Development of a Selective, Solvent-free Epoxidation of Limonene Using Hydrogen Peroxide and a Tungsten-based Catalyst

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Abstract

The development of a limonene epoxidation process using environment-friendly H₂O₂, with high H₂O₂ conversion (~95%) and selectivity to the epoxide (100%), is reported in this paper. Parametric studies of temperature, oxidant, solvent, acid concentration and sodium sulphate amounts were performed with the focus on establishing a rapid and highly selective process. Approximately 95% conversion of H₂O₂ at 100% selectivity to limonene-1,2-epoxide was achieved in 15 minutes with a single-step addition of oxidant. The operating conditions included a 323 K temperature in a solvent-free environment, with a limonene/H₂O₂/catalyst molar ratio of 4:1:0.005, using a tungsten-based polyoxometalates. To prevent the hydrolysis of the epoxide, the reaction mixture was saturated with sodium sulphate. An acid concentration of lower than 0.04 M was used and found to have significant effect on the selectivity. Kinetic studies were performed to allow modelling of the reaction scheme. The activation energy was determined to be ~36 kJ mol⁻¹.

1.0 Introduction

Waste biomass is of increasing interest as a source of sustainable bio-based industries, as it reduces waste and helps maintain carbon dioxide (CO₂) neutrality.¹ Waste biomass-derived limonene, have many applications, especially in the fragrance, flavour and cosmetic industries.²⁻⁹ Over recent decades, there has been many research into the use of limonene as a chemical feedstock, especially for limonene oxide, a monomer for bio-based polymers.^{10, 11} Limonene oxide has many possible uses in the polymer industry and has been investigated as a means of incorporating CO₂ into the synthesis of polycarbonates.¹²⁻¹⁷

Epoxidation of alkenes with hydrogen peroxide (H₂O₂), has been extensively studied.¹⁸⁻²⁹ The main benefit of using H₂O₂ as an oxidant is its environment-friendly nature; it only produces water (H₂O) as a by-product. However, the epoxidation of limonene with H₂O₂ remains a challenging area because in the presence of H₂O, the epoxide is prone to hydrolytic ring-opening reaction. The formation of many oxidative by-products and the decomposition of H₂O₂ in the presence of a metal catalyst are also common issues.³⁰ The epoxidation of limonene using H₂O₂ as an oxidant is very exothermic, which is typically mitigated by an excess solvent or by drop-wise addition of the oxidant. This method artificially lowered the rate of reaction and lengthened the reaction time. The use of a solvent also affected the 'greenness' of such process.

Amongst the various types of catalysts used for this epoxidation, a tungsten based polyoxometalates has been shown as effective with H₂O₂.³¹⁻³⁴ This polytungstophosphate has attracted much attention, as it is more active than other transition metals and does not cause substantial H₂O₂ decomposition. In this work, a highly selective process was developed for the epoxidation of limonene with H₂O₂ in a solvent-free environment. A

comprehensive parametric study of the various conditions that affect the epoxidation of limonene has been performed. The study has been used to develop a predictive kinetic model incorporating all the processes involved. A competitive reaction rate was able to be achieved by using a single-step addition of oxidant as compared to the typical drop-wise method. The exothermicity is mitigated by using limonene itself as a solvent. It is reasoned that this process, utilising a waste biomass-driven limonene, would allow further development of a rapid and intensified process for sustainable bio-based industries.

2.0 Experimental

2.1 Reagents

Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), H_2O_2 (30% wt. in H_2O), 42.5% phosphoric acid (H_3PO_4), 48.5% sulphuric acid (H_2SO_4), anhydrous sodium sulphate (Na_2SO_4), (R)-Limonene, limonene-1,2-diol, p-cymene, acetonitrile, toluene, 1,2-dichloroethane and Adogen 464® phase transfer catalyst were all purchased from Sigma-Aldrich (Gillingham, UK).

