Catalyst-Free Epoxidation of Limonene to Limonene Dioxide

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Supporting Information

ABSTRACT: Limonene dioxide is a platform molecule for the production of new biopolymers. First attempts at limonene epoxidation were made by using low-coordination titanium supported on SBA-16 as the catalyst using *tert*-butyl hydroperoxide as the oxidizing agent, but no limonene dioxide was obtained. When limonene was substituted by 1,2-limonene oxide, the yield of limonene dioxide was only 13% in the same conditions. Two other techniques, both using in situ generated dimethyl dioxirane by the reaction of acetone with Oxone, have been studied and compared. These reactions are carried out in semibatch conditions and at room temperature. The first double epoxidation of limonene was performed in a conventional biphasic organic–water system and the other in excess acetone. The former epoxidation of limonene using ethyl acetate as the organic phase allowed reaching 95% conversion and yielding 33% of limonene dioxide. In comparison, when the reaction was performed in acetone, a limonene dioxide yield of 97% was observed under optimized conditions. The double epoxidation of limonene should be carried out at room temperature with a flowrate of 4 mL min^{−1} of aqueous Oxone for a period of 45 min with a stoichiometric excess of 30% of Oxone.

KEYWORDS: Limonene, Green epoxidation, Catalyst-free, Limonene dioxide, Biomonomer

INTRODUCTION

Polymer scientists have been urged to find sustainable and renewable alternatives to petroleum-based polymers. Their substitution by biopolymers will lead to important contributions to reduce our dependency on nonrenewable fossil fuels, through the positive impact on reducing CO₂ emissions in the atmosphere.¹ Furthermore, it has been underlined that biomass-derived monomers offer excellent potential substitutes to traditional monomers.^{1,2} Biomass-derived monomers were classified in four categories: oxygen-rich monomers (lactic acid, succinic acid), hydrocarbon monomers (bio-olefins), non-hydrocarbon monomer (carbon dioxide), and finally hydrocarbon-rich monomers (vegetable oils, fatty acids, terpenes).³ Biopolymers have been the subject of numerous scientific publications.^{4–8}

Limonene is a low-cost terpene easily obtained by extraction from citrus oil. In 2013, the global annual production reached 70 000 t, and it is mostly used for the fragrance and the food industries.⁹ The primary product of limonene epoxidation, 1,2-limonene oxide, has gained attention since it was used to produce polycarbonates.^{10–12} Limonene polycarbonate is produced through the polymerization of 1,2-limonene oxide and carbon dioxide in the presence of a catalyst. Limonene dioxide has gained less attention, but is a promising molecule it can be used as a cross-linker or adhesive, epoxy resin.¹³ Limonene dioxide, when reacting with carbon dioxide, produces limonene dicarbonate. This new type of monomer

is applied for the preparation of isocyanate-free polyurethane.¹⁴ These types of polymerization techniques are excellent ways to valorize carbon dioxide and use it as a monomer. Rough estimates of the potential reduction of CO₂ emissions associated with complete substitution of present polymers including polycarbonates, polyurethane, and epoxy resins have been made. The potential reductions have been roughly estimated to 600 kt per year in the Quebec province region only. The main goal of the present work is to develop a process to obtain limonene dioxide in high yield in the cheapest and greenest possible way, to support the large-scale need to produce these three types of polymers.

Epoxidation of olefins can be carried out using hydroperoxides, ClO[−], PhIO, or molecular oxygen. These act as oxygen source in the presence of a catalyst such as supported metal oxides or organometallic complexes. The most employed metals are V, Mo, W, Ti, Mn, Cr, or Co.^{15,16} Hydrogen peroxide is used as the oxygen donor when methyltrioxorhenium or tungstic acid and its derivatives are the catalysts. Organometallic complexes and supported metal oxides are the most efficient catalysts to achieve high epoxide yield. Epoxidation of limonene to limonene dioxide using organometallic catalysts has been reported in the literature.^{17,18} These

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catalysts afford very high yields of limonene dioxide. However, most of the transition metals used for epoxidation of olefins are toxic and not considered environmentally friendly.¹⁶

