

Contents lists available at ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Epoxidation of soybean oil using a homogeneous catalytic system based on a molybdenum (VI) complex

Maritana Farias^{a,*}, Márcia Martinelli^b, Diana Pagliocchi Bottega^b

^a Curso de Química, Instituto Federal de Educação, Ciência e Tecnologia Sul-rio-grandense, Campus Pelotas, Praça Vinte de Setembro, 455, 96015-360 Pelotas, RS, Brazil ^b Departamento de Química Inorgânica, Universidade Federal do Rio Grande do Sul, Avenida Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil

ARTICLE INFO

Article history: Received 1 February 2010 Received in revised form 14 June 2010 Accepted 19 June 2010 Available online 25 June 2010

Keywords: Molybdenum (VI) acetylacetonate complex Epoxidation Homogeneous catalysis Soybean oil ¹H NMR

ABSTRACT

The ability of bis(acetyl-acetonato)dioxo-molybdenum (VI) [MoO₂(acac)₂] to catalyse the epoxidation of soybean oil in the presence of *tert*-butyl hydroperoxide as oxidizing agent has been investigated. The influence of reaction time and temperature in the course of the epoxidation reaction was evaluated by quantitative ¹H NMR. When epoxidation was carried out in refluxing toluene at 110 °C for 2 h, a 70.1% conversion of substrate was obtained, producing 54.1% epoxidation with a selectivity of 77.2%. The ¹H NMR spectroscopic method selected for the purpose of this work allowed a simple and rapid evaluation of the mono- and diepoxides obtained following the epoxidation of soybean oil.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The epoxidation of vegetable oils is commercially important since the epoxides produced from these renewable raw materials present numerous applications, including the formation of polyurethane foams (via oxirane ring opening to generate polyols) [1–3], synthetic detergents [4,5], coatings [6–9] and lubricants [10–13]. Within the concept of "Green Chemistry", the production of biodegradable lubricants from epoxidized vegetable oils is of particular interest considering the undesirable impact on the environment associated with the use of mineral oil-based lubricants.

The epoxidation processes most commonly employed in industry utilize peracids as oxidizing agents together with strong mineral acids as catalyst. Such methods, however, present a number of disadvantages in that they are not selective, cause corrosion of the equipment and generate considerable amounts of residue [14]. In contrast, the use of transition metal complexes as catalyst eliminates many of these problems and also provides a reaction that is very selective. Although various types of metallic catalysts are able to promote epoxidation reactions, complexes of Mo (VI) probably represent the best catalysts for olefin epoxidation and a vast literature is available in this specific area [15–19]. In epoxidations with homogeneous systems, rhenium catalysts in particular give excellent results [20–23]. Oxomolybdenum compounds are less effective catalysts for olefin epoxidations than organorhenium oxides [24,25]. However from an economic and environmental perspective, the use of simple, affordable and commercially available molybdenum compounds in such a capacity would offer significant advantages [26].

Alongside the peracids, various alternative oxidizing agents may be employed in epoxidation reactions. In this regard, hydrogen peroxide and organic peroxides, such as tert-butyl hydroperoxide (TBHP), have the capacity to epoxidize olefins in the presence of metallic catalysts. Indeed, the properties of Mo (VI) complex catalysts are closely associated with the capacity of the metal to react with peroxides to form peroxomolybdenum complexes [27,28]. In its highest oxidation state (d°), Mo (VI) is a Lewis acid and hence possesses a low redox potential and is thus labile to the substitution of ligands. Complexes of transition metals in high oxidation states facilitate the heterolysis of hydrogen peroxide and alkyl peroxides forming, with the latter, transition metal-alkyl hydroperoxide complexes (Scheme 1). Complexes formed with alkyl hydroperoxides are, from a synthetic point of view, more useful than those produced with hydrogen peroxide because of their superior solubility in non-polar solvents [15,29-31]. The application of alkyl hydroperoxides as epoxidation agents offers a number of advantages since the compounds are easy to obtain, give high yields and selectivities, and may be used in diluted form thus reducing the element of risk during epoxidation. Additionally, opening of epoxide rings by hydroperoxides during the epoxidation reaction is minimal and, in any case, gives rise to by-products that may be reduced to commercially valuable alcohols [32].

