Kinetics of *in situ* Epoxidation of Jatropha Seed Oil using Peroxyacetic Ac

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ABSTRACT

Jatropha seed meal was extracted with n-hexane and the oil obtained was found to have iodine value 157.37gI_2/100g, acid value 5.61 mg KOH/g and peroxide value 5.11 meq/kg. The fatty acid profile of the oil showed that oleic acid (31.35%), palmitic acid (20.92%) stearic acid (15.68%) and caprylic acid (10.45%) were the major fatty acid components. Epoxidation of the seed oil using peroxyacetic acid generated in situ by reacting various acetic acid/hydrogen peroxide molar ratios was carried out at different temperatures (323 — 343K). It was found that epoxidation with almost complete conversion of unsaturated carbon was attained by the in situ technique with rate constants of the order of 10^{-6} l mol^{-1} s^{-1} and activation energy, E_a of 65.75kJ mol^{-1} The enthalpy $\Delta H^{\neq}$, entropy $\Delta S^{\neq}$ and free energy $\Delta G^{\neq}$ of activation of epoxidation of Jatropha seed oil were determined to be 67.74kJmol^{-1} - 128.47J$mol^{-1}K^{-1}$ and 103.63kJmol^{-1} respectively.

INTRODUCTION

Epoxidation is the formation of an oxirane group by the reaction of peroxyacids (peracids) with olefinic and aromatic double bonds. Epoxides are extremely valuable commercially because of the many reactions they undergo. Epoxidised oils and epoxidised esters of unsaturated fatty acids are widely used in combination with other substances to impart a range of properties such as heat and light stability, superior ageing, low temperature flexibility, etc, on polyvinyl chloride and its copolymers[1]. The annual production of epoxidised esters used as plasticizers and additives for polyvinyl chloride exceeds 700,000tonnes[2]. Soybean oil is the major starting material for the production of epoxy esters[3]. Other epoxidised oils used commercially are prepared from linseed, olive and sunflower[4]. Although the physico-chemical characteristics of locally available vegetable oils have been reported to be similar to those of the standard oils used in the production of epoxy esters[4], reports on the utilisation of the former as starting material in epoxy ester production are scanty[5,6]. In this report, the epoxidation of *Jatropha multifida* seed oil using peroxyacetic acid is examined.

Jatropha multifida is a medium-sized woody plant with simple palmate or lobed leaves and umbel inflorescence. The plant has brightly coloured flowers which makes it an ornamental plant. The fruit tends to be capsular, green when tender, yellow when strong and dark-brown when dry. The dry fruits contain three seeds which are wind dispersed. The plant exudes a whitish sap, which is used locally in the treatment of sore gum (pyorrhea).

EXPERIMENTAL

Materials

Jatropha seed oil was extracted with n-hexane from ground Jatropha seeds collected from around Benin city, and was shortly afterwards (within 48h) analysed for iodine value, saponification value, peroxide value, acid value and free fatty acid[7]. Glacial acetic acid *(99.5%)* from BDH Ltd and hydrogen peroxide (30%) from MERCK were used without further purification.

Determination of fatty acid composition of Jatropha seed oil

Methyl esters of the fatty acid components of the extracted seed oil were prepared according to the official method of the American Oil Chemists Society[7]. The fatty acid composition was determined using gas chromatograph, GC, Pye Unicam 104 equipped with a flame ionisation detector, FID. The glass column, 1.5m long with 0.4mm diameter was packed with 12% PEGS acid-washed chromsorb W.Flow rates were 33cm^3 min^{-1} nitrogen carrier gas, 35cm^3 min^{-1} hydrogen. The

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** *Department of Chemical Engineering, University of Benin, Benin City* injector and detector temperature was maintained at 573K and the oven temperature was programmed at 5K from 383K to 573K with a 30min hold at 573^{0}C. Gas chromatographic peaks were identified by comparison of retention times with those of standard methyl esters of pure fatty acids. The proportions of the fatty acids present in the seed oil were calculated on the basis of the weight of their methyl esters and from retention times of known standards using a varian model COS 401 integrator.

