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E. U. Ikhuoria[a]; R. O. Obuleke[a]; F. E. Okieimen[a]
[a] Department of Chemistry, University of Benin, Benin City, Nigeria

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Studies on the Kinetics of Epoxidation of the Methyl Esters of Parkia Biglobosa Seed Oil

E. U. IKHUORIA, R. O. OBULEKE, and F. E. OKIEIMEN
Department of Chemistry, University of Benin, Benin City, Nigeria

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Epoxidation of methyl esters of parkia biglobosa seed oil was carried out at various temperatures using paracetic acid prepared in situ by reacting hydrogen peroxide with various amounts of glecial acetic acid. The physico-chemical characteristics of the oil are its alkyl esters were determined. The rate constant and activation energy of epoxidation found to be of the order of 10^{-7} $\mathrm{Lmol^{-1}s^{-1}}$ and 51.963 $\mathrm{kJmol^{-1}}$ respectively. Thermodynamic parameters such as enthalpy, entropy and free energy of activation were found to be 13.8 $\mathrm{kJmol^{-1}}$, -3.55 $\mathrm{kJmol^{-1}}$ and 1.51 $\mathrm{kJmol^{-1}}$. These thermodynamic data show that the epoxidation of the methyl esters of parkia biglobossa seed oil is a non-spontaneous process.

Keywords: epoxidation; parkia seed oil; entropy; enthalpy; free energy

1 Introduction

The application of modified plant oils in the chemical industry is becoming more and more interesting because of their availability from renewable resources (1). The preparation of plastic materials based on natural plant oils has become one of the most promising topics in materials science. The triglycerides that constitute plant oils can be transformed into polymerizable monomers by several chemical modification such as epoxidation, acrylation of epoxies, metathesis of double bonds or transesterification (2). Thus, the versatility of the triglycerides has attracted the interest of many scientists in different research laboratories (3, 4).

Epoxidation is an important industrial process. The annual production of ethylene oxide and propylene oxide in the US is estimated to be 2.9 and 1.2 million metric tons, respectively (5, 6). Long chain olefins, unsaturated fatty acids and esters and various polymers are also subjected to epoxidation to give intermediates useful for the manufacture of commercially important materials (7). Epoxidized vegetable oils and esters derived from them have found important applications as plasticizers and additives for polyvinyl chloride (PVC) (8).

Epoxidation should be carried out to reach a maximum conversion (epoxy yield) especially if the product is to be used for further chemical transformations. On the other hand, epoxidation may be employed to obtain a product in the most economical way, e.g. aiming at the highest conversion rate, but not necessarily at the highest conversion (9). Nowadays vegetable oils represent one group of olefinic compounds that are widely used for epoxidation reactions.

Epoxidation of long chain olefins and unsaturated fatty acid derivatives, such as soybean oil and other plant oils is carried out on an industrial scale (10). One of the most important epoxidized vegetable oils is epoxidized soybean oil (ESO). Its worldwide production is about 200,000 t/year (11, 12).

In Nigeria, vegetable oil–dependent industries rely mostly on imported oils like linseed and soybean oils, which are imported and very expensive. The locally available vegetable oils like, palm oil, palm kernel oil, coconut oil and parkia seed oil have not been fully exploited. This study examines the kinetics of epoxidation of the methyl esters of Parkia biglobosa seed oil (PBSO). In Nigeria, Parkia biglobosa seed is one of our indigenous oil seeds, of the family *fabaceae*. It bears fruits and the matured and ripe pods have edible pulp. The seeds are processed into a product (*Iru* in Yoruba) used as a vital ingredient in soup.

2 Materials and Methods

Parkia seeds were obtained from Benin City, Edo State, Nigeria. The oil was extracted from the powdered meal using n-hexane in a Soxhlet apparatus. All the reagents were of analytical grade, obtained from BDH Ltd., Poole, England.

Address correspondence to: E. U. Ikhuoria, Department of Chemistry, University of Benin, Benin City, Nigeria. E-mail: esyikhuoria@yahoo.com or ikhuoria@uniben.edu

2.1 Physico-chemical Characteristics of PBSO

The physico-chemical properties of the oil (color, specific gravity, retractive, index, acid value, free fatty acid, saponification value and iodine value) were determined according to standard methods (13).

2.2 Preparation of Methyl Esters of PBSO

The methyl esters of PBSO were prepared by the alcoholysis process. In a typical experiment, 10 ml of 0.1 M sodium methoxide solution was introduced into 5 grams of oil in a conical flask. The mixture was heated under reflux in a water bath at 60°C for one hour, cooled and extracted with n-hexane in a separating funnel. The extract was washed free of soap with distilled water, n-hexane was separated by distillation and the esters dried over anhydrous sodium sulphate. This procedure was repeated using different concentrations of sodium alkoxides. The alkyl esters were analyzed for their physico-chemical properties using ASTM methods.

