Epoxidation of Karanja (*Pongamia glabra*) Oil by H_2O_2

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ABSTRACT: Epoxidation of karanja oil (KO), a nondrying vegetable oil, was carried out with peroxyacetic acid that was generated *in situ* from aqueous hydrogen peroxide and glacial acetic acid. KO contained 61.65% oleic acid and 18.52% linoleic acid, respectively, and had an iodine value of 89 g/100 g. Unsaturated bonds in the oil were converted to oxirane by epoxidation. Almost complete epoxidation of ethylenic unsaturation was achieved. For example, the iodine value of the oil could be reduced from 89 to 19 by epoxidation at 30°C. The effects of temperature, hydrogen peroxide-to-ethylenic unsaturation ratio, acetic acid-to-ethylenic unsaturation ratio, and stirring speed on the epoxidation rate and on oxirane ring stability were studied. The rate constant and activation energy for epoxidation of KO were 10^{-6} $L\cdot mol^{-1}\cdot s^{-1}$ and 14.9 $kcal\cdot mol^{-1}$, respectively. Enthalpy, entropy, and free energy of activation were 14.2 $kcal\cdot mol^{-1}$, –51.2 $cal\cdot mol^{-1}\cdot K^{-1}$, and 31.1 $kcal\cdot mol^{-1}$, respectively. The present study revealed that epoxides can be developed from locally available natural renewable resources such as KO.

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KEY WORDS: Hydrogen peroxide, *in situ* epoxidation, karanja oil, kinetics, peroxyacetic acid, sulfuric acid.

Renewable raw materials are environmentally friendly, biodegradable, low cost, and readily available (1). The possible use of these resources as a substitute for petrochemical derivatives has attracted the attention of many researchers (2). Plant oils and animal fat are members of this group of renewable resources.Vegetable oils rich in oleic, linoleic, and linolenic acyl groups may be used to introduce functional groups such as epoxides.

Epoxidation of plant oils, commonly termed "vegetable oils," is a commercially important reaction because the epoxides obtained from these renewable raw materials and from methyl oleate, their transesterification product, have applications in such materials as plasticizers and polymer stabilizers (3). Owing to the high reactivity of the oxirane ring, epoxides also act as a raw material for a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds, and polymers, e.g., polyesters, polyurethanes, and epoxy resins.

Epoxidation of long-chain olefins and unsaturated FA derivatives of vegetable oils such as soybean, linseed, rapeseed, olive, corn, safflower, melon seed, and cotton seed is carried out on an industrial scale (4). Today, one of the most important epoxidized vegetable oils is epoxidized soybean oil. Its worldwide production is about 200,000 t/yr (5).

Four technologies are used to produce epoxides from olefinic-type molecules: (i) epoxidation with percarboxylic acids (6), which is widely used in industry and can be catalyzed by acids or by enzymes (7); (ii) epoxidation with organic and inorganic peroxides, which includes alkaline and nitrile hydrogen peroxide epoxidation as well as transition metal-catalyzed epoxidation (8); (iii) epoxidation with halohydrins, using hypohalous acids (HOX) and their salts as reagents for the epoxidation of olefins with electron-deficient double bonds (6); and (iv) epoxidation with molecular oxygen (6).

Halohydrins are prepared by the addition of HOX to olefinic compounds; subsequent treatment with alkali produces the epoxide. This system is highly unfriendly environmentally, apart from being a classical stoichiometric synthesis that is characterized by an extensive use of reactants and the production of by-products such as dihalides, halogen ethers, and salts.

Epoxidations with molecular oxygen that are catalyzed by compounds of elements belonging to groups IV-B, V-B, and VI-B show high selectivity but low activity. With elements from groups I-B, VII-B, and VIII-B, the epoxidations are more active but less selective. Silver is a unique catalyst for heterogeneous epoxidation with molecular oxygen, but unfortunately, it is mostly restricted to a few substrates such as ethylene and butadiene. In the epoxidation of other alkenes, it gives very low yields (6). Thus, although O_2 is the cheapest and most environmentally friendly oxidant, its scope is limited to a small number of simple petrochemicals (9). For the vegetable oils investigated, epoxidation with O_2 leads to the degradation of the oil to smaller volatile compounds such as aldehydes and ketones as well as short-chain dicarboxylic acids. Therefore, oxidation with O_2 is not an efficient method for epoxidation of vegetable oils.

