necessary to limit the conversion.

Conclusions

Solvent-free oxidation of dec-1-ene over 1 wt.% Au/graphite in the presence of AIBN as a radical initiator reveals a number of features. First there is a well-defined induction period during which the products of allylic oxidation are formed initially and their formation could be due to a homogeneous reaction in the liquid phase. The allylic products then participate to form the epoxide product *via* surface catalysed reactions. We have shown that alcohols can be oxidised *in situ* to aldehydes and these enhance the formation of the epoxide. In particular, we clearly show that aldehydes and primary alcohols can be added in sub-stoichiometric amounts to engender enhanced epoxide formation; enhancements are substantially greater than 1: 1 with respect to the amount of additive.

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Table 1 Effect of different additives on the oxidation of dec-1-ene^a

Entry	1	2	3	4	5	6	7	8	9
Additives	none	decane	octanoic acid	dec-1-en-3-ol	dec-2-en-1-ol	dec-2-enal	heptanal	octanal	nonanal
Conversion (%)	12	11.8	11.8	11.8	15.4	16.8	18.4	17.5	16.8
Product distribution (mmol)									
Epoxide (sel%)	1.90(38.2)	1.91(38.0)	1.96(38.3)	2.29(45.4)	3.10(47.9)	3.71(51.7)	3.80(48.8)	3.85(51.5)	3.51(48.3)
1-Decen-3-one	0.35	0.70	0.08	0.38	0.42	0.39	0.18	0.19	0.24
1-Decen-3-ol	0.29	0.38	0.31	0.25	0.35	0.26	0.24	0.24	0.29
2-Decenal	0.43	0.46	0.37	0.53	0.44	0.39	0.43	0.44	0.44
2-decen-1-ol	0.49	0.37	0.50	0.34	0.47	0.34	0.44	0.38	0.34
1,2-Decanediol	0.15	0.12	0.08	0.06	0.09	0.11	0.13	0.10	0.15
2-Decenoic acid	0.27	0.18	0.12	0.15	0.28	0.43	0.35	0.29	0.29
2-Decanone	0.03	0.03	0.03	0.04	0.03	0.04	0.03	0.05	0.05
C ₈ + C ₉ aldehyde	0.07	0.10	0.06	0.08	0.08	0.08	0.06	0.09	0.09
C ₇ + C ₈ Alcohol	0.09	0.06	0.04	0.08	0.09	0.10	0.10	0.09	0.19
C ₇ + C ₈ + C ₉ acids	0.66	0.42	1.33	0.56	0.70	0.87	1.49	1.26	1.25
3-Nonen-1-ol	0.05	0.04	0.05	0.05	0.08	0.06	0.07	0.05	0.05
3-Nonanone	0.19	0.26	0.19	0.23	0.34	0.39	0.47	0.44	0.38

^aReaction Condition: dec-1-ene (53 mmol), AIBN (35 μmol), 1wt% Au/graphite (0.10 g), additives (150 mg), 24 h, 90°C.

^bSelectivity to the epoxide is given in parenthesis.

Table 2 Effect of the addition of dec-2-enal and benzaldehyde on the yield of epoxide in the oxidation of dec-1-ene^a

entry	additive	Amount/mmol	Epoxide/ mmol	Δ /mmol ^b
1	none	-	1.90	-
2	dec-2-enal	0.20	2.20	0.30
3	dec-2-enal	0.50	2.70	0.80
4	dec-2-enal	1.00	3.72	1.82
5	benzaldehyde	1.40	3.80	1.90
6	benzaldehyde	5.00	5.60	3.60
7	benzaldehyde	10.00	6.30	4.40

^a Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μ mol), 1wt% Au/graphite (0.1 g), 24 h, 90 °C.

^b Increase in epoxide yield (mmol) due to the addition of the aldehyde.