2.2 Epoxidation reactions

The polyoxometalates preparation followed the procedure outlined in the literature.³⁵ The reaction was performed in a 150-ml jacketed flask. The temperature was monitored by using a thermocouple, and a water bath supplied the heating. In a typical epoxidation reaction, H_2O_2 (30% wt, 122 mmol), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.2 g), H_3PO_4 (42.5%, 0.06 mmol) and Na_2SO_4 (5.2 g) were stirred for 30 minutes to form the catalyst complex. H_2SO_4 (48.5%) was used to adjust the initial pH of the aqueous phase (4 mmol). The reaction began when limonene was added (122 mmol), together with a phase transfer catalyst, Adogen 464® (1 g). In the reactions in the presence of a solvent, toluene was typically used (100–500 mol%). Following the completion, the reaction mixture was placed in a separating funnel. To the organic phase, 0.1 M sodium chloride (NaCl) was added to destabilise the phase transfer catalyst. The separated organic phase was dried using an anhydrous Na_2SO_4 . A vacuum evaporator fitted with a silicone oil bath was used to separate limonene from limonene oxide at a temperature of 423 K and a pressure lower

than 50 mbar. The purity of the products obtained as confirmed by Gas Chromatography (GC) is more than ~98%.

2.3 *In situ* Fourier transform infra-red (FTIR) analysis

The reaction was continuously monitored by using the React IR-4000 Fourier transform infra-red (FTIR) analysis equipment from Mettler Toledo (USA). The scanning ranged from 4000 to 650 cm^{-1} , with the sampling typically performed every 15 sec. Peaks for limonene and limonene oxide were monitored at the wavelengths of 1150 cm^{-1} and 841 cm^{-1} , respectively.

2.4 Product analysis (gas chromatography)

Analysis using gas chromatography (GC) was performed to monitor the formation of by-products with higher accuracy. Organic samples were taken periodically during the reaction at designated time intervals for GC analysis. About 40 μL of each sample was measured into a 2-mL GC vial and diluted with 1960 μL of chloroform (CHCl_3) to be within the range of the flame ionisation detector (FID). About 10 mg of naphthalene was later added to the diluted sample. A calibration curve was prepared beforehand to calibrate the GC responses to the internal standard and all reagents and possible products. About 0.5 μL of the sample mixture was injected into the column manually, using a 5- μL GC syringe (SGE). The samples were analysed by using a 5890 Hewlett Packard Series II GC equipped with a CP Wax Capillary column (BPX70). Reaction conversion and yield were calculated from GC analysis based on the internal standard response factor. Pure sample of limonene, limonene-1,2-epoxide, limonene-1,2-diol, and limonene-bis-epoxide were

used as standards to calculate the response factor. Analysis from parallel experiments shows less than ~2% error for mean value. The following expression determined the conversion:

$$Conversion (\%) = \frac{C_0 - C_i}{C_0} \times 100\% \quad (1)$$

Where C_0 is the initial concentration of limonene and C_i is the concentration of limonene in the sample as determined by GC. When H_2O_2 is the limiting reactant, the concentration of H_2O_2 and its conversion were determined by the titration method. The yield of products is calculated using the following expression:

$$Yield (\%) = \frac{X_i}{C_0} \times 100\% \quad (2)$$

Where X_i is the concentration of products in the sample as determined by GC.

3.0 Results and Discussion

3.1 Reaction scheme

The catalytic epoxidation of limonene with H_2O_2 could generate many oxidative products (Figure 1).

Figure 1. Typical reaction scheme for the epoxidation of limonene with hydrogen peroxide (H_2O_2) as oxidant. Limonene **1**, limonene-8,9-epoxide **2**, limonene-1,2-epoxide **3**, limonene-bis-epoxide **4**, limonene-1,2-diol **5**, carveol **6** and carvone **7**.

Epoxidation of limonene with H_2O_2 would produce both limonene-8,9-epoxide and limonene-1,2-epoxide (a mixture of *cis*- and *trans*-). Due to the electrophilic nature of the oxidant, epoxidation would more likely occur at more substituted double bonds, causing limonene-1,2-epoxide to be the primary product.²² Limonene-bis-epoxide (a

mixture of four isomers) would be produced by the epoxidation of external double bonds of limonene-1,2-epoxide. Moreover, limonene-1,2-epoxide could undergo hydrolytic decomposition to form limonene-1,2-diol in the presence of acid (H^+) and H_2O . Limonene could also in principle undergo allylic oxidation to form carveol, which could be further converted to carvone by oxidative dehydrogenation.

3.2 Kinetics and modelling

To model the epoxidation reaction of limonene with H_2O_2 , the reaction scheme in Figure 2 is proposed to summarise the overall reactions.

Figure 2. Proposed overall reaction scheme for the epoxidation of limonene, the formation of polyoxometalates, the decomposition of H_2O_2 and the hydrolytic decomposition of the epoxides. The schematic diagram visualises the phase where each reaction occurs (blue background: aqueous phase, gold background: organic phase).

