

Article

Catalytic Epoxidation of a Technical Mixture of Methyl Oleate and Methyl Linoleate in Ionic Liquids Using $\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}$ (QOH = 8-quinilinol) as Catalyst and NaHCO_3 as co-Catalyst

Shuang-Fei Cai, Li-Sheng Wang * and Chuan-Lei Fan

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China

* Author to whom correspondence should be addressed; E-mail: lishengwang@btamail.net.cn;
Fax: + 86-10-68911040

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Abstract: The oxo-diperoxo molybdenum(VI) complex $\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}$ (QOH = 8-quinilinol) was prepared and characterized by elemental analysis, IR and UV-Vis spectra. The ionic liquids (ILs) $[\text{bmim}][\text{BF}_4]$, $[\text{hydemim}][\text{BF}_4]$, and $[\text{bmim}][\text{PF}_6]$ were characterized by $^1\text{H-NMR}$ and UV-Vis spectra. The epoxidation of a technical mixture of methyl oleate and methyl linoleate with H_2O_2 , in $[\text{bmim}][\text{BF}_4]$, $[\text{hydemim}][\text{BF}_4]$ and $[\text{bmim}][\text{PF}_6]$, catalyzed by $\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}$ (QOH = 8-quinilinol) and with NaHCO_3 as co-catalyst has been studied for the first time. It was found that high conversions of methyl oleate and methyl linoleate to their respective oxidation products, as well as the total selectivity of their oxidation products to oxirane in $[\text{hydemim}][\text{BF}_4]$ were obtained. Also, the IL phases containing the Mo(VI) catalyst can be readily recycled by washing with diethyl ether and drying, and the Mo(VI) catalyst can be reused at least five times.

Keywords: ionic liquids; epoxidation of vegetable oil; molybdenum; hydrogen peroxide

1. Introduction

In recent years, much emphasis has been placed on the utilization of renewable resources as an alternative to petrochemical-based feedstocks. In this context, vegetable oils are undoubtedly promising candidates. Not only they are widespread, inexpensive, eco-compatible, renewable and non-

noxious, but, above all, several multi-functionalised molecules can be obtained by their chemical modification. For example, the unsaturated olefinic bonds in vegetable oils can be epoxidized to give epoxy oils, which have been already used widely as PVC-plasticizers and stabilizers, as reactive diluents for paints, as additives in lubricants, etc. [1]

Traditionally, the only commercial source of epoxidized oils is based on the Prileshajev peracid process [2]. This procedure, however, has several drawbacks that require improvement: (i) selectivity to epoxidized products is relatively low due to acid-catalyzed oxirane ring opening side reactions; (ii) the separation of acidic by-products, whose presence may be detrimental for further applications, is not easy; (iii) the handling of highly-concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems. For all these reasons there is considerable interest in finding an alternative epoxidation route for these substrates [3-6].

To this end, efficient metal-catalyzed epoxidations of vegetable oils have been investigated, especially using high-valence catalysts based on titanium [7], tungsten [8] and rhenium [9]. The use in oxidation of molybdenum(VI) catalysts [10] containing the stable oxo-peroxo core [11] is well-established, and with them a variety of organic substrates [12-14], including alkenes, alcohols, amides and nitro compounds, can be catalytically oxidized under homogeneous as well as heterogeneous conditions [15]. Recently, several interesting oxo-peroxo molybdenum(VI) complexes such as $[\text{MoO}(\text{O}_2)_2\text{L}_2]$ ($\text{L} = 8\text{-quinilinol}$) [16], have proven to be excellent room temperature (rt) catalysts for the epoxidation using the $\text{H}_2\text{O}_2/\text{NaHCO}_3$ system of many alkenes such as styrene, 1-octene, etc. in CH_3CN solutions. Not only is this catalyst-oxidant system economical and the reaction conditions mild, but hydrogen peroxide is a readily-available and green oxidant [17], so, it would be undoubtedly noteworthy if this catalytic system could also be used in the epoxidation of vegetable oils, an area in which to our knowledge no work has been conducted.