From the foregoing discussion, it is evident that for clean and efficient epoxidation of vegetable oils, the available technologies that are suitable are epoxidation with percarboxylic acids and epoxidation with organic and inorganic peroxides. These technologies can be rendered cleaner by using heterogeneous catalysts in place of the traditional homogeneous catalysts (10).

The FA composition of karanja *(Pongamia glabra)* oil (KO) was as follows: specific gravity (at 30°C) = 0.923; acid value (mg KOH/g) = 34.71; iodine value (g iodine/100 g) = 89; saponification value (mg KOH/g) = 187.78; oleic acid (18:1) = 61.65%; linoleic acid (18:2) = 18.52%. These values are similar to those of other vegetable oils currently used for the commercial production of epoxy esters (11,12). However, epoxida-

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tion studies for KO as a starting material have not been addressed. The main purpose of this study is to develop value-added products from locally available renewable resources in India. The epoxidation of KO by peroxyacetic acid generated *in situ* is therefore explored here. KO is abundantly available in India and neighboring countries, where it is used as a lighting oil (fuel), in pharmacy, in soaps, and in tanning.

EXPERIMENTAL PROCEDURES

Materials. KO was obtained from Mandal Oil Ltd. (Jhargram, West Bengal, India). Glacial acetic acid, 100% (AR Grade), aqueous hydrogen peroxide (~30 wt%), and iodine trichloride were procured from Merck (Mumbai, Maharashtra, India). Sulfuric acid was obtained from Qualigens Fine Chemicals (Mumbai, Maharashtra, India). HBr in acetic acid was obtained from SISCO Research Laboratories (Mumbai, Maharashtra, India) and then diluted with glacial acetic acid to prepare 0.1 N HBr.

Experimental setup. Epoxidation reactions were carried out in a fully baffled, mechanically agitated contactor (6.5 cm i.d. and 250 mL capacity) made of glass that was equipped with a 2-cm diameter six-bladed glass turbine impeller and reflux condenser. The contactor assembly was immersed in a thermostatic water bath, whose temperature could be controlled within ±1°C.

Epoxidation procedure. The epoxidation method reported by Swern (13) was used. The required amount of KO was placed in the contactor just described. The calculated amounts of acetic acid and sulfuric acid were added, and the mixture with oil was stirred for 30 min. Then 17 g of 30% aqueous hydrogen peroxide was added dropwise over 30 min. After addition of hydrogen peroxide, the reaction was continued to achieve the desired time duration. The reaction mixture was stirred continuously to avoid zones of high peroxide concentration that could lead to explosive mixtures. The course of reaction was followed by withdrawing aliquots, the first being taken after 1 h, considering the completion of hydrogen peroxide addition as being zero time. The collected samples were then extracted with diethyl ether and washed with water until they were acid free. The washed samples were analyzed for oxirane content and iodine value.

Analytical techniques. The percentage of oxirane oxygen was determined by the direct method with hydrobromic acid solution in acetic acid. Iodine value was obtained using the Wij method (14), and glycol content was determined by the method reported by May (15). From the oxirane content values, the relative fractional conversion to oxirane was calculated from the following expression:

$$\text{relative conversion to oxirane} = \frac{OO_e}{OO_t} \qquad [1]$$

where OO_e is the experimentally determined content of oxirane oxygen in 100 g of oil and OO_t, theoretical maximum oxirane oxygen in 100 g oil, which was determined to be 5.31% from the Equation 2 (16):

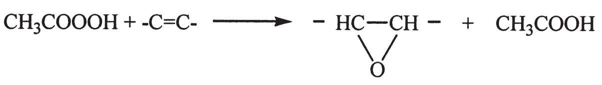
$$OO_t = \left\{ \frac{(IV_o/2A_i)}{[100 + (IV_o/2A_i)A_o]} \right\} \times A_o \times 100 \qquad [2]$$

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

RESULTS AND DISCUSSION

Epoxidation runs were conducted with the following range of variables: stirring speed, 800 to 2500 rpm; temperature, 30 to 85°C; hydrogen peroxide-to-ethylenic unsaturation ratio (mole per mole), 1.1 to 2.5; acetic acid-to-ethylenic unsaturation ratio (mole per mole), 0.3 to 0.8. The catalyst concentration was expressed as the percentage of "total weight of hydrogen peroxide and acetic acid added together" (17). The epoxidation reaction was followed in each case by plotting relative fractional conversion to oxirane as a function of reaction time. The reaction mechanism as suggested by Gan *et al.* (18) is as follows:

$$\mathrm{CH_3COOH + H_2O_2 \overset{H^+}{\longleftrightarrow} CH_3COOOH + H_2O} \qquad [3]$$



$$\mathrm{CH_3COOOH + {-C{=}C-} \longrightarrow -\underset{\diagdown\,O\,\diagup}{HC{-}CH}- + CH_3COOH} \qquad [4]$$

$$\mathrm{-\underset{\diagdown\,O\,\diagup}{HC{-}CH}- + CH_3COOH \longrightarrow -CH(OH)-CH(OCOCH_3)-} \qquad [5]$$