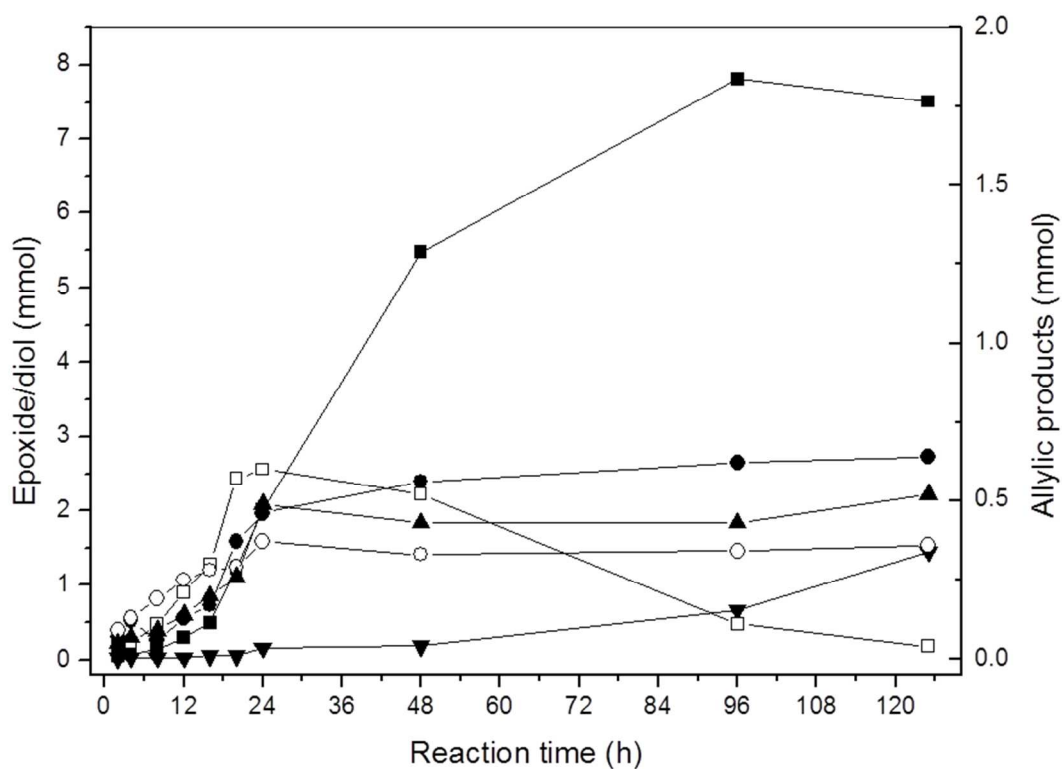


Figure 1 The yield of the main products (mmol) for the epoxidation of dec-1-ene using 1 wt.% Au/graphite: ■ = epoxide, □ = dec-1-en-3-one, ● = dec-2-enal, ○ = dec-1-en-3-ol, ▲ = dec-2-en-1-ol, ▼ = 1,2-decanediol. Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μ mol), 1wt% Au/graphite (0.1 g), 90 °C.