Furthermore, increased awareness in recent years of the detrimental environmental effects of organic solvents has resulted in rapid growth of research on alternative reaction media, and more attention has been given to the reusability of solvents and catalysts for the development of cost-effective protocols. Ionic liquids (ILs) are a promising alternative to classical solvents because ILs, especially those based on 1,3-dialkylimidazolium cations, such as 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}][\text{BF}_4]$) and its hexafluorophosphate analog ($[\text{bmim}][\text{PF}_6]$), are air and moisture stable, and possess negligible vapor pressure, low viscosity, high thermal and chemical stability and a wide electrochemical window [18-21]. They can also be recycled in many cases. Various classical reactions such as Friedel-Crafts [22], Diels-Alder [23], alkylation [24], hydrogenation [25], Heck [26], hydroformylation [27] and oligomerisation [28] using ILs as solvents have been reported. They have also emerged as ideal immobilization media for catalysts, which combine the advantages of ILs and heterogeneous supports, such as increased reaction rates, enhanced catalytic efficiency, simplified product separation together with improved catalyst recyclability, therefore, the use of ILs as solvents in organic reactions has become a particular focus of research [29].

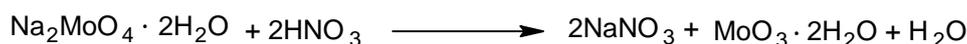
To our knowledge, however, there is no literature describing the catalytic epoxidation of vegetable oils using ILs as reaction media/immobilization media for transition metal complex catalysts. In this paper, we report the epoxidation of a technical mixture of methyl oleate and methyl linoleate with H_2O_2 , catalyzed by $[\text{MoO}(\text{O}_2)_2\cdot 2\text{QOH}]$ ($\text{QOH} = 8\text{-quinilinol}$) and NaHCO_3 as a co-catalyst. For comparison, the ILs $[\text{bmim}][\text{BF}_4]$, $[\text{hydemim}][\text{BF}_4]$, and $[\text{bmim}][\text{PF}_6]$ were used as solvents, respectively.

2. Results and Discussion

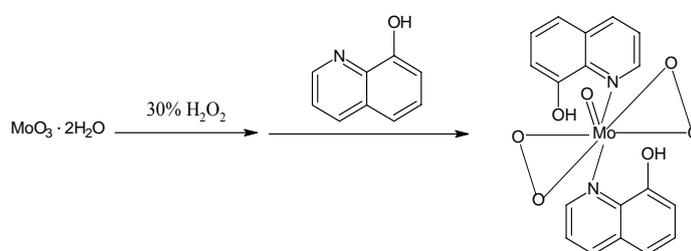
2.1. Catalyst preparation

Briefly, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, prepared according to a published procedure [30] (Scheme 1) was dissolved in 30% H_2O_2 and mixed with an acetic acid solution of 8-quinolinol to give the $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) catalyst (Scheme 2), which was characterized by elemental analysis, IR and UV spectroscopy.

Scheme 1. The preparation of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$.



Scheme 2. The preparation of di-8-quinolinolate $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol).

