

KINETIC MODELING OF A LIQUID-LIQUID REACTION: EPOXIDATION OF OLEIC ACID UNDER CONVENTIONAL HEATING AND MICROWAVE IRRADIATION

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Abstract

Epoxidation of oleic acid by peracetic acid (PAA) was studied in a recycled reactor system under conventional heating and microwave irradiation. This reaction system consists of several steps. Thus, a kinetic modelling strategy to diminish the number of parameters to be estimated was developed by investigating each reaction step: PAA synthesis and decomposition, epoxidation and ring opening. An energy balance was included by determining the concentration of the microwave-absorbent species, and by analyzing the total input power of the microwaves. The epoxidation reaction was conducted under isothermal conditions within a temperature range of 50–70°C. The organic phase content was 32–45 %v/v. The interfacial mass transfer was supposed to be faster than the intrinsic reaction kinetics suppressing the use of mass transfer correlations. Nonlinear regression was used to estimate the kinetic parameters. Estimated rate constants and activation energies for the reactions showed to be in the same order of magnitude as the ones reported in the literature.

Keywords

Epoxidation, Vegetable Oils, Kinetic Modelling, Microwave Irradiation.

Introduction

Vegetable oils are a vast biomass resource and can be implemented to develop a wide variety of products. When unsaturated vegetable oils are submitted to epoxidation, they become chemical intermediates to valuable products, such as lubricants, plasticizers or non-isocyanate polyurethanes (Tan & Chow, 2010). Epoxidized vegetable oils are promising platform chemicals for a more sustainable and environmentally friendly economy. Epoxidation by the Prileschajew method consists of the substitution of a double bond by an oxirane ring caused by a percarboxylic acid that is formed in situ. This process consists of several steps and many chemical and physical

parameters are involved. Two liquid phases are present (oil and aqueous phases) and four reactions proceed simultaneously: the formation of the percarboxylic acid (also called perhydrolysis), the decomposition of the percarboxylic acid, the epoxidation step and the degradation of the oxirane ring (also called ring opening). Oleic acid was used as a model compound for vegetable oils since it is one major component in most plant-derived oils and presents a fairly simple structure with only one unsaturation. Acetic acid was implemented to form its correspondent peracid, peracetic acid. The chemical reactions are illustrated in Figure 1.

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Experiments with microwave (MW) heating were conducted in parallel with conventionally heated (CH) experiments in order to compare both heating methods. This work was focused on finding the most suitable mathematical model that shows good agreement with the experimental data and estimating the kinetic parameters of the model. This model could be later used to predict the progress of the reaction and the product yields.

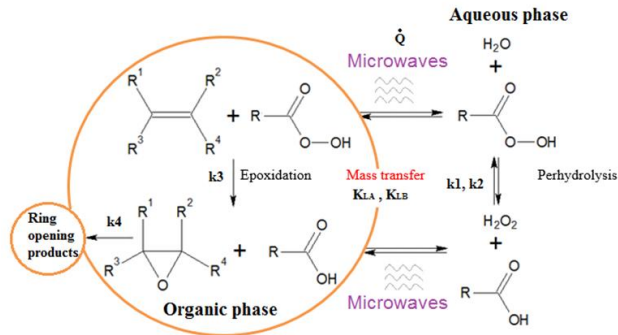


Figure 1. Reactions involved in the epoxidation of double bonds by percarboxylic acid with the Prileshajew method

Methods

Epoxidation of oleic acid was performed in a recycled batch reactor. The reaction kinetics was modeled mathematically by applying numerical methods for the solution of stiff differential equations and optimization algorithms for parameter estimation. The change in the temperature at the microwave cavity was determined by the net microwave input power and the concentrations of the microwave absorbent species.

For conventionally heated experiments, the system was considered an isothermal batch, while the mathematical model developed for MW heating consisted of the system comprising two continuous stirred tank reactors (CSTR) in series, one being the reaction vessel while the other one being the MW cavity. The solubilities of hydrogen peroxide and water in the organic phase were approximated to be negligible and the solubilities of peracetic acid was approximately 1/3 of acetic acid solubility (Cai et al., 2018). Additionally, by presuming the other organic species are not soluble in the aqueous phase, it is possible to simplify the mass balances to a system of ordinary differential equations (ODEs). Examples of the model equations are given below:

Aqueous phase (a)

$$\frac{dC_{PAA1a}}{dt} = \frac{C_{PAA2a} - C_{PAA1a}}{\tau_1} + \left(\alpha + \frac{1-\alpha}{K_{PAA}}\right)^{-1} \cdot (-\alpha R_{perh} + (1-\alpha)R_{EpoX}) \quad (1)$$

$$\frac{dC_{HP1a}}{dt} = \frac{C_{HP2a} - C_{HP1a}}{\tau_1} - R_{perh} \quad (2)$$

$$\frac{dC_{PAA1o}}{dt} = \frac{C_{PAA2o} - C_{PAA1o}}{\tau_1} + \left(\alpha + \frac{1-\alpha}{K_{PAA}}\right)^{-1} \cdot (\alpha(R_{per} - R_{decom}) - (1-\alpha)R_{EpoX}) \quad (3)$$

$$\frac{dC_{W1a}}{dt} = \frac{C_{W2a} - C_{W1a}}{\tau_1} + R_{perh} \quad (4)$$

Oil phase (o)

$$\frac{dC_{OA1o}}{dt} = \frac{C_{OA2o} - C_{OA1o}}{\tau_1} - R_{EpoX} \quad (5)$$

$$\frac{dC_{EOA1o}}{dt} = \frac{C_{EOA2o} - C_{EOA1o}}{\tau_1} + R_{EpoX} - R_{RO} \quad (6)$$

where α represents the ratio between aqueous and oil phases, τ is the mean residence time and k is the rate constant.

Modelling results and conclusions

The total number of kinetic parameters to estimate for oleic acid epoxidation by peracetic acid was 8. The route of the PAA decomposition was an assumption based on a previous work of our group. The mass transfer resistance was assumed to be negligible compared to the reaction kinetics. The model presented good correspondence with the values measured experimentally (Figure 2). The estimated rate constants and activation energies for the reactions showed to be in the same order of magnitude as the ones reported in the literature.

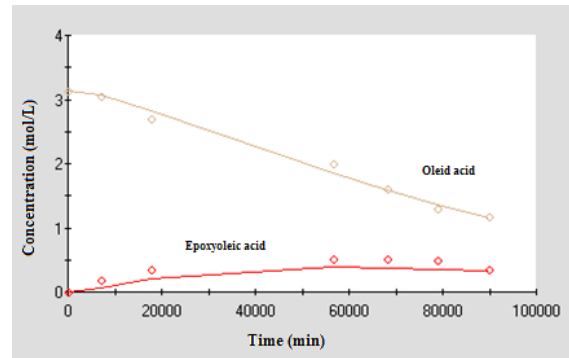


Figure 2. Data fitting for experiment under conventional heating at 40°C.

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