Effect of stirring speed. To investigate the effect of stirring speed, 28.8 g of oil (0.1 mole) was treated with 17 g of hydrogen peroxide (1.5 moles of hydrogen peroxide per mole of ethylenic unsaturation), 3 g acetic acid (0.5 moles of acetic acid per mole of ethylenic unsaturation), and 0.40 g sulfuric acid (2% of the hydrogen peroxide and acetic acid added together) at 30°C. To study the effect of mass transfer resistance, the reaction was performed at different stirring speeds ranging from 800 to 2500 rpm. The relative conversions to oxirane at different stirring speeds are shown in Table 1. The oxirane formation rate (moles of oxirane$\cdot L^{-1}\cdot s^{-1}$) was not substantially affected by stirring speeds beyond 1500 rpm, and hence it can be safely assumed that the reaction is free from mass transfer resistance beyond 1500 rpm under the given conditions of temperature and catalyst loading. All further experiments were performed at 2500 rpm to ensure that the reaction is kinetically controlled.

Effect of acetic acid-to-ethylenic unsaturation mole ratio. The effect of acetic acid concentration on the level of epoxidation of KO is shown in Figure 1. Acetic acid takes part in the overall reaction as a catalyst in the formation of oxirane rings (Eq. 4) and as a reactant in the hydrolysis of the oxirane rings (Eq. 5). To attain the maximum oxirane oxygen content, an optimal level of the acid can be used where both the effects are balanced with respect to the amount of acid required in the formation of peroxyacetic acid. Figure 1 shows the results obtained for the four levels studied (0.3, 0.5, 0.65, and 0.8 moles per mole of ethylenic unsaturation). The most favorable results occurred at the 0.5 mole ratio. Table 2 shows the effect of ace-

TABLE 1
Relative Conversion to Oxirane at Different Stirring Speeds

	Stirring speed, rpm							
	800		1500		2000		2500	
t (*h*)	5	10	5	10	5	10	5	10
Oxirane oxygen[a] (%)	1.44	2.31	1.66	2.21	1.7	2.14	1.6	2.21
Iodine value[b,c] (IV)	57.73	45.04	54.56	42.82	56.67	45.25	58.37	46.95
Conversion of IV[d] (x)	0.35	0.49	0.38	0.51	0.36	0.49	0.34	0.47
Relative conversion to oxirane	0.27	0.43	0.31	0.41	0.32	0.40	0.30	0.41

[a] Experimentally determined oxirane oxygen content (OO_e).
[b] IV_0: initial iodine value = 89.
[c] Experimentally determined iodine value.
[d] Conversion of IV (*x*): conversion of double bonds as related to IV_o, calculated as $x = [(IV_o - IV)/IV_o)]$.

tic acid concentration on iodine value of the epoxidized oil. Considering the stability of the epoxide, 47% iodine value conversion could be achieved at a 0.5 mole ratio with a relative conversion to oxirane of 0.41 at 30°C.

Effect of hydrogen peroxide-to-ethylenic unsaturation mole ratio. The effect of the hydrogen peroxide-to-ethylenic unsaturation mole ratio on relative fractional conversion to oxirane was studied in the ratio range of 1.1 to 2.5.The reaction rate increased as the concentration of hydrogen peroxide in the system increased (Fig. 2). Although the maximum relative conversion to oxirane was attained for 2.0 moles per mole of ethylenic unsaturation, the stability of the oxirane ring was very poor (Fig. 2). However, little difference was observed in the final conversion attained for mole ratios of 1.5 and 2.0. For higher H_2O_2 concentrations at the same temperature, the relative conversions to oxirane decreased more rapidly. In the experimental range explored, the optimal concentration appeared to be 1.5 moles of H_2O_2 per mole of ethylenic unsaturation. Similarly, Table 2 shows the iodine value conversions obtained for different H_2O_2 concentrations.