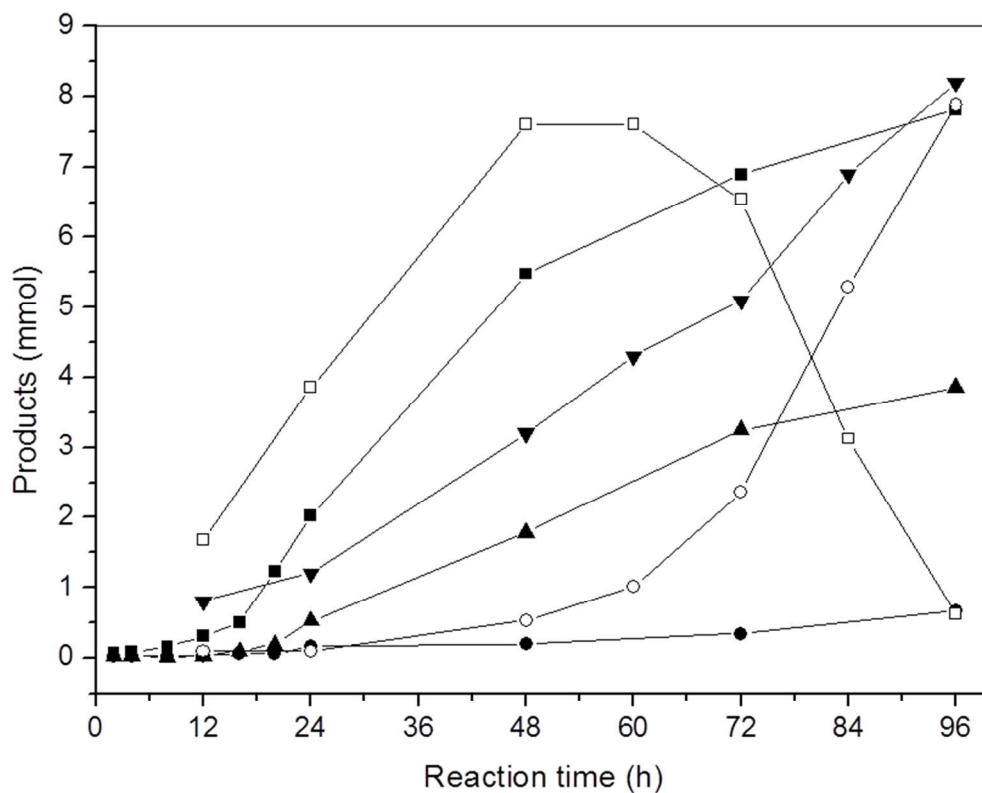


Figure 2 Effect of the addition of octanal on the oxidation of dec-1-ene. Key: ■ epoxide without octanal □ epoxide with octanal ● 1,2-decanediol without octanal ○ 1,2-decanediol with octanal ▲ C_{7,8,9} acids without octanal ▼ C_{7,8,9} acids with octanal. Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μ mol), 1 wt% Au/graphite (0.1 g), octanal (150 mg, 1.1 mmol), 90 °C.