^{*} Corresponding author. Tel.: +55 51 33086305; fax: +55 51 33087304. *E-mail address:* maritana@pelotas.ifsul.edu.br (M. Farias).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2010.06.038

Soybean oil represents an excellent model system for the investigation of epoxidation processes since more than 80% of its content is composed of unsaturated long-chain fatty acids, with approximately 52% linoleic acid, 26% oleic acid and 8% linolenic acid [33]. The double bonds present in these acids can be transformed through the use of oxidizing agents and appropriate catalysts into oxirane groups, thus transforming the original oil into a more reactive substrate.

Gas chromatography (GC) is commonly used to analyse the epoxidation products obtained from vegetable oils. In this method, the epoxidized vegetable oil must be derivatised, typically by transformation into its alkyl ester, a step that is time consuming, uses large amounts of reagent [34] and presents the possibility of opening the oxirane ring as a result of the action of the derivatising agents [35]. In contrast, methods based on quantitative proton nuclear magnetic resonance (¹H NMR) spectroscopy do not necessitate derivatisation of the analyte, require only small amounts of reagent and, compared with GC, are rapid with respect to both sample preparation and collection of data. Application of ¹H NMR in the determination of the yield of transesterification [36] and of the composition of unsaturated fatty acids in vegetable oils [37] has already been reported. Additionally, ¹H NMR, ¹³C NMR and GC-mass spectrometry have been employed in monitoring the catalytic epoxidation of methyl linoleate using transition metal complexes as catalysts [38]. Aerts and Jacobs [34] used ¹H NMR method to determine the yields of epoxidized oils and methyl esters of fatty acids, and showed that the results obtained for the epoxidation of methyl oleate and methyl linoleate were similar to those given by GC analysis with respect to the percentage conversion of double bonds and the selectivities for mono- and diepoxides. The same authors also evaluated the reproducibility of the results obtained by ¹H NMR for the selectivities for mono- and diepoxide produced in oil samples and found only small margins of error (approximately 0.2 in σ^2) in all cases. NMR techniques have also been used to characterise the products of epoxidation of castor oil and derivatives with the catalytic system [VO(acac)₂]/TBHP [39], epoxidation of soybean oil by the methyltrioxorhenium-CH₂Cl₂/H₂O₂ catalytic biphasic system [20], and the monoepoxides obtained from methyl esters of linoleic acid [40].

Considering the foregoing facts, in the present study, the ability of bis(acetyl-acetonato)dioxo-molybdenum (VI) [MoO₂(acac)₂] to catalyse the epoxidation of soybean oil using toluene as solvent and TBHP as oxidizing agent has been investigated. Quantitative analysis of the hydrogen resonances in the NMR spectra of soybean oil and of the epoxidized oils was performed in order to determine the average molar mass, the number of double bonds in the oil, the conversion of substrate, the percentage of epoxidation and the selectivity of the catalytic system. The data obtained by NMR were also compared with the ones produced by GC–MS spectrometry. The effects of reaction time and temperature on the formation of products were investigated. Additional experiments with oleic acid were also carried out.

2. Experimental

2.1. Materials

Chloroform (analytical grade) and deuterated chloroform containing 1% tetramethylsilane (TMS) were obtained from Merck, whilst toluene, methanol and n-hexane were acquired from Ecibra and used as supplied. Sodium bisulphite, sodium methoxide, disodium hydrogen citrate (Vetec) and anhydrous sodium sulphate (F. Maia) were purchased in analytical grade, and MoO₂(acac)₂ was supplied by Aldrich. In order to obtain anhydrous TBHP, a 70% aqueous solution (Merck) was extracted with



Scheme 1. Mechanism of epoxidation of an olefin by reaction with hydroperoxide in the presence of a transition metal catalyst.

toluene and the concentration of the resulting solution was determined by ¹H NMR spectroscopy. Quantofix[®] Peroxide 100 test strips (Sigma) were used for the semi-quantitative determination of peroxide. Oleic acid (analytical grade) was obtained from Synth. A sample of degummed soybean oil, donated by Oleoplan-RS-Brazil, was employed as substrate for the epoxidation reactions.