A greener approach to the epoxidation of limonene to limonene dioxide is considered in this work. Dimethyl dioxirane (DMDO) is an oxidizing agent that can be easily and safely synthesized in situ by the reaction of a ketone, most of the time acetone, and an aqueous solution of potassium peroxymonosulfate, commercially known under the trade name of Oxone (Dupont). Several reports have shown excellent yield for epoxidation of olefins.^{16,19} In situ synthesized dioxirane offers advantages in terms of reactivity and yields. Peracids such as peracetic acid or meta-chloroperbenzoic acid (mCPBA) cannot be used for acid-sensitive epoxides. Compared to perhydrates, Weitz-Schaffer conditions, or the Payne reaction, the dimethyl dioxirane can epoxidize both electron-poor and electron-rich alkenes in very high yields.^{20,21} The products of the reaction using in situ generated DMDO are the epoxides, water, HSO_4^- , and acetone which are easy to separate and safe to handle. Furthermore, compared to hydrogen peroxide, hydroperoxides, or other peracids which require a stabilizing agent, Oxone is a highly stable salt that can be safely stored. Oxone can be easily prepared at commercial scale by reacting sulfuric acid and hydrogen peroxide in the presence of potassium hydroxide.²²

The aim of this paper is to establish if the in situ generated dimethyl dioxirane, which is an oxidizing agent that does not require a catalyst, can be used for the production of limonene dioxide in high yield. The time evolution of the reaction was studied to get a better understanding of the reaction mechanism. The reaction conditions such as the molar ratio of olefin/oxidizing agent and the flowrate of Oxone were optimized. Finally, a comparison between the epoxidation of limonene using dimethyl dioxirane and low-coordination titanium on silica support using *tert*-butyl hydroperoxide (TBHP) was performed to determine which process is more convenient to obtain high limonene dioxide yield in mild conditions.

■ EXPERIMENTAL SECTION

Titanium Catalyst Synthesis. SBA-16 synthesis is similar to the one reported by Kleitz et al.^{23–25} In a typical synthesis, 5.35 g of F127 (BASF) was dissolved in a stirred solution containing 257.2 g of water and 10.6 g of concentrated hydrochloric acid (35–37%) at 45 °C. Once the F127 was dissolved, 16.1 g of *n*-butanol was added to the solution as a cosurfactant. Finally, 25.45 g of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added to the mixture. The solution was agitated for 24 h. The resulting mixture was transferred to an autoclave to allow hydrothermal aging for 24 h at 140 °C. $\text{TiO}(\text{ACAC})_2$ (Strem 98%) was dissolved in 200 mL of toluene at 45 °C. SBA-16 was previously calcined at 550 °C for 6 h, added to the solution, and agitated for 2 h. The solid was filtered, washed with 300 mL of toluene, and dried in the oven at 100 °C for 24 h. Finally, the sample was calcined at 550 °C (ramp of temperature: 2 °C min⁻¹) for 3 h.²⁶

Characterization of Ti-SBA-16. Nitrogen adsorption–desorption isotherms were measured at –196 °C using an Autosorb-1C sorption analyzer. The pore size distributions and the cumulative surface area curves were determined using the nonlocal density functional theory (NLDFT) method 31 supplied with the Autosorb-11.55 software from Quantachrome Instruments. The kernel selected was N_2 sorption on silica at –196 °C assuming a cylindrical pore geometry and implementing the model of (metastable) NLDFT adsorption isotherms (adsorption branch).

Prior to elementary analysis, the catalyst was digested in a mixture of 10% (v/v) hydrochloric acid and hydrofluoric acid 1% (v/v). Elemental analysis was performed using a PerkinElmer Atomic

Absorption M1100B spectrometer. Titanium coordination was determined by diffuse reflectance UV–vis on a Varian Cary 300 Bio instrument with a scan rate of 200 nm per second.

The characterization results for Ti-SBA-16 catalyst are reported in the Supporting Information (SI).