Epoxidation of Jatropha seed oil

Epoxidation of Jatropha seed oil, JSO, was carried out by using peroxyacetic acid prepared *in situ* by reacting various amounts of acetic acid and hydrogen peroxide in the presence of a small amount (ca 4mmol) of sulphuric acid. In a typical experiment, a known amount of JSO was placed in a IL flask equipped with a reflux condenser, thermometer and stirrer, containing the required amount of acetic acid. The flask was allowed to attain the reaction temperature in a thermostat water bath (controlled at ± I K), and hydrogen peroxide which was pre-equilibrated at the reaction temperature was added. The stirring rate was controlled so that the oil in the reaction mixture was finely dispersed. The reaction was monitored by withdrawing aliquots of the reaction mixture at various intervals of time into a large excess of cold water in a separating funnel. The aqueous layer was drawn off and the oil layer was washed successively with water until it was acid free. The extent of epoxidation of the oil was determined by the method described by Pagout and Hauffenne[8]. Epoxidation was carried out at various temperatures (323 – 343K) using various amounts of acetic acid and hydrogen peroxide.

RESULTS AND DISCUSSION

Physico-chemical characteristics and fatty acid composition of Jatropha seed oil

The physico-chemical properties of JSO are shown in Table 1. The level of unsaturation of the oil, measured in terms of iodine value is 157.4 g 1_2/100g and is about the same order of magnitude as the values reported for linseed and soybean oils[9]. Thus JSO can be classified as semi-drying, with implication for the practical application of the oil in alkyd resin preparation. The peroxide value of JSO, 5.11 meq kg^{-1} is relatively low, lower than the range (20 – 40 $meqkg^{-1}$) within which the onset of rancidity is generally observed. It can be seen from the results in Table I that oleic acid (31.4%) and palmitic acid (20.9%) are the major fatty acid components of JSO.

Table 1 Physico-chemical characteristics and fatty acid composition of Jatropha seed oil

Parameter	Value
Physico-chemical characteristics	
Acid value (mgKOH/g)	5.61
Iodine value (g 1_2/100g)	157.37
Free fatty acid (% as oleic acid)	2.70
Peroxide value (meq/kg)	5.11
Saponification value (mgKOH/g)	190.12
Specific gravity (at 30^{0}C)	0.924
Fatty acid content (%.)	
Caprylic acid	4.46
Myristic acid	2.61
Palmitic acid	20.57
Stearic acid	15.64
Arachidic acid	5.68
Behenic acid	1.61
Lignoceric acid	0.98
Palmitoleic acid	3.59
Oleic acid	30.25
Linoleic acid	6.22

kinetics of epoxidation of JSO

The rates of epoxidation of JSO by peroxy acetic acid at various temperatures are shown in Fig. I. The results show that the initial increase in the rate of epoxidation with reaction time reached

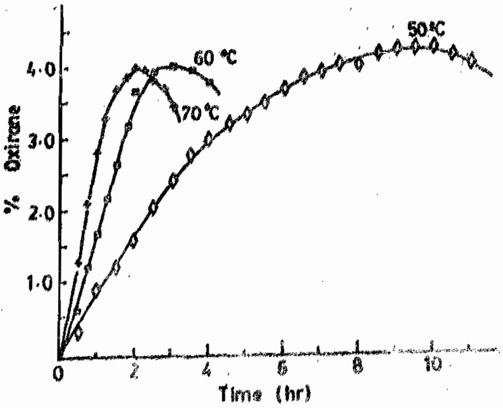


Fig. 1. Rate of in situ epoxidation of Jatropha seed oil by peroxyacetic acid at various temperatures.

maximum rates and decreased with further increase in reaction time. The time required for epoxidation to attain maximum rates and the maximum values attained at the different temperatures are shown in Table 2. The reductions in the rates of epoxidation observed for reaction are generally less than 12% (and were highest for epoxidation at 343K) and are ascribed to oxirane cleavage reactions.