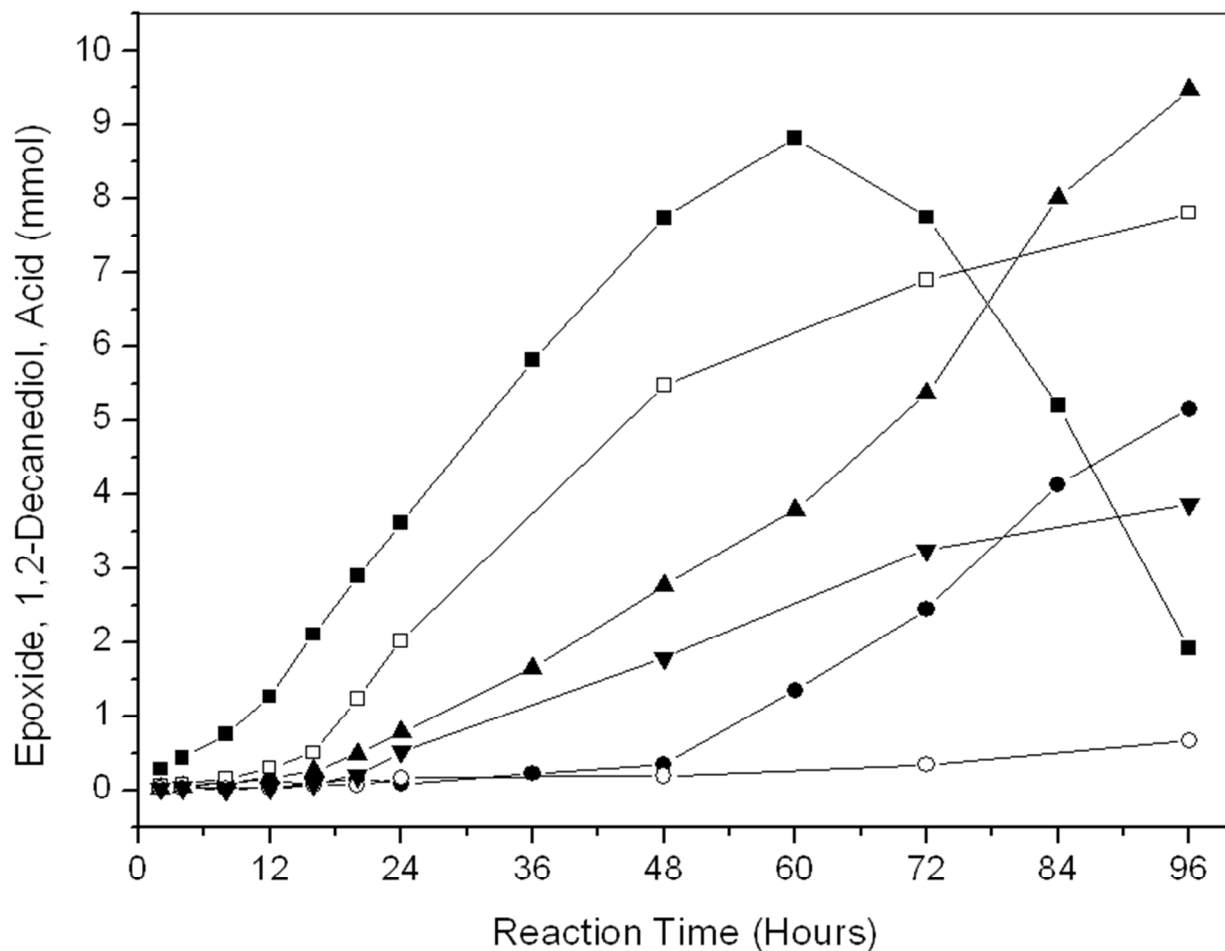


Figure 3 Effect of the addition of benzaldehyde on the oxidation of dec-1-ene. Key ■ epoxide with benzaldehyde □ epoxide without benzaldehyde ● 1,2-decanediol without benzaldehyde ○ 1,2-decanediol with benzaldehyde ▲ C_{7,8,9} acids with benzaldehyde ▼ C_{7,8,9} acids without benzaldehyde. Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μmol), 1wt% Au/graphite (0.1 g), benzaldehyde (1.4 mmol), 90 °C.