2.2. Acquisition of NMR spectra

A Varian Inova 300 MHz spectrometer was employed to measure the ¹H NMR spectra of samples (60 mg) dissolved in deuterated chloroform (0.6 mL) containing TMS as internal standard. The mean values of the relaxation times (T1) of the hydrogens involved in the quantitative determinations were \leq 2.0 s. The spectrometric parameters employed were: 7.5 µs pulse width corresponding to a flip angle of 71.1°, relaxation delay of 10 s; acquisition time of 2.049 s for 65,536 points, and spectral width of 4807.7 Hz. For each spectrum, 32 transients were accumulated in 6 min 49 s.

2.3. GC-MS analysis

The reaction products were detected in an DB-wax capillary column $(30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m})$ using a Shimadzu QP-2010 gas chromatograph coupled with a mass spectrometer with 70 eV E.I detector and MS WILEY7.LIB library. The injection volume was 1 μ L split of 1:20. The oven temperature was programmed from 50 °C at 20 °C/min to 200 °C (5 min), at 5 °C/min to 230 °C (20 min). The products were derivatised in agreement with the Rothenbacher method [35] as follows: for transesterification, 5 mL of sodium methoxide solution (6% in methanol) were added in 100 mg of the sample and shaken vigorously for 90 s. Extraction was performed by the addition of 10 mL of n-hexane and 10 mL of disodium hydrogen citrate (15% in water), and the organic phase was used for GC analysis.

2.4. Epoxidation reaction

Soybean oil (1g; 1.1 mmol; equivalent to 4.1 mmol of double bonds) in toluene (2 mL) was placed in a 50 mL round bottomed flask connected to a reflux condenser. MoO₂(acac)₂ (13 mg; 41 µmol; equivalent to 1% of double bonds present in the oil) and anhydrous TBHP (1.4 mL; 4.1 mmol; equivalent to the double bonds present in the oil) were added and the mixture was maintained under vigorous stirring at temperatures and periods of time stated in Table 1. At the end of the required reaction time, the flask was placed into an ice bath, sodium bisulphite solution (15%, w/v) was added slowly and the consumption of peroxide monitored using Quantofix Peroxide 100 test strips. The organic phase was separated, dried over anhydrous sodium sulphate, filtered and the solvent removed using a rotary evaporator. The remaining catalyst was separated by transferring the reaction product to a silica gel column, which was subsequently eluted with chloroform. All reactions were carried out in triplicate and their catalytic activities were obtained by ¹H NMR, 5% of incertitude [20,41].

Table 1

E	poxidation of sovbe	ean oil at 80°C using t	he catalytic system	MoO ₂ (acac) ₂ /TBHP. ^a	determined by	¹ H NMR spectroscopy.
				2 2 1 2 1		

Reaction time (h)	Conversion (%)	Epoxidation (%)	Selectivity (%)	TON ^b	TOF^{c} (h^{-1})
2	49.7 ± 1.0	16.3 ± 0.4	32.8	4.6	2.3
4	54.8 ± 1.1	17.6 ± 0.5	32.1	4.9	1.2
8	63.0 ± 1.0	23.6 ± 0.5	37.5	6.6	0.8
16	94.1 ± 0.4	39.4 ± 1.1	41.9	11.0	0.7
24	94.1 ± 0.9	39.0 ± 0.6	41.4	11.0	0.5

^a Reactions were carried out with toluene as solvent and molar ratio of anhydrous TBHP:number of double bonds in the oil:catalyst of 100:100:1. The results were calculated by ¹H NMR, 5% of incertitude.

^b TON: total turnover number, moles of epoxide formed per mole of catalyst.

^c TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst] \times time (h⁻¹).

2.5. Quantitative NMR analysis

The mean molecular weight (M) of the original soybean oil (equal to $872.63 \text{ g mol}^{-1}$) was calculated from its ¹H NMR spectrum (Fig. 1) according to [42]:

$$M = \frac{15.034G}{3NF} + \frac{14.026(C + D + E + F + H)}{2NF} + \frac{26.016(A - NF)}{2NF} + 173.1$$
(1)

where NF is the normalisation factor (the relative peak area of one hydrogen) calculated from the area of the signal associated with the four hydrogens of the methylene groups of the glycerol moiety (**B** in Fig. 1) by the expression:

$$NF = \frac{B}{4}$$
(2)

These hydrogens were selected because they exhibited the lowest relaxation times compared with other triglyceride hydrogens and their signals did not interfere with any others in the spectrum [42]. In Eq. (1) **C**, **D**, **E**, **F** and **H** are the peak areas associated with the methylene hydrogens (14.026 g) of the triglyceride, **G** is the peak area of the methyl hydrogens (15.034 g) of the triglyceride, and **A** is the peak area of the olefinic hydrogens (26.016 g) plus the peak area of the methine hydrogen of the glycerol moiety, which all appear in the same region. Finally, the value 173.1 represents the molecular weight of the triglyceride fragment depicted in Fig. 2.