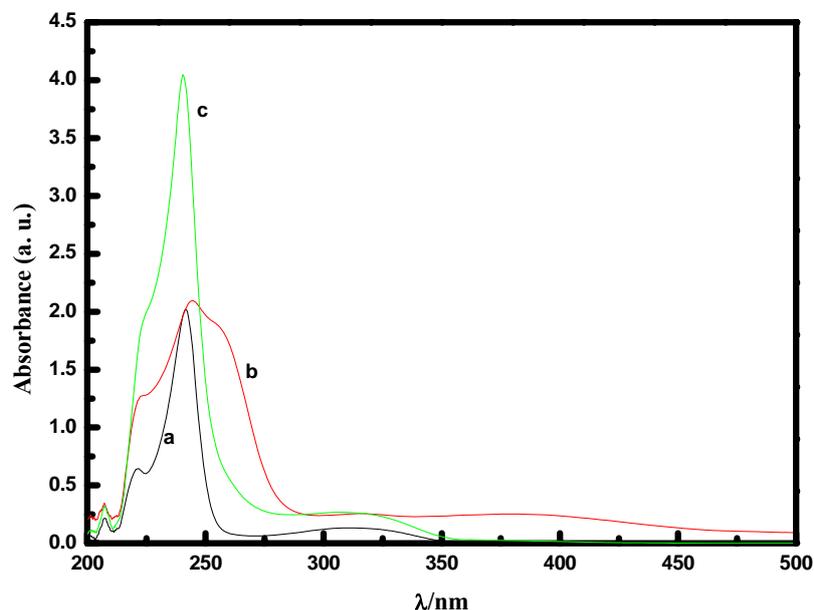


2.2. Catalytic performance

2.2.1. UV-Vis spectral study of $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) alone

The UV-Vis spectra of 8-quinilinol in CH_2Cl_2 displayed two shoulders at 242 and 311 nm (Figure 1, curve a), while the oxo-diperoxo molybdenum(VI) complex $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) showed two strong absorption bands at 244 and 380 nm (Figure 1, curve b), and a small absorption band at 315 nm. Further, it showed a very broad low intensity absorption ranging from 300 to 500 nm. The 380 nm absorption band could be assigned to the ligand-to-metal charge transfer [16]. $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) was found to be slightly soluble in the ILs used, but almost immiscible with substrate at rt. When hydrogen peroxide is added, interestingly, it dissolves immediately and gives an orange solution. To find out more about the mechanism of reaction and confirm the nature of the reactive intermediate, the UV-Vis spectrum of the reaction mixture resulting from the addition of substrate to a solution of catalyst and hydrogen peroxide was studied. Two strong absorption bands at 240 and 308 nm (Figure 1, curve c) were observed. Similarly, a small absorption band was found at 362 nm. Additionally, compared with $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol), the absorbance of the peak in the 300 to 500 nm region was decreased considerably. It is believed that the new small peak appearing at 362 nm (lit. [31] 364 nm), corresponds to the active oxo-dioxo molybdenum species which has been proposed as the catalyst precursor [32], and is generated from the oxo-diperoxo molybdenum species. Each double bond can be epoxidized in the presence of monooxidiperoxo species, and the intermediate oxo-dioxo species formed regenerates the monooxidiperoxo centers.

Figure 1. The UV-Vis spectra of 8-quinilinol (curve a), $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) (curve b), $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) + H_2O_2 + substrate (curve c).



2.2.2. Effect of NaHCO_3 as a co-catalyst

Table 1 shows the results of epoxidation of methyl oleate and methyl linoleate. In all the cases, the conversion of the former to its oxidation products was higher than that of the latter, a result of the difference in the number of double bonds in these two unsaturated esters. Without any added solvent the total conversion of methyl oleate and methyl linoleate to their oxidation products was low (41%, Entry 1), and with the use of only NaHCO_3 without catalyst, no conversion of methyl linoleate or methyl linoleate was observed (Entry 2). Further, the catalytic efficiency when H_2O_2 is used as a sole oxidant is poor (Entries 6 and 7). When NaHCO_3 is used together with H_2O_2 , however, the efficiency of the system is greatly increased. The key aspect of such a reaction is that H_2O_2 and NaHCO_3 react in an equilibrium process to produce peroxymonocarbonate HCO_4^- which is a more reactive nucleophile than H_2O_2 and speeds up the epoxidation reaction (Scheme 3) [33,34].

Scheme 3. The production of HCO_4^- .



Table 1. Epoxidation of methyl oleate and methyl linoleate with hydrogen peroxide catalyzed by $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinolinol) in ILs.^a

Entry	Solvent	Conversion (%)			Selectivity (%) ^e	TON(TOF) ^f
		methyl oleate ^b	methyl linoleate ^c	total ^d		
1	no solvent	55	31	41	90	3690(1845)
2	no catalyst	0	0	0	0	0
3	[bmim]BF ₄	92	78	84	93	7812(3906)
4	[bmim]PF ₆	75	44	57	94	5358(2679)
5	[Hydemim]BF ₄	96	89	92	95	8740(4370)
6	[bmim]PF ₆ ^g	60	32	44	92	4048(2024)
7	[Hydemim]BF ₄ ^g	84	54	67	94	6298(3149)
8	CH ₃ CN	85	63	72	92	6624(3312)
9	30% CH ₃ CN + 70% [hydemim]BF ₄	94	84	88	95	8360(4180)
10	C ₂ H ₅ OH	81	45	60	93	5580(2790)
11	30 % C ₂ H ₅ OH + 70% [hydemim]BF ₄	90	74	81	95	7695(3848)