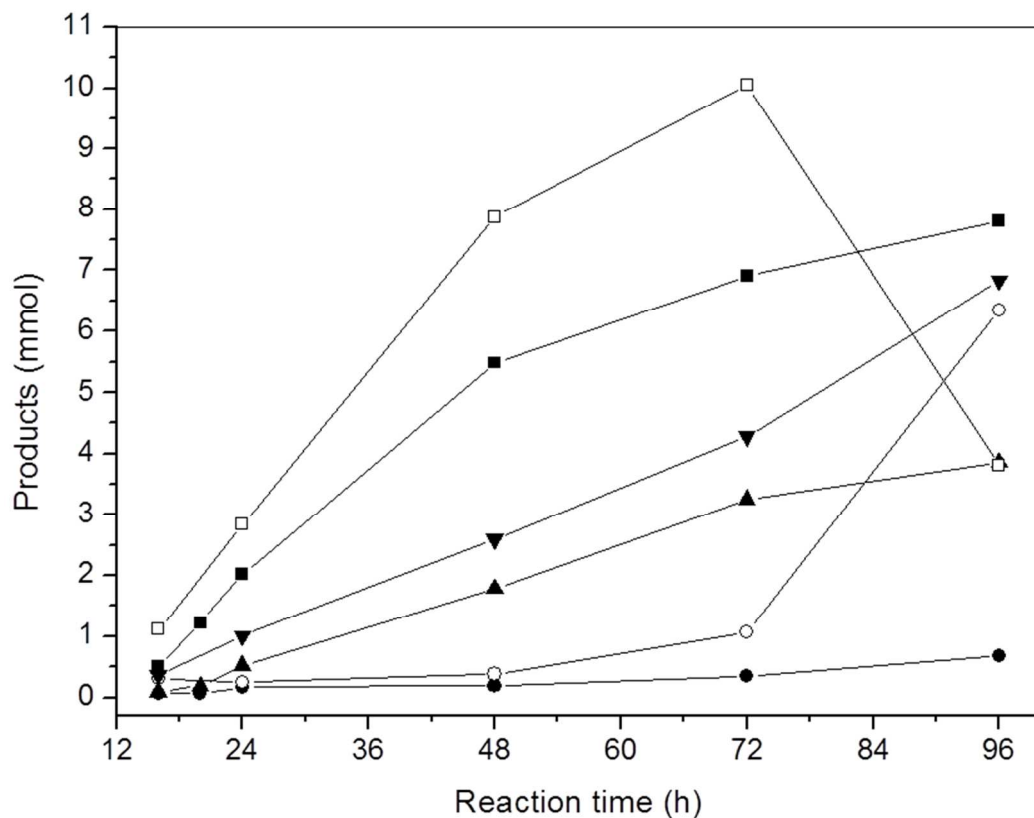


Figure 4 Effect of the addition of benzyl alcohol on the oxidation of dec-1-ene. Key ■ epoxide without benzyl alcohol □ epoxide with benzyl alcohol ● 1,2-decanediol without benzyl alcohol ○ 1,2-decanediol with benzyl alcohol ▲ C_{7,8,9} acids without benzyl alcohol ▼ C_{7,8,9} acids with benzyl alcohol. Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μmol), 1wt% Au/graphite (0.1 g), benzyl alcohol (1.4 mmol), 90 °C.