Figure 2 shows that the polytungstophosphate $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ formed from H_2O_2 , tungstate and phosphate shuttles to and from the organic phase via a phase transfer catalyst (Q^+). The details of the mechanism are elaborated in the literature.^{33, 36, 37} The active oxygen is transferred to both limonene and limonene oxide via the epoxidation reaction. The H^+ ions participate in the formation of the polyoxometalates and the protonic attack on the epoxides at the interphase. The epoxides form a diol in the presence of H_2O (nucleophile), following the protonic attack. The model also considers the decomposition of H_2O_2 as it will likely occur in the reaction.

Therefore, the rate laws for all the reactions considered by the model can be written as follows:

$$r_{decomp} = k_{decomp} [H_2O_2] \quad (3)$$

$$r_{POM} = k_{POM} [H^+] ([8H_2O_2] [4WO_4^{2-}] [PO_4^{-3}] [3Q] - K_{eq}^{-1} [Q_3POM] [7H_2O]) \quad (4)$$

$$r_{lim} = k_{lim} [limonene] [Q_3POM] \quad (5)$$

$$r_{bis} = k_{bis} [limonene\ oxide] [Q_3POM] \quad (6)$$

$$r_{diol} = k_{diol} [limonene\ oxide] [H_2O] [H^+] \quad (7)$$

$$r_{bisdiol} = k_{bisdiol} [bis-epoxide] [H_2O] [H^+] \quad (8)$$

In this work, the kinetic study was performed by applying the initial rate method based on pseudo first-order conditions. A prior mixing study ensured that the kinetic study was performed without mass transfer limitation.

To determine the reaction order with respect to the catalyst, the concentrations of the catalysts precursor, Na_2WO_4 were varied between 0.003 M and 0.009 M. The initial concentrations of limonene, H_2O_2 and solvent were kept constant.

Figure 3. The plot of the natural log between the initial reaction rate and A) catalyst concentration. B) limonene concentration. C) H₂O₂ concentration.

The plot of the natural log between the initial rates and the catalyst concentration produces a straight line with a gradient of ~ 1 , indicating that the reaction is not diffusion limited (Figure 3(A)). The reaction order with respect to limonene was determined by varying the initial concentration of limonene from 0.25 M to 1.25 M. The concentrations of H₂O₂ were kept constant and in excess. Figure 3(B) confirms a first-order reaction from the gradient of the plot of the natural log between the initial rates and limonene concentration.

The reaction order with respect to H₂O₂ was determined by varying the initial concentration of H₂O₂ from 0.25 M to 1.25 M. The initial concentration of limonene was kept constant and in excess. The gradient obtained from Figure 3(C) shows a fractional reaction order of ~ 0.5 , indicating a complex mechanism. According to Figure 2 and Equation (4), increasing the concentration of H₂O₂ increases the formation of the polyoxometalates but is limited to the concentration of tungstate and phosphate. This also implied that the epoxidation of limonene, as shown by Equation (5), would most probably be the rate-determining step. Yadav and Satoskar reported similar behaviour for the epoxidation of undecylenic acid, where the rate was independent of the H₂O₂

concentration when the ratio of the $[\text{H}_2\text{O}_2]/[\text{catalyst}]$ was high.³⁷ Kamata *et al.* also found an apparent zero-order dependence on the H_2O_2 concentration for the epoxidation of alkene.³⁸

3.3 Effect of temperature

The effects of temperature on the epoxidation of limonene were investigated. The temperature varied between 303 K and 333 K.

Figure 4. The effects of temperature on limonene epoxidation. A) conversion of limonene, B) yield of limonene oxide, C) yield of bis-epoxide and D) yield of limonene diol. Reaction conditions: limonene (1.25 M), H_2O_2 (1.25M), Na_2WO_4 (0.006 M), H_2SO_4 (0.06M) and toluene (500 mol%). The lines are fitted to the kinetic model by using Equations (3)–(8) and the rate constant in Table 1.