2.3 Epoxidation of Methyl Esters of PBSO

Epoxidation of methyl esters of PBSO was carried out at 29°C using paracetic acid prepared *in situ* by reacting hydrogen peroxide (30% v/v) with various amounts of glacial acetic acid in the presence of small quanties of concentrated sulphuric acid (14).

In a typical experiment, a known amount of the methyl esters of PBSO was placed in a 500 ml flask containing the required amount of acid (acetic acid and sulphuric acid), condenser, thermometer and stirrer. The flask was allowed to attain the reaction temperature in a thermostated bath (controlled to better than ±2°C) and hydrogen peroxide, previously equiliberated at the reaction temperature, was added. The stirring rate was controlled so that the oil in the mixture was finely dispersed. The reaction was monitored by withdrawing aliquots of the reaction mixture at various time intervals into a large excess of cold water in a separatory funnel. The aqueous layer was drawn off and the oil layer was washed successively with warm water until it was acid free. Epoxidation was carried out at various temperatures (50, 60 and 70°C) and using various initial amounts of acetic acid and hydrogen peroxide. The resulting epoxidized methyl esters of PBSO were characterized using standard methods (13).

3 Results and Discussion

3.1 Physical Chemical Properties

The physico-chemical properties of PBSO and the methyl esters obtained are given in Table 1. These results show that the acid, iodine, free fatty acid, and saponification values obtained for the esters are much lower than those of the crude PBSO. The decrease in the values obtained for the esters may be due to the removal of other constituents of triglycerides and the incorporation of alkyl groups to obtain the alkyl esters. The color was observed to change from 24Y, 4R for the raw oil to 15Y, 1.6R for the esters. However, these properties are similar to those of soybean, linseed, and rubber seed oils which are the conventional oils used principally for coating formulation, epoxy compounds and linoleum (14, 15).

Table 1. Physico-chemical properties of parkia biglobosa seed oil (PBSO) and alkyl esters

Properties	PBSO	Methyl ester	Ethyl ester	Propyl ester
Acid value (mg KOH/g)	6.67	0.59	0.69	0.69
Iodine value (gI_2/100 g)	103.37	43039	45.57	45.63
Saponification value (mg KOH/g)	184.48	159.24	166.39	166.56
Free fatty acid (% wt)	3.36	0.344	0.347	0.349
Specific gravity (at 30°C)	0.898	0.845	0.840	0.837
Colour (Lovibond 1st cell)	24Y, 4R	15Y, 1.6R	15Y, 1.6R	15Y, 1.6R
Physical state	Liquid	Liquid	Liquid	Liquid

3.2 Effect of Temperature on the Rate of Epoxidation

The effect of temperature on the rate of epoxidation of methyl esters of PBSO, determined at 50, 60 and 70°C, is shown in Figure 1. It can be seen from the plots that the epoxide content increases linearly with reaction time during the initial stages of the reaction and later starts to decrease. The region where these plots deviate from linearity is believed

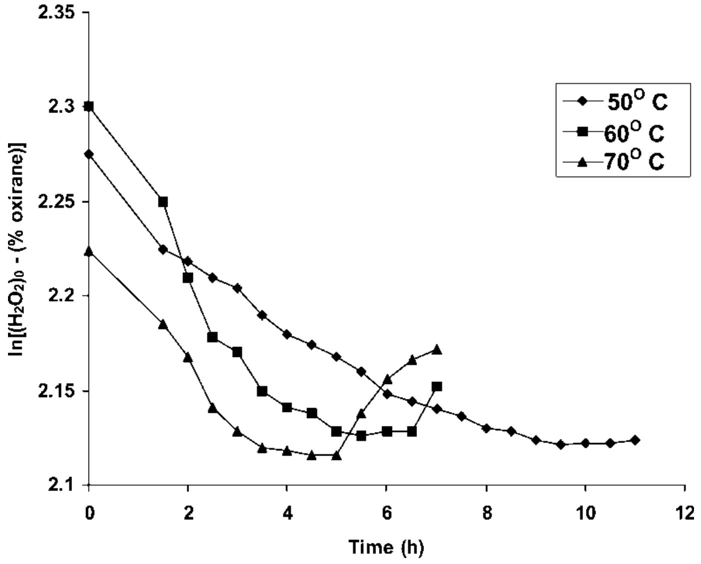

Fig. 1. Plot of $\ln[H_2O_2]_0 - (\% \text{ Oxirane})]$ vs. time for epoxidation of methyl esters of PBSO by paracetic acid.

to mark the onset of oxirane cleavage. The oxirane content obtained at incipient cleavage is given in Table 2. The epoxide contents was observed to be 1.40, 1.36 and 1.34 at 70, 60 and 50°C, respectively. The change in maximum oxirane content for the 20°C increase in temperature appears insignificant and leads to the suggestion that moderate temperatures of 50–60°C appear appropriate for optimum oxirane levels.