In order to determine the values of conversion, epoxidation and selectivity, the number of double bonds (ND) present in the original



Fig. 1. ¹H NMR spectrum of the original soybean oil sample represented by a triglyceride of linoleic acid (R₁ and R₂ are alkyl groups).

soybean oil (ND_i equal to 3.58 mol) was determined from:

$$ND_{i} = \frac{\mathbf{A} - NF}{2NF}$$
(3)

Eqs. (4)–(6) were then applied in order to calculate the further parameters of the reactions studied:

Conversion (%) =
$$\left[\frac{ND_i - ND_f}{ND_i}\right] \times 100$$
 (4)

Epoxidation (%) =
$$\left[\frac{(\mathbf{I} + \mathbf{J})/2}{NF \cdot ND_i}\right] \times 100$$
 (5)

Selectivity (%) =
$$\left[\frac{\text{Epoxidation (%)}}{\text{Conversion (%)}}\right] \times 100$$
 (6)

where ND_f is the number of double bonds that remain unreacted, obtained by substitution into Eq. (3) of the appropriate peak areas in the spectrum of the epoxidized oil. I and J are the peak areas associated with the hydrogens of the epoxide groups and occur at chemical shifts of 2.9 (monoepoxide) and 3.1 (diepoxide) ppm, respectively (Scheme 2) [34].

3. Results and discussion

In preliminary experiments, appropriate conditions for the epoxidation of soybean oil using the $MoO_2(acac)_2/TBHP$ catalytic system were evaluated, with particular emphasis given to the effects of employing an aqueous solution or anhydrous TBHP as oxidizing agent. Tests using TBHP in solution gave lower percentage of epoxide than anhydrous TBHP and after 2 h of reaction, large amounts of hydroxilated products were found. Since the best results were obtained by using anhydrous TBHP, the study reported herein employed the oxidizing agent in this form. The temperature conditions were also investigated. At temperatures below 80 °C, epoxidation products were not observed. Therefore, the reactions were carried out at 80 °C and at 110 °C, which is the temperature of toluene reflux. Temperatures above 110 °C were not considered because epoxy ring opening could occur.

The main experimental conditions can be seen from Table 1, when soybean epoxidation was carried out at 80 °C, the values for conversion, epoxidation and selectivity of reaction increased with time. The results shown are the average of triplicates. It can





Scheme 2. Principal chemical shifts (ppm) of hydrogens influenced by double bonds and/or epoxide groups in (a) methyl linoleate; (b) methyl linoleate diepoxide; and (c and d) methyl linoleate monoepoxide (R = Me). Adapted from [34].

be observed that the results show no difference when referred to the elapsed time from 16 to 24 h of ongoing reactions and that 16 h reaction time gives the most satisfactory marks in this series of experiments. Throughout the catalytic procedure, it was also observed that there was no color change during the reaction, being observed by the persistent yellow color of the catalyst [43]. This possibly indicates that the catalyst does not decompose into Mo(V) species during the reaction [44]. On the characterization of the reaction products after 8 h of reaction at 80 °C, the formation of monoepoxide products could be verified from the appearance of a hydrogen signal related to the formation of the epoxide group at 2.9 ppm in the ¹H NMR spectrum (Fig. 3a). However, following 16 h



Fig. 3. ¹H NMR spectra of soybean oil showing: (a) oil epoxidized at 80 °C for 8 h; (b) oil epoxidized at 80 °C for 16 h; (c) oil epoxidized at 110 °C for 2 h: (R_1 and R_2 are alkyl groups).

of reaction, the presence of diepoxides could also be detected as evidenced by the hydrogen signals of the epoxide groups at both 2.9 and 3.1 ppm (Fig. 3b). Table 2, which gives the results for reactions carried out under conditions of toluene reflux (110 °C), shows that conversion increased slightly with reaction time, but epoxi-

Table 2

Epoxidation of soybean oil at 110 °C using the catalytic system MoO₂(acac)₂/TBHP,^a determined by ¹H NMR spectroscopy.