^a Reaction conditions: $[\text{M}_{\text{c=c}}:\text{H}_2\text{O}_2:\text{catalyst}:\text{NaHCO}_3]$, 1:4:0.0001:0.3; $\text{M}_{\text{c=c}}$ was the total amount (mmol) of c=c and calculated by $\text{M}_{\text{c=c}} = \text{M}_{\text{methyl oleate}} + 2 \text{M}_{\text{methyl linoleate}}$; $\text{V}_{\text{solvent}}$, 2 mL; T, 303 K; t, 2 h. ^b The relative percentage conversion of methyl oleate to oxidation products, was calculated by expression (3) (see Appendix). ^c The relative percentage conversion of methyl linoleate to oxidation products, was calculated by expression (4) (see Appendix). ^d Total conversion of double bonds of methyl oleate and methyl linoleate to the oxidation products, was calculated by expression (10) (see Appendix). ^e Total Selectivity of oxidation products to the epoxidized methyl oleate and methyl linoleate, was calculated by expression (16) (see Appendix). ^f TON was defined as the ratio of the number of mol of product obtained to the number of mol of catalyst used. TOF was calculated by the expression of $\text{TON} \cdot \text{time}$ (h^{-1}). ^g This is the control experiment, excluding the catalyst, but not NaHCO_3 .

2.2.3. Effect of ILs

Both [bmim][BF₄]- and [hydemim][BF₄]-containing systems showed higher activity (84% in Entry 3 and 92% in Entry 5, respectively) than the [bmim][PF₆]-containing system (57 %, Entry 4), which suggested the hydrophobic-hydrophilic properties of the ILs may play a key role in the epoxidation processes of methyl oleate and methyl linoleate. As a comparison with ILs, when using instead organic solvents, including CH₃CN and C₂H₅OH, relatively lower total conversions of methyl oleate and methyl linoleate were obtained (72%, Entry 8 and 60%, Entry 10, respectively). In order to illustrate the effect of ILs more clearly, a mixed solvent of [hydemim][BF₄] and CH₃CN or C₂H₅OH was used. When 1.4 mL of [hydemim][BF₄] was added to 0.6 mL of CH₃CN or C₂H₅OH to form a homogeneous solution, about 88 and 81% of methyl oleate and methyl linoleate was converted, respectively (Entries 9 and 11), which suggested the catalytic activity was enhanced by the use of [hydemim][BF₄].

2.3. Recycling of the catalyst

Recycling of the $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ in the epoxidation of methyl oleate and methyl linoleate was examined with $[\text{hydremim}][\text{BF}_4]$ as solvent (Table 2). As shown, the Mo(VI) catalyst immobilized in $[\text{hydremim}][\text{BF}_4]$ can be reused at least up to five cycles. The slightly decrease in conversion observed might result from some leaching of $[\text{hydremim}][\text{BF}_4]$ into the diethyl ether during the washing.

Table 2. The recycling experiment for the epoxidation of methyl oleate using H_2O_2 as oxidant catalyzed by $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ (QOH = 8-quinilinol) and NaHCO_3 as co-catalyst in $[\text{hydremim}][\text{BF}_4]^a$ (^{a-c} same as in Table 1).

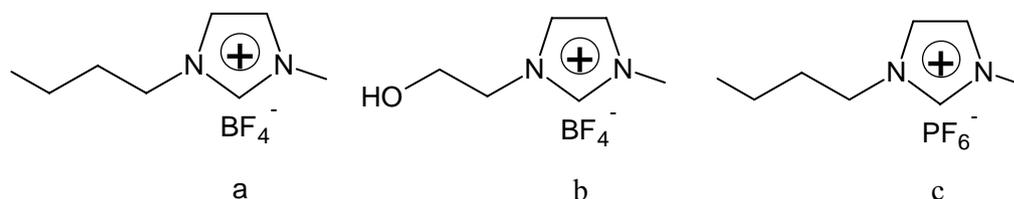
Run		1	2	3	4	5
Conversion (%)	methyl oleate ^b	96	92	89	89	87
	methyl linoleate ^c	89	87	86	82	82
	total ^d	92	89	87	85	84
Selectivity (%) ^e		95	95	95	95	95

3. Experimental

3.1. Materials

The ILs $[\text{bmim}][\text{BF}_4]$, $[\text{hydremim}][\text{BF}_4]$, and $[\text{bmim}][\text{PF}_6]$ (their structures are shown in Figure 2) were purchased from the Shanghai Chengjie Chemical Co., Ltd, and the mass fraction purities were all above 99%. The mass fraction of water in these ILs was less than 1×10^3 ppm. Fatty acid methyl esters (C. P.) was purchased from the Beijing Jinlong Chemical Co., Ltd., and contained methyl oleate (28.26%), methyl linoleate (19.43%), methyl palmitate (32.69%), methyl octadecanoate (7.28%), methyl dodecanoate (7.05%), methyl tetradecanoate (4.29%), *iso*-propyl myristate (0.53%) and decanoic acid 2-ethylhexyl ester (0.47%) according to GC-MS analysis. Standard samples of methyl oleate (100%, GC-MS) and methyl linoleate (99%) were purchased from Alfa Aesar and Sigma, respectively. Hydrogen peroxide (G. R., 30%) and the other reagents (A. R., >95%) were all provided by the Beijing Chemical Reagents Company and used without further purification.