Epoxidation Using Ti-SBA-16. The catalytic tests were performed in a 50 mL round-bottom flask with 300 mg of catalyst with Ti/Si atomic ratio of 7.9%, 10 mL of acetonitrile, 6.2 mmol of R(+)-limonene, and 11.2 mmol of TBHP in decane solution at 75 °C for 24 h with an agitation at 500 rpm using a Fisher Scientific thermoplate equipped with a thermocouple. The catalyst was separated from the solution by centrifugation.

Conventional Biphasic Epoxidation of Limonene. The biphasic reaction of limonene with Oxone was performed following the procedure reported by Hashimoto and Kanda.²⁷ A 40 mL portion of water, 3.55 g of sodium bicarbonate, 4.90 g of acetone, 40 mL of ethyl acetate, and 8.5 mmol of R(+)-limonene (Sigma-Aldrich, 97%) were mixed in a three-neck round-bottom flask. A 50 mL aqueous solution which contained 5.20 g of Oxone was added dropwise at a flowrate of 1 mL min⁻¹ using a syringe pump at room temperature. The reaction was then run under vigorous agitation for another hour. The reaction mixture was liquid–liquid extracted with ethyl acetate, evaporated, and finally analyzed by GC-FID to determine the conversion and yield of epoxides.

Epoxidation of Limonene by Dimethyl Dioxirane in Excess Acetone. The reaction was carried out at room temperature in semibatch conditions. A 30 mL portion of acetone, 4 g of sodium bicarbonate, and 10 mmol of R(+)-limonene (Sigma-Aldrich, 97%) were added to a three-neck round-bottom flask. A 26 mmol portion of potassium peroxymonosulfate (Oxone) was dissolved in 50 mL of water (0.52 M) and added to the three-neck flask using a syringe pump connected to a Tygon tube with an internal diameter of 4 mm to ensure a constant flowrate. The reaction mixture was separated by liquid–liquid extraction by diethyl ether. The organic layer was dried on magnesium sulfate and evaporated. The conversion and yield of epoxides were determined by GC-FID. The reaction mixture was also analyzed by ¹H NMR spectroscopy in CDCl_3 and by GC-MS.

Characterization of the Reaction Medium. All reaction mixtures were analyzed using a CP-3800 gas chromatograph (Varian Inc.) equipped with a flame ionization detector (FID) and a Stabilwax column (30 m × 0.53 mm × 1 μm) coupled with a 5 m guard column. The limonene conversion was determined using eq 1.

$$\text{conv (\%)} = \frac{n_0(\text{limonene}) - n_f(\text{limonene})}{n_0(\text{limonene})} \times 100 \quad (1)$$

The yield for limonene oxide and limonene dioxide was calculated using eq 2:

$$\text{yield (\%)} = \frac{n_{\text{epoxide}}}{n_0(\text{limonene})} \times 100 \quad (2)$$

Both limonene oxide and limonene dioxide standards were purchased from Sigma-Aldrich. Methoxybenzene was used as the internal standard. To ascertain the presence of limonene dioxide, the reaction mixture composition was confirmed by GC-MS. The GC-MS instrument was a Hewlett-Packard HP 5890 series GC system and MSD Hewlett-Packard Model 5970. The GC-MS was equipped with a Zebron ZB-5MS capillary column (30 m × 0.25 mm × 0.25 mm).

¹H NMR of the limonene dioxide spectrum was compared with that of limonene and reported in the Supporting Information.

■ RESULTS AND DISCUSSION

Epoxidation of Limonene to Limonene Dioxide Using Ti-SBA-16 as the Catalyst. One of the most studied heterogeneous catalysts for the epoxidation reaction is low-coordination titanium supported on silica. Different impregnation techniques of the titanium source and support have been published to produce active Ti catalysts.^{26,28–33} Examples of the epoxidation of limonene by hydrogen peroxide using different

supported low-coordination titanium catalysts are reported in Table 1.