Reaction time (h)	Conversion (%)	Epoxidation (%)	Selectivity (%)	TON ^b	$TOF^{c}(h^{-1})$
2	70.1 ± 0.9	54.1 ± 0.9	77.2	15.0	7.5
4	69.3 ± 1.1	53.1 ± 0.8	76.6	14.8	3.7
8	77.6 ± 0.5	49.7 ± 0.7	64.0	13.9	1.7
16	79.3 ± 0.6	43.7 ± 0.5	55.1	12.2	0.8
24	83.2 ± 1.3	40.9 ± 0.7	49.2	11.4	0.5

^a Reactions were carried out with toluene as solvent and molar ratio of anhydrous TBHP: number of double bonds in the oil: catalyst of 100:100:1. The results were calculated by ¹H NMR, 5% of incertitude.

^b TON: total turnover number, moles of epoxide formed per mole of catalyst.

^c TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst] × time (h⁻¹).



Scheme 3. Proposed mechanism for the epoxidation of olefins by the catalytic system MoO₂(acac)₂/TBHP. Adapted from [15].

dation and selectivity diminished. However, with the increase in temperature from 80 to 110 °C, with only 2 h of reaction, the conversion reached 70% and there was a significant gain in the amount of epoxidized product and selectivity. The turnover numbers in Table 2 were higher than the ones in Table 1, indicating increased activity of the catalyst at this temperature. Color change that could be related to the decomposition of the catalyst was not observed, even under drastic conditions of 110°C, although TON started to decline for longer reaction times. Comparing Mo catalysts for epoxidation reactions of other substrates, our catalytic system has similar activity and stability [44,45] or lower [17,46]. As far as we could investigate, data for epoxidation reactions using molybdenum catalytic systems and unsaturated fatty acids [18] as substrates have not been reported so far. However, values of TON and TOF for the catalytic epoxidation of a mixture of methyl oleate and methyl linoleate in ionic liquids, using the Mo (VI) complex as catalyst [47], are higher than those found in this work. The characterization of the reaction products by ¹H NMR revealed that after only 2 h of reaction at 110°C, the formation of diepoxides had already occurred (Fig. 3c), and similar diepoxide formation was observed under several other conditions. Evidence of the generation of hydroxylated products, formed by the opening of the oxirane ring, can also be observed in the 3.4–4.0 ppm region of the ¹H NMR spectrum shown in Fig. 3c. Perhaps these products are likely to decrease the activity of the catalyst.

The formation of *cis* epoxides, under all the conditions studied, was confirmed from the observed hydrogen chemical shift (2.9 ppm) associated with the epoxide. This shift is characteristic of authentic *cis* epoxide, whilst the epoxide hydrogens of *trans* epoxide resonate at 2.63 ppm [38]. The present findings indicate that the *cis* configuration, present in the majority of the unsaturated fatty acids of vegetable oils [48], is maintained in the corresponding epoxides. Indeed, the *trans* configuration is rarely found in natural products such as vegetable oils, and great care must be taken in representing the molecular structure of such compounds.

It is proposed that the mechanism (Scheme 3) of epoxidation of olefins, using the catalytic system $MoO_2(acac)_2/TBHP$, occurs via formation of a catalytic species **A**, by the reaction of the complex $MoO_2(acac)_2$ with TBHP. Subsequently, the species **A** transfers an oxygen to the olefin generating the species **B**. The *tert*-butyl alcohol formed during the course of the reaction acts as a competitive inhibitor of TBHP attack, since this by-product can also coordinate to the molybdenum center [49]. This could lead to a



Fig. 4. Total ion chromatogram of the methyl esters of epoxidized soybean oil with the catalytic system $[MoO_2(acac)_2]/TBHP$, 110 °C, 2 h.



Fig. 5. Mass spectrum fragmentation of epoxidized methyl oleate obtained from Fig. 4, under the catalytic system $[MoO_2(acac)_2]/TBHP$, 110 °C, 2 h.

significant reduction in the catalytic activity as the reaction time elapses.