Effect of temperature. To prevent the uncontrolled exothermic reaction, two temperature levels, separated by 10°C, were used in each run. The lower temperature was maintained during addition of H_2O_2; immediately thereafter the temperature was allowed to reach the higher level and was maintained there until the end of the reaction. Figure 3 represents the result obtained at 30°C and for three levels: 35 to 45°C, 55 to 65°C, and 75 to 85°C. Increasing temperatures favored the formation of peroxyacetic acid. This resulted in a more rapid epoxidation rate, but also in higher rate of hydrolysis (oxirane cleavage) of the product. The time required for epoxidation to attain the maximal oxirane content at different temperatures is shown in Figure 3. Reactions at lower temperatures had lower rates but gave a more stable oxirane ring (Table 2). These results suggest that the optimal epoxidation level was obtained in a shorter time at moderate reaction temperature range (55 to 65°C), at which the hydrolysis rate was not high. The highest fractional conversion (0.79) to oxirane was, however, obtained at 85°C in a short period of 3.5 h.

To check the effect of using one single temperature level, one set of experiments was carried out at 60°C. Our results were equivalent to those obtained when using two temperature levels. Higher operating temperatures gave higher initial rates of reaction, and the maximum oxirane oxygen content was attained in less time. There is a practical reason for using a lower temperature during the addition of hydrogen peroxide: The exothermic nature of the reaction may cause an excessive temperature rise in the peroxide-reacting mixture, with potential explosion hazards.

Epoxidation kinetics. An *in situ* epoxidation reaction generally takes place in two steps: (i) formation of peroxyacetic acid and (ii) reaction of peroxyacetic acid with the unsaturated bond. If the first step is rate determining and the concentration of peroxyacid is assumed to be constant throughout the reaction, then the following rate law applies (18):

$$\frac{d[\mathrm{EP}]}{dt} = k\{[\mathrm{H_2O_2}]_o - [\mathrm{EP}]\}\cdot[\mathrm{RCOOH}]_o \qquad [6]$$

where the subscript *o* denotes the initial concentration and EP denotes epoxide.

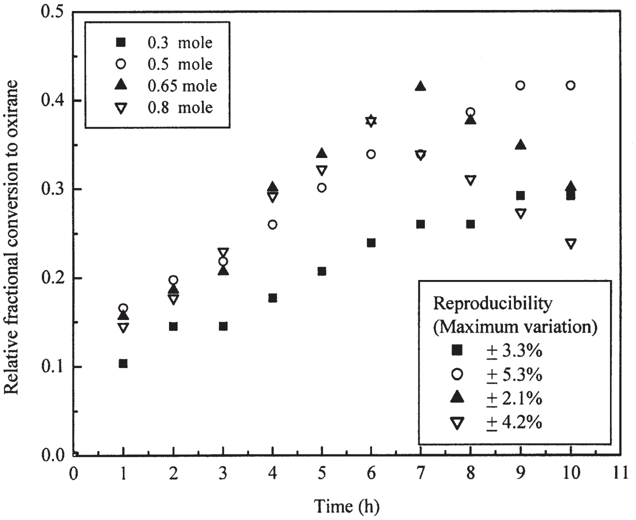


FIG. 1. Effect of acetic acid per mole of ethylenic unsaturation on relative fractional conversion to oxirane. Conditions: karanja oil, 28.8 g; H_2O_2, 17 g; sulfuric acid (2%), 0.40 g; stirring speed, 2500 rpm; temperature, 30°C.

TABLE 2
Effects of Hydrogen Peroxide and Acetic Acid Concentrations and Temperature on Iodine Value

	mole H_2O_2/mole unsaturation							
	1.1		1.5		2.0		2.5	
t (h)	5	10	5	10	5	10	5	10
Iodine value[a,b] (IV)	63.45	57.73	58.37	46.95	41.87	26.01	40.29	19.03
Conversion of IV[c] (x)	0.28	0.35	0.34	0.47	0.52	0.70	0.54	0.78
	mole CH_3COOH/mole unsaturation							
	0.3		0.5		0.65		0.8	
t (h)	5	10	5	10	5	10	5	10
Iodine value[b] (IV)	61.45	53.29	58.37	46.95	56.47	41.87	54.56	30.45
Conversion of IV[c] (*x*)	0.30	0.40	0.34	0.47	0.36	0.52	0.38	0.65
	Temperature (°C)							
	30		45		65		85	
t (h)	5	10	5	10	4	8	2.5	5
Iodine value[a,b] (IV)	58.37	46.95	52.66	30.89	40.66	22.2	34.26	13.32
Conversion of IV[c] (*x*)	0.34	0.47	0.40	0.65	0.54	0.75	0.61	0.85

[a] IV_o: initial iodine value = 89.