Table 1. Epoxidation of Limonene by H₂O₂

Ti catalyst	oxidizing agent	solvent	conversion (%)	limonene dioxide selectivity (%)
TS-1 ³⁰	H ₂ O ₂	CH ₃ OH	24	0
Ti-MCM-41 ³⁴	H ₂ O ₂	CH ₃ CN	43	14
Ti-SBA-15 ³⁰	H ₂ O ₂	CH ₃ OH	46	0

Table 1 shows that Ti-based catalysts lead to low yield of limonene dioxide. Hydrogen peroxide is an ecofriendly oxidizing agent. A review of different epoxidation methods with its use has been published for a wide variety of catalysts (organometallic complexes or supported metals).³⁵ Even though H₂O₂ is a green oxidizing agent, other considerations must be taken in to account. During the epoxidation reaction, the oxidation of limonene also occurs by its reaction with the radicals formed by the decomposition of hydrogen peroxide. The secondary products from the oxidation of limonene are carvone, carveol, and perillyl alcohol. H₂O₂, or TBHP, is often sold as aqueous solutions. Epoxides are very reactive molecules, which can react with the water molecules of the reaction mixture to produce diols. The presence of acid also catalyzes diol formation.³⁶ The amount of diols formed will depend on the reaction conditions. Hydrogen peroxide or other hydroperoxides in water have led to the formation of diols by the reaction of water molecules with the already produced epoxides, when the reaction is carried out at moderate temperature.^{33,34,37,38} The yield of limonene dioxide is very low meaning that the titanium catalysts are not active enough to interact with the second unsaturation of limonene at position 8,9.^{33,37–39} When TBHP is used as the oxidizing agent, the diol formation is greatly reduced in favor of the epoxides, especially in anhydrous conditions.^{40,41} For a full coverage of the literature pertaining to Ti-based catalysts, the reader may consult ref 26.

Charbonneau and Kaliaguine have recently studied coordinatively unsaturated Ti on SBA-16 as catalyst for the epoxidation of limonene by TBHP, and some improvements have been reported.²⁶ It was determined that the 3D pore structure of the SBA-16 compared to the 2D pore structure of the SBA-15 allows faster diffusion of reactants and products to and from active sites, leading to higher 1,2-limonene oxide yield. On the other hand, in this previous report, no limonene dioxide was detected in the reaction products which suggests that the catalyst activity is not optimal.²⁶ *tert*-Butyl hydroperoxide (TBHP) in decane was the oxidizing agent. One limitation in these reaction conditions is the molar ratio of TBHP/olefin. It is now known that increasing this molar ratio above two favors the reaction of auto-decomposition of TBHP which forms radicals in the reaction mixture.^{15,26} These radicals

decrease the selectivity for the epoxides by the oxidation reaction.⁴² To avoid this problem, attempts were made to directly epoxidize 1,2-limonene oxide to determine if Ti-SBA-16 could also allow producing limonene dioxide. The results are summarized Table 2.

After 24 h of reaction, the epoxidation of 1,2-limonene oxide using Ti-SBA-16 catalyst resulted in a conversion of 62% yielding only 13% of limonene dioxide. It seems that Ti-SBA-16 using TBHP as the oxidizing agent was not active enough to achieve the second epoxidation on position 8,9. Given the importance of limonene dioxide to the biopolymers development, other alternatives have been considered to obtain high yield.

Conventional Biphasic Reaction and Reaction in Excess Acetone. Hashimoto and Kanda have developed a catalyst-free process for the epoxidation of monoalkenes. The reaction is carried out in semibatch biphasic conditions by using in situ formation of dimethyl dioxirane as the oxidizing agent in the presence of sodium bicarbonate as the buffer.²⁷ The DMDO was produced in the aqueous phase by the nucleophilic attack of Oxone on acetone dissolved in this phase. The first step consists of the nucleophilic attack of the peroxymonosulfate on the carbon bearing the carbonyl functional group of acetone. Following this step, an intramolecular rearrangement occurs leading to the formation an oxygen–oxygen bond which results in the formation of the dimethyl dioxirane and HSO₄[−]. After its formation, DMDO migrates by phase transfer from the aqueous phase to the organic phase where the epoxidation reaction of limonene takes place as represented in Scheme 1.