The conversion of limonene reaches a maximum of 80% at a reaction time of 120 min for all temperatures (Figure 4(A)). However, at a temperature higher than 323 K, the yield of limonene oxide and bis-epoxide attains a maximum of 73% and 7%, respectively before gradually decreasing (Figure 4(B) and 4(C)). The decrease in both limonene oxide and bis-epoxide yields over the reaction time can be explained by the rate of hydrolysis, which results in the formation of limonene diol and bis-diol, respectively. On the other hand, the yield of limonene diol at 333 K is over 15% at a reaction time of 120 min (Figure 4(D)). This result is more than double the yield at 323 K (7%). The kinetic model is able to predict the formation of bis-epoxide and limonene diol at temperatures up to 333 K and validates the experimental data. To ensure the highest selectivity towards the formation of limonene oxide, it is suggested that the epoxidation reaction be performed at a temperature below 323 K.

The Arrhenius dependence for the formation of the desired product, limonene oxide and a major by-product, limonene diol was determined by varying the reaction temperature between 303 K and 333 K. Figure 5 shows the temperature dependence of limonene oxide and limonene diol formation as plots of $\ln(k_{epox})$ and $\ln(k_{diol})$ versus $1/T$.

Figure 5. Temperature dependence of the rate constant for the formation of limonene oxide and limonene diol.

The activation energy for the formation of limonene oxide obtained from the gradient of Figure 5 was determined to be $\sim 36 \text{ kJ mol}^{-1}$. This figure is higher than the $16 \text{ kJ} \cdot \text{mol}^{-1}$ reported by Cagnoli *et al.*²⁰ However, Villa *et al.* reported a much higher value (76 kJ mol^{-1}), but they had used a heterogeneous catalyst.²⁵ On the other hand, the activation energy for the formation of limonene diol was determined to be $\sim 79 \text{ kJ mol}^{-1}$. This result confirms that the formation of a by-product, limonene diol proceeds slowly at a lower temperature compared with limonene oxide. However, at a temperature above 323 K , the reaction rate becomes more significant, resulting in a higher yield of limonene diol. Table 1 lists the kinetic parameters obtained from the study.

Table 1. The pre-exponential factor and the activation energy for the formation of limonene oxide, bis-epoxide and limonene diol.

		Activation energy (kJ mol ⁻¹)	
		This work	References
k _{epox} ^a	5.9 x 10 ⁴	36	16 ²⁰ 76 ²⁵
k _{bis} ^a	8.6 x 10 ⁴	43	
k _{diol} ^b	4.9 x 10 ⁸	79	

^aunit of L¹ mol⁻¹ s⁻¹; ^bunit of L² mol⁻² s⁻¹

3.4 Effect of oxidant amount

The effect of the oxidant amount was studied by varying the concentration of H_2O_2 from 100 mol% to 200 mol%.

Figure 6. The effect of the oxidant amount on limonene epoxidation. (A) conversion of limonene, (B) yield of limonene oxide, (C) yield of bis-epoxide and (D) yield of limonene diol. Reaction conditions: temperature (323 K), limonene (1.25 M), Na_2WO_4 (0.006 M), H_2SO_4 (0.06 M) and toluene (500 mol%).

The conversion of limonene decreases from 82% to 58% when the oxidant amount is increased from 100 mol% to 200 mol% (Figure 6(A)). Since there is no significant decomposition of H_2O_2 during the catalyst preparation, the decrease in limonene conversion, might be attributed to the dilution of the polyoxometalates in the aqueous

phase. This finding is similar to the observation of Wang and Huang, who reported a decrease in conversion for 1,7-octadiene with an increasing amount of oxidant (H_2O_2).³⁹ The yield of limonene oxide also decreases with an increasing oxidant amount (Figure 6(B)). The yields are 74% and 30% for oxidant amounts of 100 mol% and 200 mol%, respectively. Above 125 mol%, the yield of limonene oxide attains a maximum before decreasing with time, becoming more pronounced as the oxidant amount increases.

The yield of bis-epoxide is highest when the oxidant amount used is 100 mol% (Figure 6(C)). The yield attains a maximum of 8% before gradually decreasing. Interestingly, increasing the oxidant amount from 100 mol% to 200 mol% decreases the yield of bis-epoxide. This finding is in contrast with the observation of Takumi *et al.*⁴⁰ where they reported an increase of up to 40% yield of bis-epoxide with an increasing oxidant amount, which might be attributed to the lower temperature and acid concentration used in their study.