In the present study, the catalytic activity of $MoO_2(acac)_2$ in the epoxidation of soybean oil using TBHP was compared with the epoxidation of oleic acid using anhydrous cumene hydroperoxide (CHP) and chlorobenzene as solvent [18]. Oleic acid subjected to epoxidation for 140 min at 80 °C underwent 48.4% conversion with a selectivity of 50.3%. In our system involving soybean oil and $MoO_2(acac)_2/TBHP$, conversion after 120 min at 80 °C was 49.7% with a selectivity of 32.8% (Table 1), whereas at 110 °C the conversion was 70.1% with a selectivity of 77.2% (Table 2). At 110 °C the results obtained by using the system described in this paper were superior to those available in the literature at 80 °C [18], while at 80 °C the results were similar to those reported previously.

For further comparison, our system was used for the epoxidation of oleic acid. As can be seen from Table 3, the results obtained by using our system were again superior to those available in the literature with $MoO_2(acac)_2/CHP$ and chlorobenzene as solvent [18].

The total ion chromatogram (TIC) of the epoxidation products obtained for best reaction condition for epoxidation of soybean oil, at 110°C and 2h, can be seen in Fig. 4. Peaks until 15 min corresponded to the saturated and unsaturated fatty esters from the unreacted soybean oils and peaks around 20-22 min corresponded to epoxidation products. The signal of the precursor ion with a mass to charge ratio (m/z) of 155 amu, which evidences the formation of the epoxidized methyl oleate [50] is shown at Fig. 5 with its fragmentations (Scheme 4). However, the electron impact ionization (EI) detector produces a strong high sensitivity fragment and at (m/z) 155, which points to epoxidized methyl oleate, it is little selective because the fragment does not include the other product expected from the NMR data obtained, epoxidized methyl linoleate (m/z 344). Chemical ionization (CI) with ammonia is supposed to be more suitable for such characterization [51,52].

Table 3

Epoxidation of oleic acid using the catalytic system MoO₂(acac)₂/TBHP^a, determined by ¹H NMR spectroscopy.

Reaction temperature (°C)	Conversion (%)	Epoxidation (%)	Selectivity (%)	TON ^b	$TOF^{c}(h^{-1})$
80 110	$67.2 \pm 0.6 \\ 62.5 \pm 0.9$	$\begin{array}{l} 40.6 \pm 0.6 \\ 42.2 \pm 0.9 \end{array}$	60.3 67.9	40.6 42.2	20.3 21.1

^a Reactions were carried out with toluene as solvent, 2 h and molar ratio of anhydrous TBHP: oleic acid:catalyst of 100:100:1. The results were calculated by ¹H NMR, 5% of incertitude.

^b TON: total turnover number, moles of epoxide formed per mole of catalyst.

^c TOF: turnover frequency which is calculated by the expression [epoxide]/[catalyst] \times time (h⁻¹).



Scheme 4. Fragmentations of epoxidized methyl oleate.

4. Conclusions

The results obtained demonstrate the catalytic potential of the system $MoO_2(acac)_2/TBHP$ in the epoxidation of soybean oil. This catalytic system shows great promise and may substitute for classical methods of epoxidation, particularly since it offers lower environmental impact with a minimization of residues. Under the conditions tested, the best results obtained for conversion, epoxidation and selectivity occurred when the reaction was carried out at 110 °C for 2 h. For vegetable oils that are composed predominantly of triglycerides, the positions of unsaturation within the fatty acids may be less susceptible to epoxidation in comparison with terminal double bonds of short chain alkenes.

The use of ¹H NMR techniques allowed facile and rapid identification and quantification of the products of vegetable oil epoxidation. Through analysis of the characteristic signals of the hydrogens present in soybean oil and epoxidized oil, it was possible to determine the yield and selectivity of the reactions, thereby permitting evaluation of the reaction conditions employed in the catalytic epoxidation.