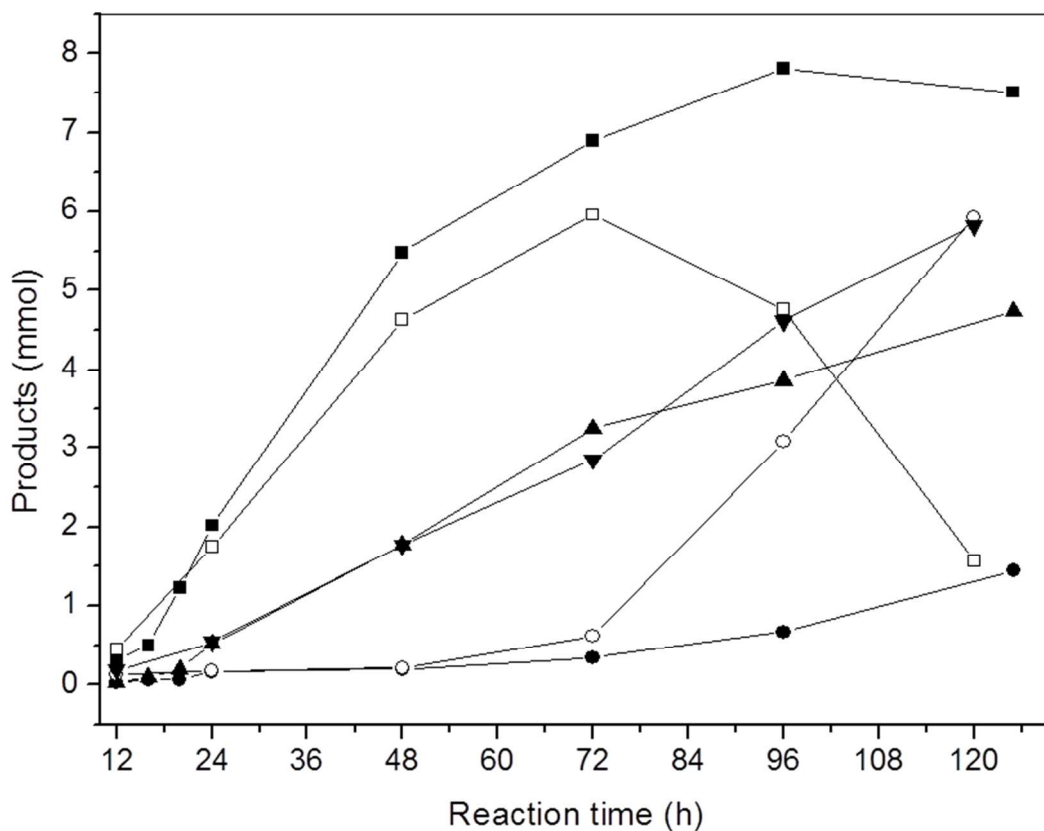


Figure 5 Effect of the addition of benzoic acid on the oxidation of dec-1-ene. Key ■ epoxide without benzoic acid □ epoxide with benzoic acid ● 1,2-decanediol without benzoic acid ○ 1,2-decanediol with benzoic acid ▲ C_{7,8,9} acids without Benzoic acid ▼ C_{7,8,9} acids with Benzoic acid. Reaction conditions: Dec-1-ene (53 mmol), AIBN (35 μmol), 1wt% Au/graphite (0.1 g), benzoic acid (150 mg), 90 °C.