The yield of limonene diol increases dramatically with an increasing oxidant amount (Figure 6(D)). The yield at a reaction time of 120 min rises from 8% to about 40% with an increasing oxidant. The formation of diol is influenced by the concentrations of both H^+ and H_2O . The increased H_2O concentration is in proportion to the increase in the oxidant amount since 30% (wt/wt) H_2O_2 solution is used. To maintain the highest selectivity towards limonene oxide and to minimise the formation of limonene diol, using an equivalent amount (100 mol%) of oxidant to limonene is therefore suggested.

3.5 Effect of sodium sulphate (Na_2SO_4)

The presence of H_2O in an H_2O_2 solution was found to adversely affect the selectivity of limonene oxide due to the hydrolysis of the epoxide ring. Many methods have been developed to suppress the hydrolysis process, including the addition of an inorganic salt, Na_2SO_4 , which has been found to improve the selectivity of terpenes oxide.^{30, 35} In this work, the effect of Na_2SO_4 to limonene epoxidation was investigated. The amount of Na_2SO_4 used varied from 2.5 g to 7.5 g.

Figure 7. The effect of the Na_2SO_4 amount on limonene epoxidation. (A) conversion of limonene, (B) yield of limonene oxide, (C) yield of bis-epoxide and (D) yield of limonene diol. Reaction conditions: temperature (323 K), limonene (1.25 M), H_2O_2 (1.25 M), Na_2WO_4 (0.006 M), H_2SO_4 (0.06 M) and toluene (500 mol%).

In the absence of Na_2SO_4 , the pH of the aqueous phase is lower; thus, more protons (H^+) are present in the system, causing an increase in the reaction rate (Figure 7(A)). On the other hand, the addition of Na_2SO_4 increases the yield of limonene oxide (Figure 7(B)). The yield at a reaction time of 120 min increases from less than 5% to 75% when the amount of Na_2SO_4 is increased from 0 g to 5.7 g. There is no decrease in the yield of limonene oxide over time when more than 5.7 g of Na_2SO_4 is used. In the presence of Na_2SO_4 , the ionic strength of the aqueous phase increases³⁰. Although the mechanism of the salt effect is difficult to determine, it is postulated that the salt ionised into its respective ions, inducing a 'salting-out' process⁴¹. The ions repulse nonelectrolyte compound such as limonene oxide in the aqueous phase, minimising the epoxide solubility at the interphase, which in turn suppressed the hydrolysis process.

A slight limitation of this effect can be seen in Figure 7(C), where the hydrolysis of bis-epoxide is only suppressed at a much higher salt concentration (7.5 g). This might be due to the higher affinity of bis-epoxide towards the aqueous phase due to the presence of two epoxide ring in its molecule. Figure 7(D) confirms the importance of Na_2SO_4 , where the yield of limonene diol decreases from 30% to about 5% with an increasing amount of Na_2SO_4 . The utilisation of Na_2SO_4 effectively reduces the hydrolysis of limonene oxide. The epoxidation of limonene using H_2O_2 achieves the highest selectivity to limonene oxide when the aqueous phase is 100% saturated with Na_2SO_4 (5.7 g).

3.6 Effect of acid concentration

The concentration of acid (H_2SO_4) in the reaction media affects the stability of the catalyst^{30, 31, 34, 40, 42, 43}. The effect of acid on limonene epoxidation was studied by varying the initial concentration of H_2SO_4 from 0.02 M to 0.06 M. The initial pH for all cases was lower than 1.

Figure 8. The effect of acid concentration on limonene epoxidation. A) conversion of limonene, B) yield of limonene oxide, C) yield of bis-epoxide and D) yield of limonene diol. Reaction conditions: temperature (323 K), limonene (1.25 M), H_2O_2 (1.25 M), Na_2WO_4 (0.006 M) and toluene (500 mol%).

The conversion of limonene reaches 80% for all acid concentrations at a reaction time of 120 min (Figure 8(A)). The yield of limonene oxide and bis-epoxide rises from

57% to 71% and 5% to 10%, respectively when the acid concentration is decreased from 0.06 M to 0.02 M (Figure 8(B) and 8(C)). At an acid concentration of more than 0.05 M, the yield of bis-epoxide attains a maximum before gradually decreasing. The yield of limonene diol is only quantifiable when the acid concentration is more than 0.05 M (Figure 8(D)). At an acid concentration lower than 0.04 M, no limonene diol is present in the reaction mixture over the reaction time.