Table 2: Kinetics of *in situ* epoxidation of Jatropha seed oil at different temperatures

Temp. (K)	Maximum oxirane content attained (% oxirane)	Time for max. oxirane to be attained (min)	Rate constant epoxidation 10^6k ($l mol^{-1}s^{-1}$)
323	3.03	245	1.38
333	3.79	150	3.37
343	3.74	94	5.06

The chemistry of *in situ* epoxidation may be explained using the following reaction scheme[10]

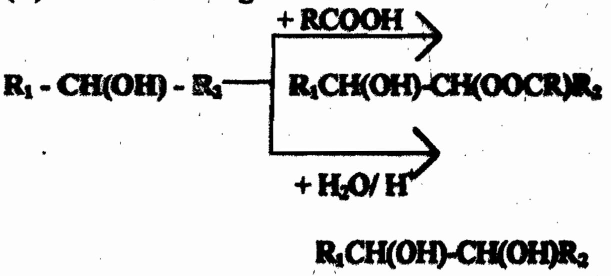
(a) Formation of peroxy acid

$$RCOOH + H_2O_2 \longleftrightarrow RCOOOH + H_2O$$

(b) Epoxidation

$$RCOOOH + R_1CH = CHR_2 \rightarrow R_1CHOCH - R_2 + RCOOH$$

(c) Oxirane clearage



$$R_1 - CH(OH) - R_2 \xrightarrow{+RCOOH} R_1CH(OH)\text{-}CH(OOCR)R_2$$

$$R_1 - CH(OH) - R_2 \xrightarrow[+H_2O/H^+]{} R_1CH(OH)\text{-}CH(OH)R_2$$

The rate of *in situ* epoxidation may be described using the relationship[11].

$$ln\{[H_20_2]_0 - [Ep]\} = k[RCOOH]_0 t + ln[H_2O_2]_0 \quad (1)$$

Where Ep is the epoxide and the subscript o denotes initial concentration.

The plot of ln{$[H_2O_2]$ - [Ep]} versus reaction time, t, should yield a straight line from which the rate constant of epoxidation can be determined. Fig. 2 shows such plots for the *in situ* epoxidation of JSO at the different temperatures.

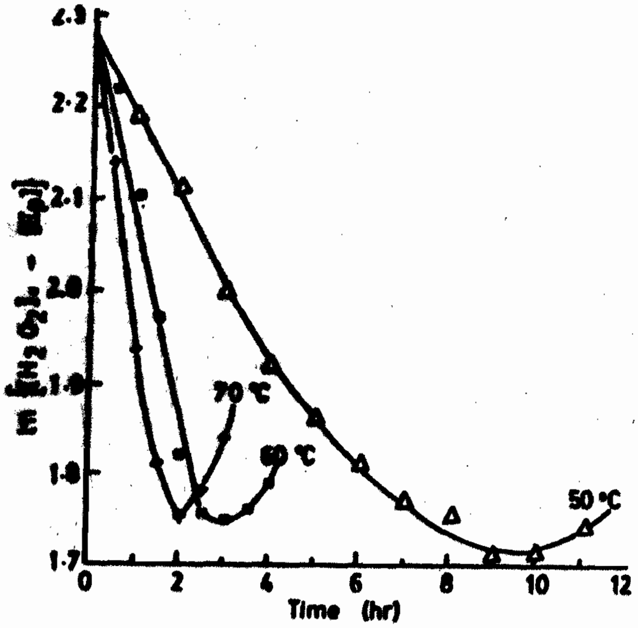


Fig. 2. Kinetics of in situ epoxidation of Jatropha seed oil by peroxyacetic acid.