Acknowledgements

The authors wish to thank Prof. Dr. Paulo H. Schneider (UFRGS, Porto Alegre, RS, Brazil) for the determination of the parameters used in the acquisition of the ¹H NMR spectra, Prof. Dr. Norberto P. Lopes (USP, Ribeirão Preto, SP, Brazil) for GC/MS analyses and FAPERGS and CNPq for financial assistance to the project. M. Farias is indebted to the Instituto Federal de Educação Ciência e Tecnologia Sul-rio-grandense (Pelotas, RS, Brazil) for granting study leave, and to CAPES for scholarship.

References

- L.L. Monteavaro, E.O. Silva, A.P.O. Costa, D. Samios, A.E. Gerbase, C.L. Petzhold, J. Am. Oil Chem. Soc. 82 (2005) 365–371.
- [2] A. Guo, W. Zhang, Z.S. Petrovic, J. Mater. Sci. 41 (2006) 4914-4920.
- [3] S.C. Godoy, M.F. Ferrão, A.E. Gerbase, J. Am. Oil Chem. Soc. 84 (2007) 503-508.
- [4] Y. Guo, J.H. Hardesty, V.M. Mannari, J.L. Massingill Jr., J. Am. Oil Chem. Soc. 84
- (2007) 929–935.
- [5] K.M. Doll, S.Z. Erhan, J. Surfactants Deterg. 9 (2006) 377–383.

- [6] T. Tsujimoto, H. Uyama, S. Kobayashi, Macromol. Rapid Commun. 24 (2003) 711-714.
- [7] Z. Zong, J. He, M.D. Soucek, Prog. Org. Coat. 53 (2005) 83-90.
- [8] M.A. de Luca, M. Martinelli, M.M. Jacobi, P.L. Becker, M.F. Ferrão, J. Am. Oil Chem. Soc. 83 (2006) 147–151.
- [9] M.A. de Luca, M. Martinelli, C.C.T. Barbieri, Prog. Org. Coat. 65 (2009) 375-380.
- [10] H.H. Masjuki, S.M. Sapuan, J. Am. Oil Chem. Soc. 72 (1995) 609-612.
- [11] B.K. Sharma, A. Adhvaryu, Z. Liu, S.Z. Erhan, J. Am. Oil Chem. Soc. 83 (2006) 129–136.
- [12] X. Wu, X. Zhang, S. Yang, H. Chen, D. Wang, J. Am. Oil Chem. Soc. 77 (2000) 561–563
- [13] P.S. Lathi, B. Mattiasson, Appl. Catal. B 69 (2007) 207–212.
- [14] A. Campanella, M.A. Baltanás, M.C. Capel-Sánchez, J.M. Campos-Martin, J.L.G. Fierro, Green Chem. 6 (2004) 330–334.
- [15] K.A. Jorgensen, Chem. Rev. 89 (1989) 431–458.
- [16] J.M. Mitchell, N.S. Finney, J. Am. Oil Chem. Soc. 123 (2001) 862-869.
- [17] R.M. Calvente, J.M. Campos-Martin, J.L.C. Fierro, Catal. Commun. 3 (2002) 247–251.
- [18] J.M. Sobczak, J.J. Ziólkowski, Appl. Catal. A 248 (2003) 261–268.
- [19] M.G. Topuzova, S.V. Kotov, T.M. Kolev, Appl. Catal. A 281 (2005) 157-166.
- [20] A.E. Gerbase, J.R. Gregório, M. Martinelli, M.C. Brasil, A.N.F. Mendes, J. Am. Oil Chem. Soc. 79 (2002) 179–181.
- [21] F.E. Kühn, A. Scherbaum, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 4149-4164.
- [22] G.S. Owens, J. Arias, M.M. Abu-Omar, Catal. Today 55 (2000) 317-363.
- [23] M.D. Refvik, R.C. Larock, J. Am. Oil Chem. Soc. 76 (1999) 99–102.
- [24] F.E. Kühn, A.M. Santos, M. Abrantes, Chem. Rev. 106 (2006) 2455-2475.
- [25] F.E. Kühn, A.M. Santos, W.A. Hermann, Dalton Trans. (2005) 2483-2491.
- [26] M. Herbert, F. Montilla, R. Moyano, A. Pastor, E. Álvarez, A. Galindo, Polyedron 28 (2009) 3929–3934.
- [27] N.A. Koshel, V.N. Sapunov, B.S. Turov, V.V. Popova, B.F. Ustavshchikov, Polym. Sci. 22 (1980) 2642–2647.
- [28] S. Gil, R. Gonzalez, R. Mestres, V. Sanz, A. Zapater, React. Funct. Polym. 42 (1999) 65–72.
- [29] M.L.A. Von Holleben, M.C. Schuch, Quim. Nova 20 (1997) 58-71.
- [30] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U.F. Schuchardt, Acc. Chem. Res. 31 (1998) 485–493.
- [31] C.C.L. Pereira, S.S. Balula, F.F.A. Paz, A.A. Valente, M. Pillinger, J. Klinowski, I.S. Gonçalves, Inorg. Chem. 46 (2007) 8508–8510.
- [32] P.J. Martinez de la Cuesta, E.R. Martinez, J.M.R. Maroto, F.M. Jimenez, Ann. Qui. A: Fis. Tec. 84 (1988) 231–235.
- [33] P. Wang, B.Y. Tao, J. Am. Oil Chem. Soc. 75 (1998) 9-14.
- [34] H.A.J. Aerts, P.A. Jacobs, J. Am. Oil Chem. Soc. 81 (2004) 841-846.
- [35] T. Rothenbacher, W. Schwack, Rapid Commun. Mass Spectrom. 21 (2007) 1937–1943.
- [36] G. Gelbard, O. Brès, R.M. Vargas, F. Vielfaure, U.F. Schuchardt, J. Am. Oil Chem. Soc. 72 (1995) 1239–1241.
- [37] Y. Miyake, K. Yokomizo, N. Matsuzaki, J. Am. Oil Chem. Soc. 75 (1998) 1091–1094.
- [38] G. Du, A. Tekin, E.G. Hammond, L.K. Woo, J. Am. Oil Chem. Soc. 81 (2004) 477–480.
- [39] M.R.S. Nunes, M. Martinelli, M.M. Pedroso, Quim. Nova 31 (2008) 818-821.
- [40] P.H. Cui, R.K. Duke, C.C. Duke, Chem. Phys. Lipids 152 (2008) 122-130.