[b] Experimentally determined iodine value.

[c] Conversion of IV (*x*): conversion of double bonds as related to IV_o, calculated as $x = [(IV_o - IV)/IV_o]$.

Hence,

$$\ln\{[H_2O_2]_o - [EP]\} = -k[RCOOH]_o \cdot t + \ln[H_2O_2]_o \qquad [7]$$

According to Equation 7, a plot of ln $\{[H_2O_2]_o$ - [EP]} vs. time should yield straight lines for those reactions with negligible degradation of oxirane. Deviations from linearity were observed for the reaction with substantial ring opening. In such cases, rate constants were obtained from the initial slopes. Figure 4 shows plots for *in situ* epoxidation of KO at different temperatures. The rate constants obtained for the reaction were of the order of 10^{-6} L·mol^{-1}·s^{-1} (Table 3) and are in agreement with the values reported for methyl esters of palm olein and soybean oil (18,19). Activation energy for the *in situ* epoxidation of KO obtained from the Arrhenius plot (Fig. 5) was 14.9 kcal·mol^{-1}. This value is comparable with values of 17.6 and

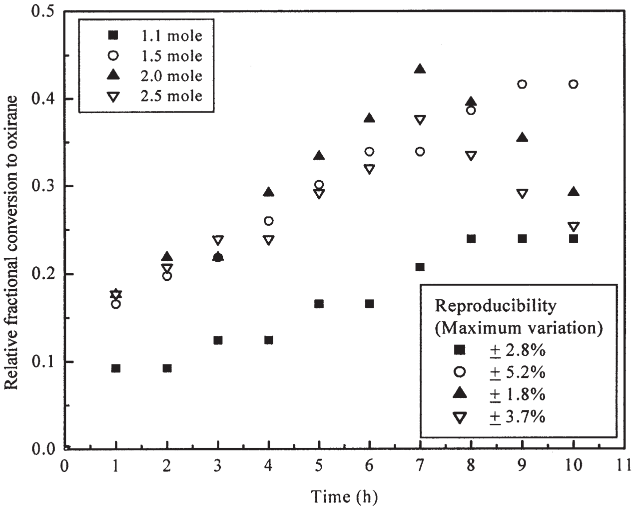


FIG. 2. Effect of H_2O_2 per mole of ethylenic unsaturation on relative fractional conversion to oxirane. Conditions: karanja oil, 28.8 g; acetic acid, 3 g; sulfuric acid (2%), 0.40 g; stirring speed, 2500 rpm; temperature, 30°C.

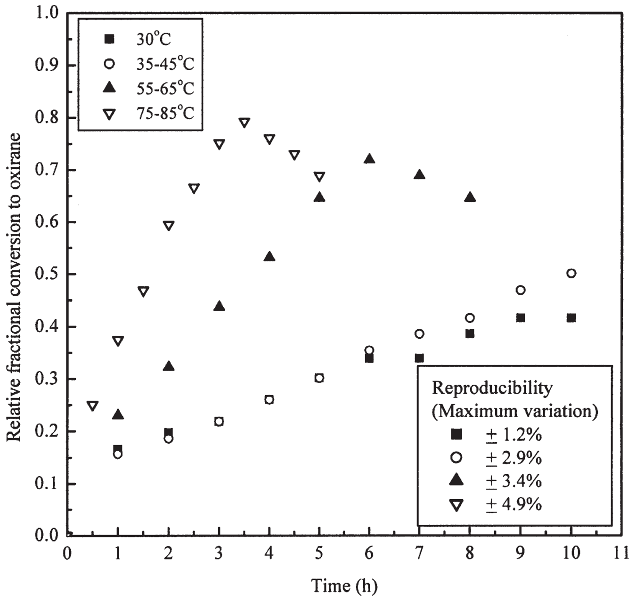


FIG. 3. Effect of temperature on relative fractional conversion to oxirane. Conditions: karanja oil, 28.8 g; H_2O_2, 17 g; acetic acid, 3 g; sulfuric acid (2%), 0.40 g; stirring speed, 2500 rpm.