Figure 2. The structures of the ILs $[\text{bmim}][\text{BF}_4]$ (a), $[\text{hydremim}][\text{BF}_4]$ (b) and $[\text{bmim}][\text{PF}_6]$ (c) .



3.2. Instruments

Chemical analyses for C, H, and N were performed by elemental microanalysis (Elementar Vario EL analyzer). IR spectra were measured on a Nicolet MAGNA 750 instrument fitted with a Nic-plan IR microscope. The electronic spectra were recorded on a 756 PC UV/VIS spectrometer. ^1H NMR spectra were recorded on a Varian Unity Inova-400 spectrometer. The reactions mixtures and their

respective fatty acid methyl ester contents were analyzed by GC-MS [DSQ (Thermo Fisher)] with a capillary column (DB-5, 30 m × 0.25 μm × 0.25 mm), equipped with an FID detector. Oven program: 100 °C for 2 min, 5 °C/min to 300 °C and held for 10 min. Both the injector port temperature and the detector transfer line temperature were 250 °C, and helium was used as carrier gas, 1 mL/min. Spilt sampling, split ratio was 50:1. Sample volume was 0.1 μL. MS: electron ionization, 70 eV. The reaction products were analyzed on a GC2010 with a capillary column (AB-1, 30 m × 0.25 μm × 0.25 mm), equipped with an automatic sampler (AOC-20i) and an FID detector. Oven program: 100 °C for 2 min, 5 °C/min to 300 °C and held for 10 min. Both the injector port temperature and the detector transfer line temperature were 250 °C, and helium was used as carrier gas, 2 mL/min. Spilt sampling, split ratio was 50:1. Sample volume was 2 μL.

3.3. Preparation

3.3.1. Preparation and characterization of MoO₃·2H₂O

MoO₃·2H₂O was prepared according to the published procedure [30] (Scheme 1). Na₂MoO₄·2H₂O (50 g) was dissolved in H₂O (100 mL) and added to 5 N HNO₃ (300 mL) at rt. The precipitate was filtered, washed with 4 N HNO₃ (100 mL) and H₂O (100 mL), and dried at rt. Yield 25 g, yellow powder (68 %). IR (cm⁻¹): 3,520, 3,406, 3,223, 1,623, 968, 905, 744; UV-Vis λ_{max} (nm): 219.40 (ε = 5,836 M⁻¹ cm⁻¹).

3.3.2. Preparation and characterization of [MoO(O₂)₂·2QOH] (QOH = 8-quinilinol)

[MoO(O₂)₂·2QOH] (QOH = 8-quinilinol) was prepared based on the published procedure (Scheme 2) [16]. An aqueous solution (25 mL) of MoO₃·2H₂O (1.25 g; 6.0 mmol) was dissolved in 30 % (w/v) H₂O₂ (40 mL; 13.9 mmol) by stirring at rt to give a pale yellow solution. Addition of 8-quinolinol (2.02 g; 13.9 mmol) dissolved in 4 M acetic acid (10 mL) to the above solution with stirring (about 10 min) gave a yellow solid. It was filtered off, washed with water, 95% ethanol and finally with diethyl ether and dried under vacuum. Yield: 2.68 g (83%). Found, C, 46.21; H, 2.99; N, 6.21. Calc. for C₁₈H₁₄N₂O₇Mo: C, 46.35; H, 3.00 and N, 6.01%. IR (cm⁻¹): 1,620 (w), 1,594 (w), 1,577 (w), 1,558 (m), 1,497 (s), 1,467 [s; ν(C–N)], 1,419 (w), 1,406 (w), 1,375 (s), 1,321 (s), 1,306 (w), 1,271 (m), 1,225 (w), 1,210 (w), 1,175 (w), 1,143 (w), 1,107 [s; ν(C–O)], 1,062 (w), 1,029 (w), 956 [s; ν(Mo=O)], 914 (w), 852 [s; ν(O–O)], 820 (s), 749 (s); UV-Vis λ_{max} (nm): 244, 315 (sh), 380 (ε = 4,806 M⁻¹ cm⁻¹).