3.3 *Kinetics of Epoxidation*

The rate law for the epoxidation of vegetable oils can be expressed as follows:

$$\ln[(H_2O_2)_0 - (\%\text{oxirane})] = -k(RCOOH)_0 t + \ln(H_2O_2)_0] \quad (1)$$

Where $(H_2O_2)_0$ is initial concentration of hydrogen peroxide, $(RCOOH)_0$ is the initial concentration of formic acid, t is reaction time, and k is the rate constant.

From Equation (1), plots of $\ln[(H_2O_2)_0 - (\%\text{ oxirane})]$ vs. reaction time, is expected to give a straight line for those reaction with negligible degradation of oxirane (12), with a slope equal to k(RCOOH). Deviation from linearity was observed in this study as the reaction progressed (Figure 1). This could be due to epoxide degradation. The values of the rate constant, obtained from the linear portion of the plots are presented in Table 2. These values ranged from 3.09×10^{-7} for epoxidation at 50°C to 5.42×10^{-7} $\text{Lmol}^{-1}\text{s}^{-1}$ for epoxidation at 70°C. This variation in the magnitude of k shows that an increase in reaction temperature increases the reaction rate. There is an over three–fold increase in the rate of reaction when the reaction temperature was increased from 50 to 70°C. These values are comparable with the values reported for soybean oil (16, 17) and rubber seed oil (14). The activation energy, E_a of producing *in situ* epoxidized methyl esters of PBSO was calculated from the Arrhenius relationship:

$$k = Ae^{-E_a/RT} \quad (2)$$

Where A is a constant known as the frequency factor, T is the absolute temperature, R is the gas constant.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3)$$

Table 2. Levels of epoxidation and rate constant of epoxidation of (PBSO) at various temperatures

Temperature	Maximum oxirane attained (%)	Time of maximum oxirance to be attained (h)	Rate constant of epoxidation $k \times 10^{-7}$ (Lmol^{-1})
50	1.34	9.5	3.00
60	1.36	5	4.06
70	1.40	4	5.42

Table 3. Thermodynamic properties for the epoxidation of PBSO

Temperature (K)	Kinetic parameters		
	ΔH	$\Delta S^{\#}$	$\Delta G^{\#}$
323	-2.63×10^3	-3.42	1.53
333	-2.72×10^3	-3.89	1.42
343	-2.80×10^3	-3.35	1.51

A plot of lnk against $^1/_T$ gives a straight line with a slope equal to $-^{Ea}/_R$. The activation energy, E_a of 51.963 kJmol^{-1}, was obtained from a linear Arrhenius plot for in *situ* epoxidation of methyl esters of PBSO by paracetic acid.

3.4 *Thermodynamics of Epoxidation*

The enthalpy of activation, ΔH, was calculated using the following equation (17):

$\Delta H = E_a - RT$. The enthalpy of activation was found to be 13.8 kJmol^{-1}. The average entropy of activation, $\Delta S^{\#}$, and free energy of activation $\Delta G^{\#}$ were obtained using the relationship (18):

$$k = \frac{RT}{Nh} e^{\Delta S/R} e^{-E/RT} \quad (4)$$

Where k is the rate constant; R gas constant; T, absolute temperature and h, Planck's constant.

The average values of the thermodynamic parameters were found to be $\Delta S^{\#} = -3.55\ \text{kJmol}^{-1}\text{k}^{-1}$ and $\Delta G^{\#} = 1.51\ \text{kJmol}^{-1}\text{k}^{-1}$. These values obtained for the $\Delta S^{\#}$ and $\Delta G^{\#}$ show that the reaction for the epoxidation of the methyl esters of parkia biglobosa seed oil is a non-spontaneous process (Table 3).

4 Conclusions

This study shows that it is possible to develop epoxides from locally available natural renewable resources such as parkia biglobosa seed oil. It also shows that epoxidation of the methyl esters of parkia biglobosa seed oil using *in situ* generated paracetic acid could be carried out in a moderate temperature range of 50–70°C.

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