Electrochemistry Communications 54 (2015) 46–50

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

A new approach for epoxidation of fatty acids by a paired electrosynthesis

Wanjie Li, Meifeng Tian, Haiyan Du, Zhenhai Liang *

College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, PR China

ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form 4 March 2015
Accepted 4 March 2015
Available online 12 March 2015

Keywords:
Unsaturated fatty acids
Paired electrosynthesis
Epoxidation
Castor oil

ABSTRACT

This paper reports a novel and effective electrochemical method to prepare epoxides using a paired electrosynthesis. The electrochemical epoxidation of unsaturated fatty acids by HCOOOH generated in situ from H_2O_2 (by oxygen reduction) and HCOOH in the catholyte, and by HOCl also generated in situ in the anolyte by oxidation of chloride ions was studied using HCl as a catalyst. The FTIR spectra of the epoxidised castor oil, soybean oil, and corn oil were compared to those of the parent unreacted oils. The highest relative epoxy yield of castor oil (40%) was achieved at 25 °C and pH 6.5 after 3 h, and the epoxy value of castor oil reached 0.12 mol/100 g. The optimal passing oxygen rate, molar ratio of castor oil double bonds to HCOOH and current density were determined to be 3 $cm^3\ s^{-1}$, 8 and 0.3 A cm^{-2}, respectively.

1. Introduction

Vegetable oils comprise the largest proportion of current renewable raw material consumption in the chemical industry [1]. Vegetable oils and their unsaturated fatty acids are converted to epoxides because of the promising applications of the resulting epoxides. In particular, these epoxides are widely used as environmental-friendly lubricants, plasticisers, polymer stabilisers and paint and coating components; they also serve as intermediates for various chemicals, including alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds and polymers such as polyesters, polyurethanes and epoxy resins [2–5]. Srikanta Dinda et al. studied the epoxidation of cottonseed oil by peroxyacetic acid generated in situ from hydrogen peroxide and glacial acetic acid in the presence of liquid inorganic acid catalysts. A 78% relative conversion to oxirane with minimal oxirane cleavage can be obtained using in situ techniques [6]. Snězana Sinadinovíc-Fīser et al. studied the epoxidation of castor oil in benzene with peracetic acid generated in situ from acetic acid and hydrogen peroxide in the presence of an ion-exchange resin catalyst. The highest relative epoxy yield of 78.32% was achieved at 323 K after 8 h when 0.5 mol of acetic acid and 1.5 mol of 30 wt.% aqueous hydrogen peroxide per mole of double bond in oil were used in the presence of 15 wt.% of Amberlite IR-120 [7]. Epoxide preparation still presents deficiencies, such as high equipment demand, large energy consumption, high cost, formation of by-products, and environmental pollution. Castor oil, soybean oil and corn oil are abundant in unsaturated fatty acids. Therefore, these oils can become a good material for various applications [8,9]. In the present paper, we provide a novel and effective electrochemical method to synthesise epoxides. The same compound is synthesised in both the cathodic and anodic compartments with this paired electrosynthesis method. A schematic of the epoxide preparation is shown in Scheme 1. Compared with the current technology, the proposed method presents considerable advantages, such as simpler equipment and technological process, lower cost, less environmental pollution and easier reaction control.

2. Experimental

2.1. Materials

Castor oil, soybean oil, corn oil and HCOOH (85%) and other chemicals were obtained from Tianjin Petrochemical Corporation (China). HCl (37.5%) was formulated as 0.1 mol L^{-1} solution to be the catalyst and maintain pH. $NaHCO_3$ was formulated as 0.02 mol L^{-1} solution to adjust pH. All reagents were analytical grade and all aqueous solutions were prepared with deionized water.

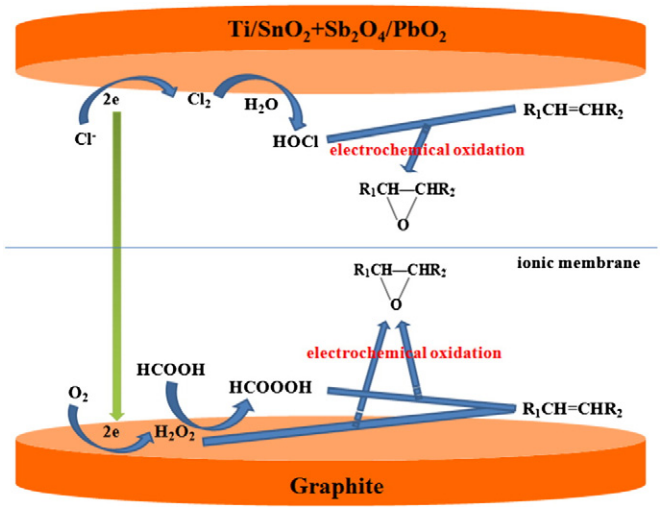
DC Regulated Power Supply (WYJ-30V10A) was obtained from Shanghai Hong Ji Electrical Equipment Co. Ltd. (China). Cation exchange membrane (N117) was obtained from Beijing Foxconn Technology Co. Ltd. (China). Electronic energy-saving temperature control device (ZNHW-II, Zhengzhou Asia-Instrument Co. Ltd., Zhengzhou, China) controlled the temperature with sensor into the solution.