3.3.3. Characterization of the ILs [bmim][BF₄], [hydemim][BF₄], and [bmim][PF₆]

¹H-NMR: 0.877–0.914 (3H), 1.234–1.290 (2H), 1.732–1.805 (2H), 3.846 (3H), 4.139–4.175 (2H), 7.654 (1H) and 7.720–7.724 (1H) for [bmim][BF₄] (CDCl₃); δ = 3.98 (3H), 3.99–4.02 (2H), 4.37–4.40 (2H), 4.79 (1H), 7.52 (1H), 7.57 (1H) and 8.77 (1H) for [hydemim][BF₄] (D₂O); 0.927–0.964 (3H), 1.357–1.413 (2H), 1.906–1.944 (2H), 4.038 (3H), 4.327–4.363 (2H), 7.673–7.727 (2H) and 8.929 (1H) for [bmim][PF₆] (CD₃COCD₃). UV-Vis (in C₂H₅OH): λ_{max} (nm) = 211.60 (ε = 4,403 M⁻¹ cm⁻¹) for [bmim][BF₄]; λ_{max} (nm) = 210.95 (ε = 4,109 M⁻¹ cm⁻¹) for [hydemim][BF₄]; λ_{max} (nm) = 211.10 (ε = 3,957 M⁻¹ cm⁻¹) for [bmim][PF₆].

3.4. Epoxidation

Catalyst (0.265 μmol) and NaHCO_3 (7.950 mmol) were placed in a 50 mL round bottomed flask equipped with a magnetic stir bar. The catalyst was dissolved in the IL (2 mL) by heating and then cooled to rt. To this substrate (ca. 11.66 g) was added and the reaction mixture stirred at 30 °C. To maintain a constant flow of peroxide during the entire period of reaction, 30 % H_2O_2 (106 mmol) was added dropwise periodically over 2 h, then the reaction mixture was cooled to rt and extracted with diethyl ether (3×20 mL). The diethyl ether layers were combined and concentrated under reduced pressure, and a sample was taken for GC analysis and measurement of oxirane oxygen (see Appendix). The IL phase including the catalyst was washed with diethyl ether, and dried prior to being recycled.

4. Conclusions

The oxo-diperoxo molybdenum(VI) complex $\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}$ (QOH = 8-quinilinol) was prepared, and characterized by its elemental analysis, IR and UV-Vis spectra. The ILs $[\text{bmim}][\text{BF}_4]$, $[\text{hydemim}][\text{BF}_4]$, and $[\text{bmim}][\text{PF}_6]$ were characterized by their $^1\text{H-NMR}$ and UV-Vis spectra. Furthermore, the epoxidation of a technical mixture of methyl oleate and methyl linoleate with H_2O_2 , catalyzed by $\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}$ (QOH = 8-quinilinol) and NaHCO_3 as a co-catalyst in the ILs $[\text{bmim}][\text{BF}_4]$, $[\text{hydemim}][\text{BF}_4]$ and $[\text{bmim}][\text{PF}_6]$ has been reported in this paper for the first time. High conversions of methyl oleate and methyl linoleate, as well as the total selectivity of their respective oxidation products in $[\text{hydemim}][\text{BF}_4]$ were obtained. The IL phase including the Mo(VI) catalyst can be readily recycled by washing with diethyl ether and drying, and the Mo(VI) catalyst can be reused at least five times.

Appendix: Analysis of products

Determination of the conversion of methyl oleate or methyl linoleate

The relative percentage conversion of methyl oleate or methyl linoleate to its oxidation products, C_1 or C_2 , can be calculated by the following expressions:

$$C_1 = \left(1 - \frac{m_1'}{m_1}\right) \times 100 \quad (1)$$

$$C_2 = \left(1 - \frac{m_2'}{m_2}\right) \times 100 \quad (2)$$

where m_1' and m_2' are the content of methyl oleate and methyl linoleate unconverted after the epoxidation reaction, respectively. By comparing the retention times of their standard samples with the reaction products, both the content of methyl oleate and methyl linoleate can be determined by GC, using the area normalization method. In addition, m_1 and m_2 are the initial content of methyl oleate and methyl linoleate in the substrate, respectively. They were known by GC-MS analysis ($m_1 = 28.26\%$ and $m_2 = 19.43\%$, respectively).