Scheme 1. Epoxidation of Limonene by DMDO

The epoxidation of mono-olefins under the biphasic conditions developed by Hashimoto and Kanda has the advantages that no catalyst is required and that the unreacted olefin and the reaction products are easily separated by simple decantation.²⁷

Table 2. Epoxidation of Limonene over Ti-SBA-16

substrate	catalyst	conversion ^a (%)	1,2-limonene oxide yield ^a (%)	limonene dioxide yield ^a (%)
limonene ^{b,c}	Ti-SBA-16	80	64	0
1,2-limonene oxide ^d	Ti-SBA-16	62		13

^aConversion and yields were determined by GC-FID after purification (identification of byproducts, see ref 26). ^bA 300 mg portion of Ti-SBA-16 (Ti/Si = 7.9%), 10 mL of acetonitrile, 6.2 mmol of limonene, and 11.2 mmol of TBHP in decane solution at 75 °C for 24 h. ^cPreviously published results.²⁶ ^dA 300 mg portion of Ti-SBA-16 (Ti/Si = 7.9%), 10 mL of acetonitrile, 6.2 mmol of 1,2-limonene oxide, and 11.2 mmol of TBHP in decane solution at 75 °C for 24 h.

In their work, these authors studied the solubility of acetone in the aqueous phase when ethyl acetate, dichloromethane, and toluene were used as the organic phase. Their results have shown that, when toluene was used, 70% of acetone was present in the aqueous phase. With ethyl acetate this relative fraction was 62%, whereas 32% acetone was dissolved in the aqueous phase when dichloromethane was the organic solvent. For the epoxidation of indene, the acetone concentration was higher in toluene, but the obtained yield of the epoxide was lower compared to dichloromethane, in which the highest yield was obtained.²⁷ Hashimoto and Kanda suggested that the affinity of DMDO is less favorable with toluene even if the concentration of acetone in the aqueous phase is higher compared to dichloromethane. The two important criteria that should be considered for this usual biphasic epoxidation are therefore both the solubility of acetone in the aqueous phase and that DMDO be in the organic phase. The DMDO affinity for the organic solvent should be related to its polarity. Toluene is less polar with a relative polarity of 0.099 as compared to dichloromethane which has a relative polarity of 0.309. Due to the environmental issues of dichloromethane, Hashimoto and Kanda have found a greener alternative by using ethyl acetate as the solvent leading to the highest yield of epoxide. Ethyl acetate has a relative polarity of 0.228. In the present work, this procedure using ethyl acetate for the biphasic epoxidation of limonene to limonene dioxide was applied, and a comparison was made with two other solvents, isopropyl acetate and MTBE. The results are reported in Table 3.

Table 3. Comparison of Solvents for the Conventional Biphasic Epoxidation^a of Limonene

solvent	relative polarity	conversion ^b (%)	yield 1,2 limonene oxide ^b (%)	yield limonene dioxide ^b (%)
ethyl acetate	0.228	95	34	33
isopropyl acetate	0.214	74	42	31
MTBE	0.124	73	38	26

^aAn 8.5 mmol portion of limonene, 40 mL of solvent, 40 mL of water, 3.55 g of sodium bicarbonate, 4.90 g of acetone, at room temperature; the Oxone solution, 19 mmol in 36 mL of water, was added at a flowrate of 1 mL min⁻¹ with a reaction time of 2 h. ^bConversion and yields were determined by GC-FID after purification.

Like in Hashimoto and Kanda's work, ethyl acetate was found to be the best solvent for limonene epoxidation with a conversion of 95%, and 33% of limonene dioxide yield. When the reaction was carried out in isopropyl acetate and MTBE, the conversion dropped to 74% and 73%, respectively. These two solvents have a lower polarity than ethyl acetate. On the basis of the relative polarity, it is presumed that the solvent with a low polarity has less affinity with DMDO leading to lower epoxide yield. These results are similar to those of Hashimoto and Kanda, obtained using toluene as the solvent in the epoxidation of indene. The epoxidation of limonene under biphasic conditions has shown better limonene dioxide yield compared to the same reaction using Ti-SBA-16 as the catalyst. However, this biphasic system is rather complex and would create problems when trying to perform the epoxidation reaction of limonene in a continuous flow process.