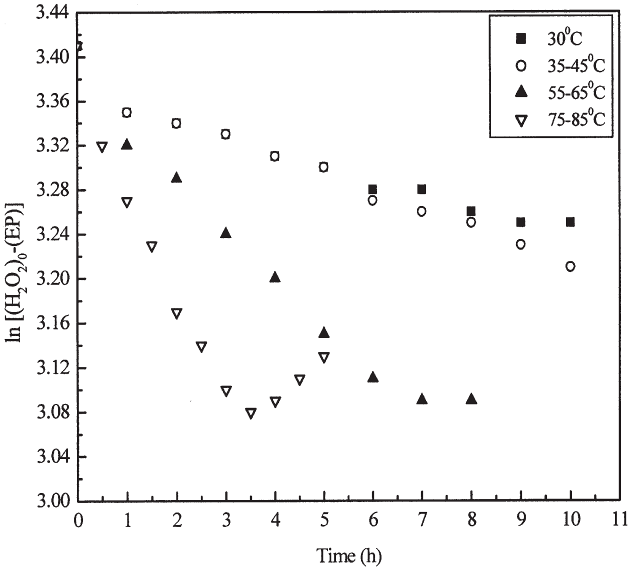


FIG. 4. Plot of ln $\{[H_2O_2]_o - [EP]\}$ vs. time for epoxidation of karanja oil by peroxyacetic acid.

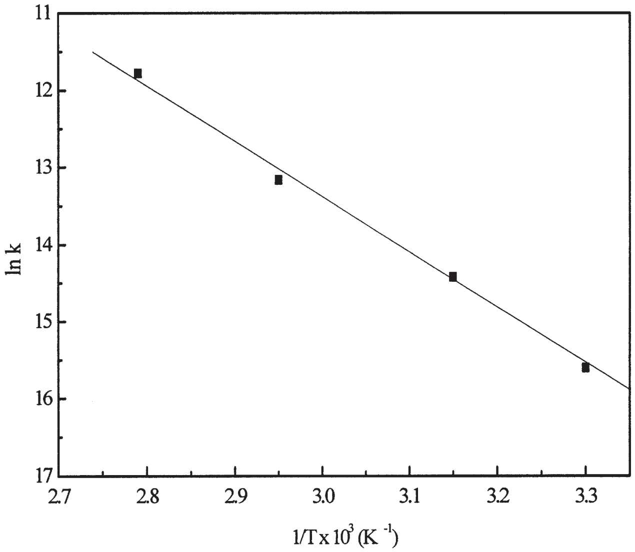


FIG. 5. Arrhenius plot for epoxidation of karanja oil by peroxyacetic acid.

TABLE 3
Rate Constants for Epoxidation of Karanja Oil at Various Temperatures

Temperature (°C)	Maximum oxirane attained (%)	Time to obtain maximum oxirane (h)	Rate constant of epoxidation, $k \times 10^6$ ($L \cdot mol^{-1} \cdot s^{-1}$)
30	2.21	10	0.17
45	2.66	10	0.54
65	3.82	6	1.91
85	4.21	3.5	7.60

15.8 kcal·mol^{-1} reported in References 18 and 19, respectively.

Thermodynamic properties of the KO epoxidation. The enthalpy of activation, ΔH, was calculated using Equation 8 (19):

$$\Delta H = E - RT \ldots \quad [8]$$

where R is the gas constant and T is the absolute temperature. The enthalpy of activation was found to be 14.2 kcal·mol^{-1}. The average entropy of activation, ΔS, and the free energy of activation ΔF, were obtained using the relationship (6)

$$k = \frac{R \cdot T}{N \cdot h} \cdot e^{\Delta S/R} \cdot e^{-E/R.T} \quad [9]$$

where k is the rate constant, N is Avogadro's constant, and h is Planck's constant. The average values of the entropy and free energy of activation were –51.2 cal·mol^{-1}·K^{-1} and $\Delta F = 31.1$ kcal·mol^{-1}, respectively.

The epoxidation of KO using *in situ*-generated peroxyacetic acid could be carried out at moderate temperature range of 55 to 65°C. The kinetic and thermodynamic parameters of the epoxidation indicate that an increase in the process temperature would increase the rate of epoxide formation. The epoxidation reaction of KO falls into a kinetically controlled regime at stirring speeds >1500 rpm. From the relative conversion data obtained for various reaction parameters, one can conclude that it is possible to develop value-added products such as epoxides from locally available natural renewable resources such as nonedible oils. Further studies are underway to maximize the oxirane content of the oil, so that the same can be taken to the theoretical maximum value.

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