So:

$$C_1 = \left(1 - \frac{m_1'}{28.26\%}\right) \times 100 \quad (3)$$

$$C_2 = \left(1 - \frac{m_2'}{19.43\%}\right) \times 100 \quad (4)$$

Since the number of double bonds for each mole of methyl oleate is one, while for methyl linoleate it is two, the total conversion of all the double bonds of these two esters, C_t , can be calculated by the following expression:

$$C_t = \frac{M_1' + 2M_2'}{M_1 + 2M_2} \times 100 \quad (5)$$

where M_1' , M_2' are the amount of methyl oleate and methyl linoleate converted (mol), respectively. M_1 and M_2 are the initial amount of methyl oleate and methyl linoleate (mol), respectively. They can be calculated respectively by the following four expressions:

$$M_1' = \frac{m_{\text{sample}}(m_1 - m_1')}{296.50} \quad (6)$$

$$M_2' = \frac{m_{\text{sample}}(m_2 - m_2')}{294.50} \quad (7)$$

$$M_1 = \frac{m_{\text{sample}} \cdot m_1}{296.50} \quad (8)$$

$$M_2 = \frac{m_{\text{sample}} \cdot m_2}{294.50} \quad (9)$$

where m_{sample} is the mass of the sample measured (g).

So:

$$C_t = \left(1 - \frac{147.25m_1' + 296.50m_2'}{99.24}\right) \times 100 \quad (10)$$

Determination of the total selectivity of oxidation products to epoxidized methyl oleate and methyl linoleate

The total yield of the different epoxides can be known by measuring the epoxy value (E) of reaction product, according to the hydrochloric acid – acetone method [35]. E is defined as the content of oxirane oxygen in a sample measured (g/100 g sample):

$$E = \frac{m_{\text{oxigen}}}{m_{\text{sample}}} \times 100 \quad (11)$$

The total percentage yield to oxirane, i.e., the total selectivity of reaction product to oxirane (S_t), can be calculated by following expression:

$$S_t = \frac{E_e}{E_c} \times 100 \quad (12)$$

where E_e and E_c are the experimentally obtained oxirane oxygen and the maximum oxirane oxygen calculated, respectively. E_e can be obtained by the following expression:

$$E_e = \frac{[V - (V_1 - \frac{V_2}{G} \times m_{\text{sample}})]N \times 0.016}{m_{\text{sample}}} \times 100 \quad (13)$$

where V is the volume of sodium hydroxide standard solution consumed (mL) for measuring the oxirane oxygen of the sample; V_1 is the volume of sodium hydroxide standard solution consumed (mL)

in the blank test for determining the oxirane oxygen; V_2 is the volume of sodium hydroxide standard solution consumed (mL) for determining the acid value of the sample; G is the mass of sample for determining the acid value (g); N is the concentration of sodium hydroxide standard solution, mol/L; 0.016 is milligram equivalent of oxygen.

The acid value of the sample, X (mg/g sample), is defined as the mass of potassium hydroxide consumed in neutralizing 1 g of sample, and determined by the addition of potassium hydroxide-ethanol standard solution to the sample [36]:

$$X = \frac{C(V_2 - V_0) \times M_{\text{KOH}}}{G} \quad (14)$$

where C is the concentration of potassium hydroxide-ethanol standard solution (mol/L); V_2 is the volume of potassium hydroxide-ethanol standard solution consumed (mL) for determining the acid value of the sample; V_0 is the volume of potassium hydroxide-ethanol standard solution consumed (mL) in the blank test for determining the acid value of the sample; M_{KOH} is the molecular mass of potassium hydroxide, 56.11 g/mol.

Since the molecular weight of the oxygen in each mol of epoxidized methyl oleate is 16, while that in epoxidized methyl linoleate is 32, E_c can be calculated by the following expression:

$$E_c = \frac{M_1 \cdot C_1 \cdot 16 + M_2 \cdot C_2 \cdot 32}{m_{\text{sample}}} \times 100 \quad (15)$$

Therefore:

$$S_t = \frac{E_c}{0.0152C_1 + 0.0211C_2} \times 100 \quad (16)$$

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Sample Availability: Samples of the compounds MoO₃·2H₂O and [MoO(O₂)₂·2QOH] (QOH = 8-quinolinol) are available from the authors.

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