The epoxidation reaction can also be performed using pure acetone as both the DMDO source and the solvent.¹⁶ Acetone

is highly soluble in water; it is therefore expected that the concentration of acetone in the aqueous phase will be at its maximum equilibrium value. Acetone possesses a relative polarity index higher than that of ethyl acetate with a value of 0.355. By the substitution of ethyl acetate with acetone, the problems of solubility of acetone in water and DMDO affinity with the solvent are both solved.

Optimization of Reaction Conditions. The time evolution of limonene epoxidation medium composition was first monitored to establish the optimum reaction time in the specified conditions. The results of this test are shown in Figure 1.

Figure 1. Time evolution of the epoxidation of limonene to limonene dioxide in semi-batch reactor in excess of acetone.

The required time to completely epoxidize limonene to limonene dioxide at room temperature using in situ generated DMDO as the oxidizing agent with a flowrate of aqueous Oxone of 1 mL min⁻¹ is 90 min, which is reached 40 min after the complete addition of the 0.52 M Oxone solution. No 8,9-limonene oxide isomer was detected in the reaction mixture which is surprising. Asouti and Hadjarapoglou performed the epoxidation of limonene using DMDO as the oxidizing agent at low temperature in dichloromethane. They also found that only the 1,2-limonene oxide and limonene dioxide isomers were present.⁴³ The 8,9-limonene oxide isomer was not detected in their reaction mixture, similar to our results. It is proposed that the epoxidation of limonene to limonene dioxide occurs in two successive reactions. On the basis of the results from Figure 1, a reaction mechanism is proposed and shown in Scheme 2.

Scheme 2. Mechanism of Epoxidation of Limonene to Limonene Dioxide by DMDO

Table 4. Effect of the Total Amount of Oxone Fed to the Reactor at Constant Flowrate^a

Oxone/limonene ratio	pH of Oxone solution	conversion ^b (%)	1,2-limonene oxide yield ^b (%)	limonene dioxide yield ^b (%)	Oxone conversion to epoxide (%)
0.65	1.78	41	16	22	92.6
1.30	1.55	65	22	38	75
2.00	1.43	98	23	75	86
2.60	1.30	100	0	100	77

^aA 10 mmol portion of limonene, 30 mL of acetone, 4 g of sodium bicarbonate, and various amounts of Oxone dissolve in 50 mL of water was added to the flask at constant flowrate of 1 mL min⁻¹, room temperature, total reaction time 2h. ^bLimonene conversion and yields were determined by GC-FID after purification.

The epoxidation of olefins using DMDO as the oxidizing agent is considered to be a concerted electrophilic oxygen transfer.⁴⁴

The stoichiometric ratio between Oxone and limonene was also studied. Reducing the concentration of Oxone fed to the reaction vessel should change the kinetics in favor of 1,2-limonene oxide by decreasing the secondary epoxidation. Different tests were performed by varying the molar ratio of Oxone/limonene. This study should also allow determining if an excess of Oxone is required to completely epoxidize the two double bonds of limonene. The obtained results are reported in Table 4.

One interesting observation is that the pH of the solution only slightly decreases by increasing the amount of Oxone. This indicates that the pH of the reaction medium with the buffer will remain relatively stable. Up to the stoichiometric ratio of Oxone/limonene of 2.00, a mixture, of both 1,2-limonene oxide and limonene dioxide, is produced. It is therefore difficult to limit the reaction of DMDO to 1,2-limonene oxide by only controlling the amount of Oxone fed. The secondary epoxidation is relatively fast. For contents of 20 mmol of Oxone, which corresponds to the stoichiometric Oxone/limonene of 2, the conversion of limonene reached 98% yielding 23% of 1,2-limonene oxide which means that the reaction is not complete. For lower Oxone amounts, the partial conversion of Oxone is between 75% and 92.6%. For the experiment conducted at the over-stoichiometric ratio of 2.60 Oxone/limonene, the obtained partial conversion in epoxidation is 77%. Oxone is an inorganic peracid and, like hydrogen peroxide or *tert*-butyl hydroperoxide, is susceptible to auto-decomposition. The reaction is carried out at slightly basic pH (8.04) at which the HSO₅⁻ and SO₅²⁻ species are in equilibrium.⁴⁵ HSO₅⁻ reacts with SO₅²⁻ which leads to the formation of HSO₄⁻, SO₄²⁻, and a molecule of O₂.⁴⁵