In all cases, the pH increases during the reaction. This might be due to the formation of H_2O as H_2O_2 was progressively consumed. The final pH was above 2 when the acid concentration is less than 0.05 M, which shows the reduction in H^+ concentration. The reduced acidity positively affects the selectivity of the epoxide as the acid-catalysed hydrolysis was suppressed. In this regard, a pH buffer might be detrimental to the epoxide selectivity since acid-catalysed hydrolysis could be enhanced throughout the reaction.

Acid concentration plays a vital role in the epoxidation of limonene using a tungsten-based polyoxometalates. The highest selectivity towards limonene oxide with little to no diol formation can be achieved by optimising the acid concentration used in the reaction. The acid-catalysed regio-isomerisation of limonene to form products such as terpinolene and terpinene has been reported.⁴⁴ However, the absence of such products in this work might be due to the lower acid concentration used and the different catalyst employed. It should be noted that prior control experiments were performed without the addition of H_2SO_4 . Without the addition of acid, the initial pH of the aqueous phase is about 4.0. No conversion of limonene is detected throughout the reaction time.

3.7 Effects of solvents

The reactivity of limonene epoxidation reaction is related to the nature and the polarity of solvents. Here, four different solvents, ranging from non-polar to polar, were used and compared for practical applications (Figure 9). A greener solvent, p-cymene was also evaluated. Additionally, a solvent-free system was studied by using limonene in a higher molar ratio (> 200 mol%).

Figure 9. The effects of solvents on limonene epoxidation. Reaction conditions: temperature (323 K), limonene (1.25 M), H_2O_2 (1.25 M), Na_2WO_4 (0.006 M), H_2SO_4 (0.06 M), reaction time (120 min) and solvent amount (500 mol%) for each solvent. Limonene is represented by the calculated conversion whereby limonene oxide, bis-epoxide and limonene diol are represented by the calculated yield.

The conversion of limonene increases when the solvents are used in the following order: acetonitrile (39%), $<$ p-cymene (65%), $<$ toluene (78%) and $<$ 1,2-dichloroethane (89%). The chlorinated solvent, 1,2-dichloroethane, significantly increases the conversion of limonene compared with the other tested solvents. However, the selectivity towards limonene oxide is reduced due to the formation of both bis-epoxide and limonene

diol. The yield of limonene diol using this solvent is the lowest of all the solvents. Toluene has been used throughout this study, and it is found to have a lower activity than that of 1,2-dichloroethane. Although the polarity of toluene is lower than that of 1,2-dichloroethane, the higher activity of the latter might be due to the chloro-compound present in the solvent.

The selectivity to limonene oxide in p-cymene is lower than in toluene and in 1,2-dichloroethane, where the yield of limonene diol is slightly higher (14%). The conversion of limonene is found to be lowest when acetonitrile is used. The selectivity towards limonene oxide is poor, which in turn results in a much higher yield of limonene diol (25%). This outcome might be due to the higher polarity of acetonitrile that enhances the hydrolysis of the epoxide.

High selectivity to limonene oxide and high H_2O_2 conversion are obtained when limonene is used in a higher molar ratio than H_2O_2 without any solvent (Figure 10). The conversion and yield were determined based on the concentration of H_2O_2 as the limiting reactant.

Figure 10. The yield of limonene oxide with an increasing amount of limonene. Reaction conditions: temperature (323 K), H_2O_2 (1.25 M), Na_2WO_4 (0.006 M) and H_2SO_4 (0.04 M). The lines are fitted to the kinetic model by using Equations (3)–(8) and the rate constant in Table 1.

Figure 10 shows the increasing yield of limonene oxide when the amount of limonene is increased up to 400 mol%. At the equimolar amount of limonene to H_2O_2 (100 mol%), the maximum yield achieved is only 73%. In this condition, the exothermic temperature not only decomposes H_2O_2 but increases the rate of hydrolysis which gradually consumes limonene oxide. However, the yield of limonene oxide is increased to 95% at 100% selectivity within 15 minutes reaction time by increasing the limonene amount up to 400 mol%. Isothermal condition was able to be achieved as the large amount of limonene helps mitigate the exotherm. Interestingly, there is no formation of bis-epoxide, and no limonene diol is detected when limonene is used in a higher ratio (> 200 mol%). This result is due to the rapid rate of formation of limonene oxide, which fully utilises the oxidant present in the system. This also prevents further epoxidation to bis-epoxide. Due to the lower acid concentration used at 0.04 M, the epoxides remain stable throughout the reaction time, and no limonene diol is formed.