- [41] A.E. Gerbase, M.C. Brasil, J.R. Gregório, A.N.F. Mendes, M.L.A. von Holleben, M. Martinelli, Grasas y Aceites 53 (2002) 175–178.
- [42] Y. Miyake, K. Yokomizo, N. Matsuzaki, J. Am. Oil Chem. Soc. 75 (1998) 15-19.
- [43] E.G. Rochow, Inorganic Syntheses, vol. 6, McGraw-Hill Book Company, Inc., New York, 1960.
- [44] H. Vrubel, K.J. Ciuffi, G.P. Ricci, F.S. Nunes, S. Nakagaki, Appl. Catal. A 368 (2009) 139–145.
- [45] S.M. Bruno, S.S. Balula, A.A. Valente, F.A.A. Paz, M. Pillinger, C. Sousa, J. Klinowski, C. Freire, P. Ribeiro-Claro, I.S. Gonçalves, J. Mol. Catal. A: Chem. 270 (2007) 185–194.
- [46] F. Chai, X. Wang, X. Zhang, J. Tao, React. Kinet. Catal. Lett. 97 (2009) 341-348.
- [47] S. Cai, L. Wang, C. Fan, Molecules 14 (2009) 2935-2946.

- [48] M. Guidotti, N. Ravasio, R. Psaro, E. Gianotti, L. Marchese, S. Coluccia, Green Chem. 5 (2003) 421–424.
- [49] F.E. Kühn, M. Groarke, E. Beneze, E. Herdtweck, A. Prazeres, A.M. Santos, M.J. Calhorda, C.C. Romão, I.S. Gonçalves, A.D. Lopes, M. Pillinger, Chem. Eur. J. 8 (2002) 2370–2383.
- [50] C. Orellana-Coca, D. Adlercreutz, M.M. Andersson, B. Mattiasson, R. Hatti-Kaul, Chem. Phys. Lipids 135 (2005) 189–199.
- [51] S. Biedermann-Brem, M. Biedermann, A. Frankhauser-Noti, K. Grob, R. Helling, Eur. Food Res. Technol. 224 (2007) 309–314.
- [52] A. Fankhauser-Noti, K. Fiselier, M. Biedermann-Brem, K. Grob, Food Chem. Toxicol. 44 (2006) 1279–1286.