The deviations from linearity were considered to be due to epoxide degradation and rate constants were obtained from the initial linear portions of the plots. The rate constants obtained for the *in situ* epoxidation of JSO by peroxyacetic acid (Table I) are of the order of 10^{-6} l $mol^{-1}s^{-1}$ and are comparable with the values reported for rubber seed oil[5], Khaya seed oil[6] and soybean oil[12, 13]. The values of the rate constant showed the expected dependence on temperature as a change in reaction temperature from 323 to 343K was accompanied by about seven-fold increase in the value of rate constant. The average value of activation energy for epoxidation, Ea, of 65.57kJmol^{-1} was obtained from the kinetic data in Table 1. The value of Ea obtained for the epoxidation of JSO compares closely with the values of 65.66kJmol^{-1}, 63.23kJmol^{-1} and 76.53kJmol $^{-1}$ reported for the epoxidation of rubber seed oil[5], methyl ester of palm olein[11] and soybean oil [12] respectively.

The enthalpy of activation, $\Delta H^{\neq}$, of epoxidation was calculated using the relationship[14]

$$\Delta H^{\neq} = E_a - RT \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Here R is the gas constant and T is the absolute temperature. An average value of 64.73kJmol^{-1} was obtained for $\Delta H^{\ddagger}$ for the *in situ* epoxidation of JSO. The entropy of activation, $\Delta S^{\ddagger}$, and free energy of activation, $\Delta G^{\ddagger}$, of epoxidation were calculated using the relationship[14].

$$k = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} e^{-E_a/RT} \quad \ldots\ldots\ldots (3)$$

Here N is Avogadro constant and h is Planck's constant. The values of the thermodynamic parameters were found to be $\Delta S^{\ddagger}$ -128.47kJmol^{-1} and $\Delta G^{\ddagger}$ - 102.63kJmol^{-1}.

CONCLUSION

The results show that epoxidation with minimum oxirane cleavage can be attained at moderate temperatures (ca 323K). The kinetic data obtained should prove useful in the scale-up production of epoxidised oils.

REFERENCES

1. Vijiayagopalan, K. and Gopolakrishnan, K. S., Indian Rubb. Board Bull., 1971, 11(2), 52.

2. United States International Trade Commission (USTIC) Synthetic Organic Chemicals, US Production and Sales (1962 — 1982) US Government Printing Office, Washington, DC, 1983.

3. Greenspan, F.P. and Gall, R. I., Ind. Eng. Chem., 1953, 45(12), 2722.

4. Milliahi, V.C., Murthy, D. and Rao, S.D., Res. Ind., 1969, 14, 74.

5. Aigbodion, A. I., Okieimen, F.E. and Bakare, O. I., Nig. J. Appl. Sci., 1999, 17, 27.

6. Okieimen, F.E. and Okieimen, C. O., J. Chem. Soc. Niger. (in press).

7. Association of Official Analytical Chemists (AOAC), Official Methods of Analysis, 13th ed., AOAC, Washington DC, 1980.

8. Pagout, C. and Hautfenne, A., Standard Methods of Analysis of Oils, Fats and Derivatives, 7th edn., Blackwell Scientific Publishing, Oxford, 1987.

9. Okieimen F. E., Ind. Jour. Sci. Ind. Res., 2000, 59, 563.

10. Rangaraja, B., Harvey, A., Grulke, E.A. and Culman, P.D., J. Am. Oil Chem. Soc., 1995, 72 (10), 1161.

11. Gan, L. H., Goh, S. H. and Ooi, K. S., J. Amer. Oil Chem. Soc., 1992, 69, 347.

12. Princen, L. H., J Am Oil Chem. Soc., 1979, 56, 845.

13. Zaher, F. A., El-Mallah, M. H. and El-hafnawy, M.A., J. Am. Oil Chem. Soc., 1989, 66, 698.

14. Frost, A.A and Pearson, R.G., Kinetics and Mechanism, 2nd edn., John Wiley and Sons Inc., New York, 1961.

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