The kinetic model validates the experimental data, especially at more than 300 mol% of limonene. The model is able to predict 93% of the limonene oxide yield, which is remarkably close to the percentage in the experimental data (95%). However, at a limonene amount of 200 mol%, the model predicts the formation of bis-epoxide (5%), which is not observed in the experimental data. Due to the absence of a solvent and the increased molar ratio of limonene to H_2O_2 , the reaction temperature is slightly exothermic at limonene amount of less than 200 mol%. This situation causes the initial reaction rate to be slightly higher than the prediction by the model, which uses a rate constant at 323 K.

From this result, rapid production of limonene oxide in short reaction time could be achieved in a solvent-free environment using a single-step addition of oxidant as opposed to the typical drop-wise method. The biphasic mixture allows the easy separation of the product from the cheap catalyst. The absence of a solvent reduces the purification steps required, while excess limonene would be recycled. Further improvement of the process will involve the recyclability of the catalyst and the development of a continuous process.

4.0 Conclusions

Limonene epoxidation using green H_2O_2 has been performed by using a tungsten-based polyoxometalates. It has been demonstrated that the epoxidation of limonene could be performed solvent-free at a high yield and selectivity by using limonene in stoichiometric excess (versus H_2O_2) with a single-step addition of the oxidant. The developed process reveals a potentially high throughput where 95% conversion of H_2O_2 could be achieved with 100% selectivity towards limonene-1,2-epoxide within a short reaction time (~15 minutes). The addition of Na_2SO_4 has been shown to inhibit the hydrolysis of epoxide. The selectivity towards limonene-1,2-epoxide is 100% when enough Na_2SO_4 is used to saturate the aqueous phase. Using the correct acid concentration suppressed the formation of any by-products. The study of the reaction kinetics shows a first-order reaction with respect to limonene. A predictive kinetic model has been developed, with a high level of agreement with the experimental data. Overall, this study has demonstrated that rapid limonene epoxidation can be performed solvent-free at an almost stoichiometric yield by using a single-step addition of oxidant with the judicious

choice of operating conditions. The identified conditions should lead to a rapid and efficient process, with a significantly improved atom economy.

Conflict of interest

There are no conflicts of interest to declare

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References

1. M. N. Belgacem and A. Gandini, *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK, 2008.
2. W. F. Erman, *Chemistry of Monoterpenes*, Marcel Dekker, New York, 1985.
3. A. Calogirou, B. Larsen and D. Kotzias, *Atmospheric Environment*, 1999, **33**, 1423-1439.
4. A. J. Silvestre and A. Gandini, in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, 2008, pp. 17-38.
5. N. Fdil, A. Romane, S. Allaoud, A. Karim, Y. Castanet and A. Mortreux, *Journal of Molecular Catalysis A: Chemical*, 1996, **108**, 15-21.
6. P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686-694.
7. H. Mimoun, *CHIMIA International Journal for Chemistry*, 1996, **50**, 620-625.
8. C. Chapuis and D. Jacoby, *Applied Catalysis A: General*, 2001, **221**, 93-117.
9. K. Bauer, D. Garbe and H. Surburg, *Common fragrance and flavor materials: preparation, properties and uses*, John Wiley & Sons, 2008.
10. M. Bähr, A. Bitto and R. Mülhaupt, *Green Chem*, 2012, **14**, 1447-1454.
11. H. Morikawa, M. Minamoto, Y. Gorou, J.-i. Yamaguchi, H. Morinaga and S. Motokucho, *B Chem Soc Jpn*, 2017, **91**, 92-94.
12. O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem*, 2016, **18**, 760-770.
13. C. Martín and A. W. Kleij, *Macromolecules*, 2016, **49**, 6285-6295.
14. M. Pagliaro, A. Fidalgo, L. Palmisano, L. M. Ilharco, F. Parrino and R. Ciriminna, 2018.
15. C. Li, M. Johansson, R. J. Sablong and C. E. Koning, *European Polymer Journal*, 2017, **96**, 337-349.
16. C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *Journal of the American Chemical Society*, 2004, **126**, 11404-11405.
17. M. Reiter, S. Vagin, A. Kronast, C. Jandl and B. Rieger, *Chemical science*, 2017, **8**, 1876-1882.
18. K. Ambroziak, R. Mbeleck, B. Saha and D. Sherrington, *Int J Chem React Eng*, 2010, **8**, 1-13.
19. A. J. Bonon, Y. N. Kozlov, J. O. Bahú, R. M. Filho, D. Mandelli and G. B. Shul'pin, *J Catal*, 2014, **319**, 71-86.
20. M. V. Cagnoli, S. G. Casuscelli, A. M. Alvarez, J. F. Bengoa, N. G. Gallegos, N. M. Samaniego, M. E. Crivello, G. E. Ghione, C. F. Pérez, E. R. Herrero and S. G. Marchetti, *Applied Catalysis A: General*, 2005, **287**, 227-235.
21. S. G. Casuscelli, M. E. Crivello, C. F. Perez, G. Ghione, E. R. Herrero, L. R. Pizzio, P. G. Vázquez, C. V. Cáceres and M. N. Blanco, *Applied Catalysis A: General*, 2004, **274**, 115-122.
22. L. Charbonneau and S. Kaliaguine, *Appl Catal a-Gen*, 2017, **533**, 1-8.
23. M. G. Egusquiza, C. I. Cabello, I. L. Botto, H. J. Thomas, S. Casuscelli, E. Herrero and D. Gazzoli, *Catalysis Communications*, 2012, **26**, 117-121.
24. Y. Mahha, L. Salles, J. Y. Piquemal, E. Briot, A. Atlamsani and J. M. Bregeault, *J Catal*, 2007, **249**, 338-348.
25. A. L. Villa, F. T. A. and C. M. de Correa, *Journal of Molecular Catalysis A: Chemical*, 2002, **185**, 269-277.