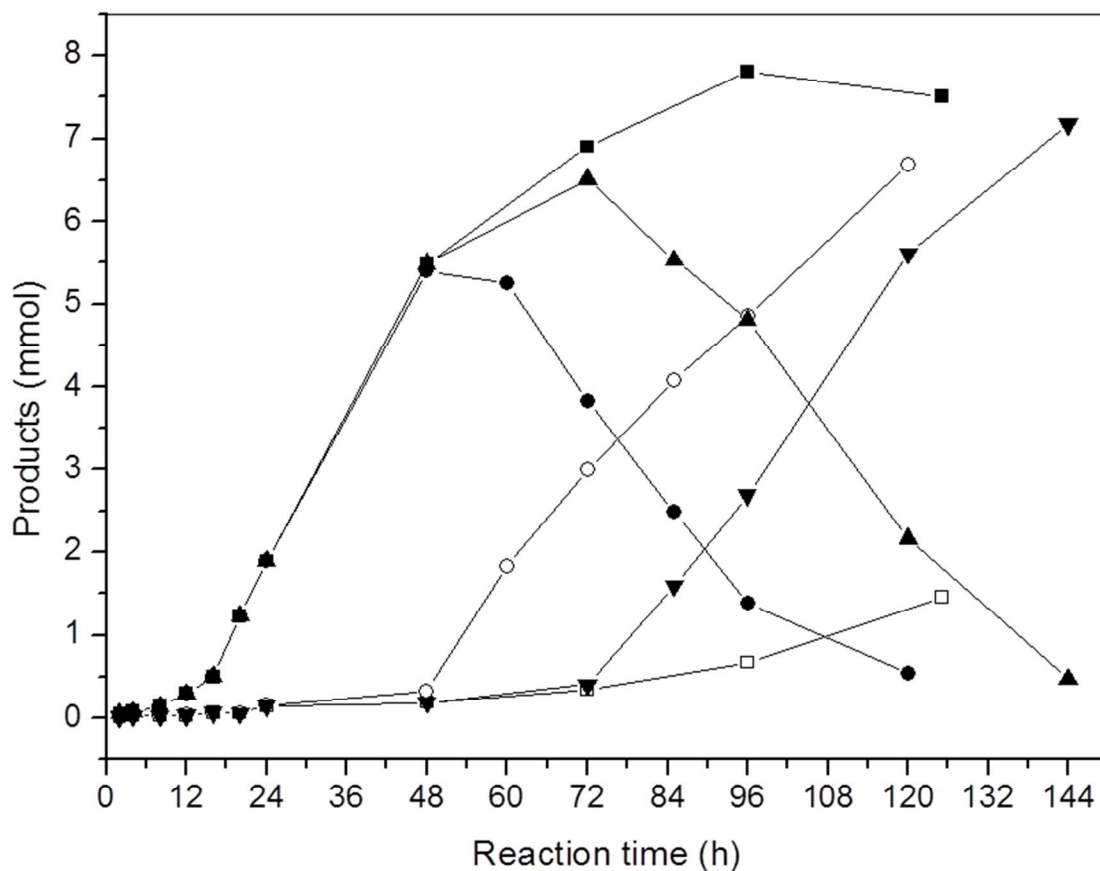


Figure 6 Effect of adding water at the yield of epoxide and 1,2-decanediol on oxidation of dec-1-ene. Key: standard reaction conditions: ■ epoxide, □ 1,2-decanediol; water added after 48 h: ● epoxide, ○ 1,2-decanediol; water added after 72 h: ▲ epoxide, ▼ 1,2-decanediol. Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μ mol), 1wt% Au/graphite (0.1 g), 90 $^{\circ}$ C, water (1g, added after 48 h and 72 h)