Several publications have mentioned that the Oxone solution should be added dropwise for a period of at least 1 h or more depending on the substrate, sometimes reaching up to 10 h.^{27,46–48} For industrial applications, it would be important to increase the flowrate to reduce reaction time and allow scaling up of the process. The effects of flowrate of the aqueous solution of Oxone on conversion and yields were studied, and the results are represented in Figure 2.

The maximum flowrate of the aqueous Oxone solution with a molar ratio of 2.60 for a complete conversion to the diepoxide at the reported conditions is 4 mL min⁻¹. At higher flowrate, the limonene conversion and diepoxide yield started decreasing. The decomposition of Oxone by reaction with DMDO occurs extremely fast which is why it is important to maintain the concentration of Oxone as low as possible in the reaction medium.

Figure 2. Effect of flowrate on the epoxidation of limonene to limonene dioxide.

This procedure using dimethyl dioxirane has allowed reaching the same performance as that reported for the methyl trioxorhenium (MTO) catalyst used with hydrogen peroxide as the oxidizing agent in the presence of *tert*-butylpyridine in homogeneous conditions at room temperature.¹⁷ Compared with these data, DMDO and MTO processes both allowed almost complete conversion of limonene and limonene dioxide (higher than 90%). The epoxidation of limonene using DMDO required, however, only 2 h compared to 24 h with the MTO catalyst. Furthermore, the epoxidation of limonene using methyltrioxorhenium homogeneous catalyst demands catalyst recovery from the reaction medium.

CONCLUSION

This work has shown that DMDO produced in situ by the reaction of Oxone with acetone is an exceptional green oxidizing agent for the epoxidation of limonene especially under excess of acetone conditions. It would offer numerous significant advantages over the oxidizing agents currently used in industrial epoxidation processes. First, it is quite stable compared to hydrogen peroxide and other hydroperoxides and does not require addition of any stabilizing agent. Second, compared to hydrogen peroxide or hydroperoxide, DMDO does not produce radical species in the reaction medium which would lead to the formation of undesired oxidation products such as carvone, carveol, and perillyl alcohol. The epoxidation of limonene to limonene dioxide has been achieved at room temperature in green conditions with a yield of 100% by this oxidizing agent. The time evolution of the reaction was monitored, and it was shown that the reaction is a two-successive-step process reaction, with first the production of 1,2-limonene oxide and the production of limonene dioxide by a secondary oxidation without passing by the formation of the 8,9-limonene oxide isomer. An important aspect of the

epoxidation of limonene by in situ generated DMDO is the need for strict control of the reaction conditions such as the excess of peroxymonosulfate, the pH, and the flowrate of the aqueous solution of Oxone. The pH of the reaction should be maintained in a narrow range between 8.00 and 9.00 to avoid both Oxone decomposition and acidic hydrolysis of the epoxide. Many advantages arise from this method of epoxidation of limonene compared to metal oxide or organometallic catalysis of limonene to limonene dioxide, which require additional separation processes. The reaction is carried out at room temperature, for a relatively short time of 45 min in green conditions. The reactants are very inexpensive and easily separated by liquid–liquid extraction and solvent evaporation. Epoxidation of olefins using this method should be considered at industrial scale as a green catalyst-free substitute to traditional epoxidation processes using hydroperoxides or peracids as the oxidizing agent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b04782.

N₂ sorption isotherms, physical properties of the catalysts, DR-UV results, and ¹H NMR results (PDF)

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Notes

The authors declare no competing financial interest.

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