26. A. Pena, S. Veiga, M. Sapelli, N. Martínez, V. Márquez, E. Dellacassa and J. Bussi, *Reaction Kinetics, Mechanisms and Catalysis*, 2012, **107**, 263-275.
27. R. B. Zapata, A. L. Villa and C. M. de Correa, *Ind. Eng. Chem. Res.*, 2009, **48**, 647-653.
28. R. B. Zapata, A. L. Villa and C. M. de Correa, *Ind Eng Chem Res*, 2006, **45**, 4589-4596.
29. E. Santacesaria, A. Renken, V. Russo, R. Turco, R. Tesser and M. Di Serio, *Ind Eng Chem Res*, 2012, **51**, 8760-8767.
30. G. Grigoropoulou and J. H. Clark, *Tetrahedron Lett*, 2006, **47**, 4461-4463.
31. C. Venturello and R. D'Aloisio, *J. Org. Chem.*, 1988, **53**, 1553-1557.
32. G. Grigoropoulou, J. H. Clark and J. A. Elings, *Green Chem*, 2003, **5**, 1-7.
33. D. C. Duncan, R. C. Chambers, E. Hecht and C. L. Hill, *Journal of the American Chemical Society*, 1995, **117**, 681-691.
34. Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida and M. Ogawa, *J Org Chem*, 1988, **53**, 3587-3593.
35. H. Hachiya, Y. Kon, Y. Ono, K. Takumi, N. Sasagawa, Y. Ezaki and K. Sato, *Synthesis-Stuttgart*, 2012, **44**, 1672-1678.
36. G. Yadav and A. Pujari, *Organic Process Research & Development*, 2000, **4**, 88-93.
37. G. Yadav and D. Satoskar, *Journal of the American Oil Chemists' Society*, 1997, **74**, 397-407.
38. K. Kamata, K. Yamaguchi and N. Mizuno, *Chemistry-A European Journal*, 2004, **10**, 4728-4734.
39. M.-L. Wang and T.-H. Huang, *Ind Eng Chem Res*, 2004, **43**, 675-681.
40. K. Takumi, N. Sasagawa, Y. Ezaki, Y. Kon, Y. Ono and K. Sato, 2014.
41. A. M. Hyde, S. L. Zultanski, J. H. Waldman, Y.-L. Zhong, M. Shevlin and F. Peng, *Organic Process Research & Development*, 2017, **21**, 1355-1370.
42. C. Venturello, E. Alneri and M. Ricci, *J. Org. Chem.*, 1983, **48**, 3831-3833.
43. K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J Org Chem*, 1996, **61**, 8310-8311.
44. N. A. Comelli, E. N. Ponzi and M. I. Ponzi, *Journal of the American Oil Chemists' Society*, 2005, **82**, 531-535.