2.2. Epoxidation procedure

An electrolytic cell was equipped with an electronic energy-saving temperature control device, a thermometer and an air bubbler. The

* Corresponding author at: No 79 Yingze West Street, Taiyuan 030024, China. Tel.: +86 351 6018193, +86 13903414089; fax: +86 351 6018554.
E-mail addresses: liangzhenh@sina.com, liangzhenhai@tyut.edu.cn (Z. Liang).

http://dx.doi.org/10.1016/j.elecom.2015.03.001
1388-2481/



Scheme 1. Schematic illustration of electrochemical epoxidation of unsaturated fatty acids.

cell contained two compartments separated with a cation exchange membrane. Graphite and $Ti/SnO_2 + Sb_2O_4/PbO_2$ were used as the cathodic and anodic electrodes, respectively. In both compartments (300 mL each), the crude oil (40 g) was mixed with an appropriate amount of HCOOH 85% (molar ratio of castor oil double bonds to HCOOH 6 to 10), then 0.1 mol L^{-1} HCl (3 mL) was added. The pH was adjusted at the desired value (pH 5 to 7) by adding an aqueous solution of $NaHCO_3$ (0.02 mol L^{-1}). The mixture was stirred in each compartment until evenly mixed. The cell was brought to the desired temperature (20 to 40 °C) using an electronic energy-saving temperature control device. The DC power source was switched on and maintained at the selected current density (0.1 to 0.5 A cm^{-2}). Oxygen was bubbled only into the cathodic compartment at a constant rate (1 to 5 cm^3 s^{-1}) using an air bubbler. The reaction progress was followed by withdrawing a 10 mL aliquot from each compartment at defined time intervals. The beginning of feeding oxygen was considered to be the 'zero time'. The separation of oil and aqueous phases was performed after quenching and centrifugation. The oil phase sample was washed with distilled water until neutralised, then subjected to reduced pressure distillation, and the residue was analysed.

2.3. Analytical methods

2.3.1. Epoxy values and relative epoxy yield

The epoxy values of all samples in both compartments were measured and averaged at each point by using a direct method with hydrobromic acid solutions in acetic acid. The relative fractional conversion of oxirane from epoxy was calculated from the following expression [7,10,11]:

Relative epoxy yield:

$$\mathrm{REY} = \left(\mathrm{EO}_{\max}^{\exp}/\mathrm{EO}_{\mathrm{the}}\right) \times 100 \quad (1)$$

where EO_{max}^{exp} is the experimentally obtained the maximum epoxy oxygen content in 100 g of oil. EO_{the}, which is defined as the theoretical maximum content of epoxy oxygen in 100 g of oil, was determined to be 4.89% from the following expression:

$$\mathrm{EO}_{\mathrm{the}} = \{(\mathrm{IN}_o/2A_i)/[100 + (\mathrm{IN}_o/2A_i)A_o]\}A_o \times 100 \quad (2)$$

where A_i (126.9) and A_o (16.0) are the atomic weights of iodine and oxygen, respectively, and IN_o(81.5) is the initial iodine value of the oil sample.

2.3.2. FTIR spectroscopy

Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR-8400 equipped with a KBr beam splitter. For thin film deposits, a diffuse reflectance system was used and a NaCl plate was used for liquid samples. A regular scanning range of 500 cm^{-1} to 4000 cm^{-1} was used for 45 repeated scans at a spectral resolution of 4 cm^{-1}. Samples from the two compartments were obtained for analysis.

3. Results and discussion

3.1. Experimental principle

The reaction steps are as follows:

Cathodic compartment:

Cathode:

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \quad (3)$$

Solution:

$$\mathrm{HCOOH} + H_2O_2 \xrightarrow{H^+} \mathrm{HCOOOH} + H_2O \quad (4)$$

$$R_1CH{=}CHR_2 + \mathrm{HCOOOH} \longrightarrow R_1CH\text{—}CHR_2 + \mathrm{HCOOH} \quad (5)$$

$$R_1CH{=}CHR_2 + H_2O_2 \longrightarrow R_1CH\text{—}CHR_2 + H_2O \quad (6)$$

Anodic compartment:

Anode:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (7)$$

Solution:

$$Cl_2 + H_2O \rightleftharpoons \mathrm{HOCl} + \mathrm{HCl} \quad (8)$$

$$R_1CH{=}CHR_2 + \mathrm{HOCl} \xrightarrow{\textit{via}\ \text{the chlorohydrin}} R_1CH\text{—}CHR_2 + \mathrm{HCl} \quad (9)$$

Composition in fatty acid of various oils [12–14] is presented in Table 1.

Soybean oil and corn oil are mainly contains oleic and linoleic acids. The formula of oleic acid and linoleic acid are as follows:

Oleic acid:

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOH$$

Linoleic acid:

$$CH_3(CH_2)_4CH = CHCH_2CH = CH(CH_2)_7COOH$$

3.2. The FTIR wave length values

The FTIR wave length values of various oils are shown in Table 2. For castor oil, the disappearance of the two C=C bands (2400 cm^{-1} to