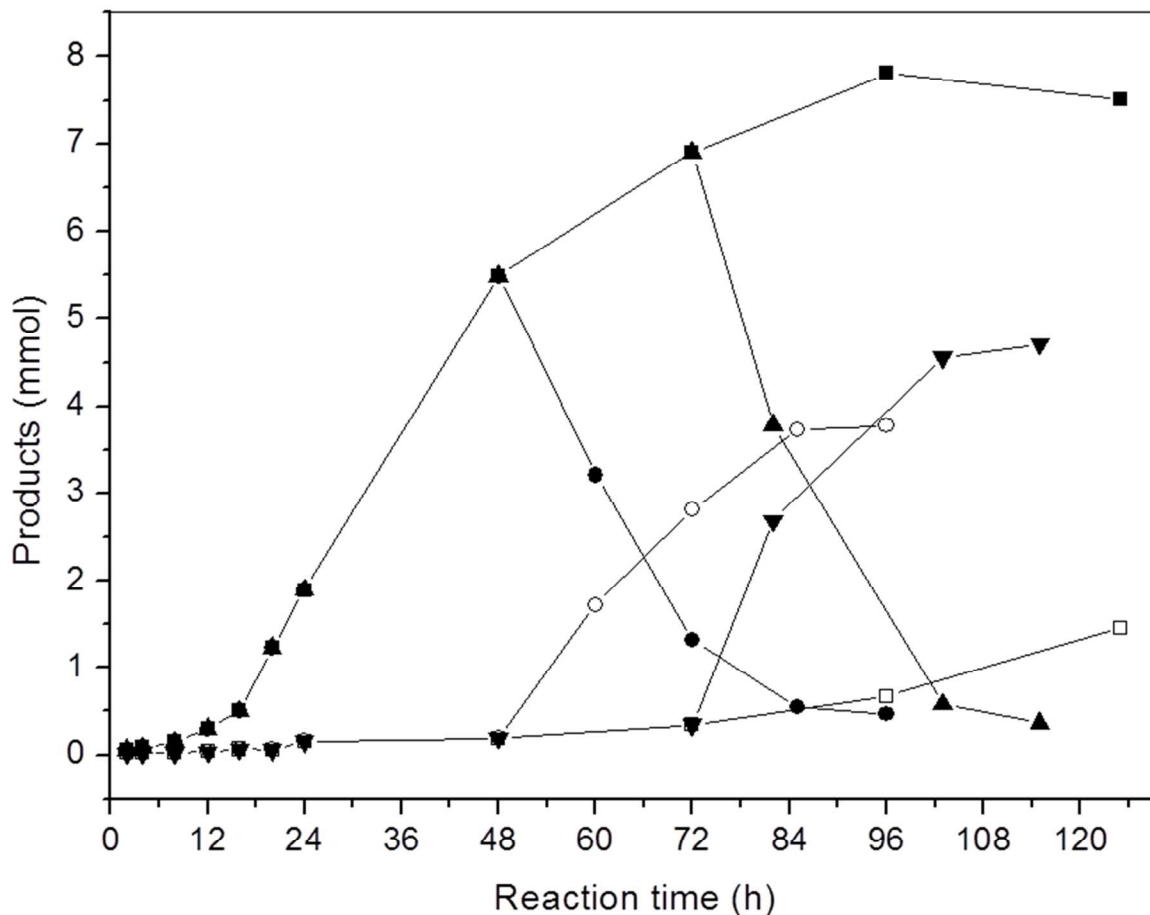


Figure 7 Effect of the addition of water and benzoic acid on the oxidation of dec-1-ene. Key: ■ epoxide without water and benzoic acid; □ 1,2-decanediol without water and benzoic acid; ● epoxide with water and benzoic acid added after 48 h; ○ 1,2-decanediol with water and benzoic acid added after 48 h; ▲ epoxide with water and benzoic acid added after 72 h; ▼ 1,2-decanediol with water and benzoic acid added after 72 h. Reaction conditions: dec-1-ene (53 mmol), AIBN (35 μ mol), 1wt% Au/graphite (0.1 g), 90 °C, benzoic acid (1.0 g), water (1.0 g).

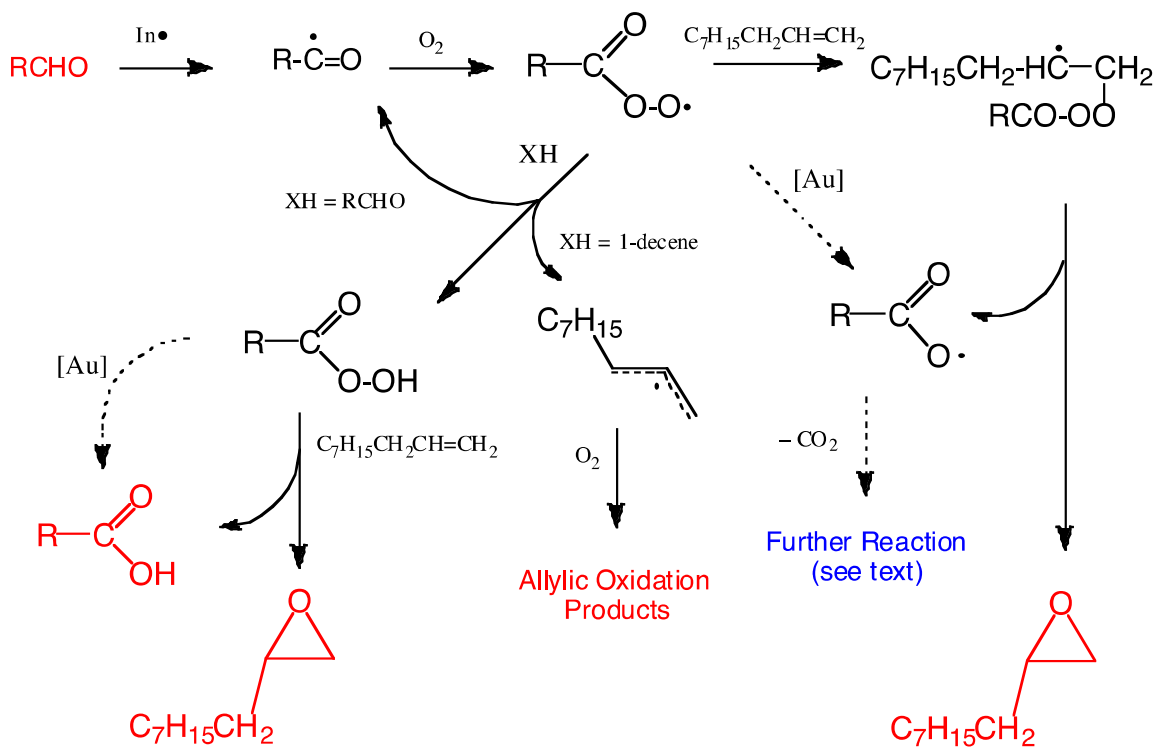


Figure 8 Proposed mechanism of dec-1-ene epoxidation with aldehyde as additive.