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EPOXIDATION OF RUBBER SEED OIL WITH PERFORMIC ACID

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SUMMARY

A study of the epoxidation of rubber seed oil with peroxyformic acid generated in situ by the reaction of 30% hydrogen peroxide with formic acid, was carried out at 303, 323, 333 and 343K. Epoxidation of rubber seed oil by performic acid is favoured by increase in temperature forming a product of high oxirane content. Kinetic analysis of the data shows that rate of epoxidation increases with temperature and the value of the rate constant (k) is of the order of 10^{-5} L mol^{-1} s^{-1}. The activation energy (E_a) and enthalpy (ΔH) of activation were found to be 57.0 KJ mol^{-1} and 54.3 KJ mol^{-1} respectively. The kinetic data obtained from this study were compared with results from epoxidation of rubber seed oil with peracetic acid.

Key words: epoxidation, oxirane, performic acid, rubber seed oil

INTRODUCTION

Epoxidised vegetable oils find wide applications as plasticizer/stabilizer for vinyl polymers and in organic synthesis (Afolabi *et al.*, 1989; Sperling & Manson, 1983). Vegetable oils such as vernonia oil naturally containing epoxy (oxirane) groups are well known (Ayorinde *et al.*, 1990 & Bryant *et al.*, 1992). However, due to the high demand for epoxidised vegetable oils as a result of the expansion in various fields of applications, ordinary triglyceride oils like linseed and soybean oils are now frequently epoxidised to supplement supply of the product from natural sources.

Current commercial requirements for epoxidised vegetable oils as plasticiser/stabilizer suggest that they have oxirane content of at least 5% and low iodine value (Sack & Wohlers, 1959). Epoxidation of vegetable oil is conveniently

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effected by a wide range of peracid such as peracetic, performic, perbenzoic acids, *etc*, usually generated by reacting hydrogen peroxide with the relevant organic acid catalysed by a mineral acid like sulphuric acid. The role of the organic acid is to shuttle the active oxygen from the aqueous phase to the oil phase as the hydrogen peroxide and the unsaturated oil alone do not react to any significant extent. The two routes of epoxidising vegetable oil are (i) the method in which the peracid acid is preformed and then used for epoxidation and (ii) the procedure in which the peracid is generated *in situ* in the reaction vessel. The latter method has been preferable for safety reasons.

Extensive work on the *in situ* epoxidation of rubber seed oil (RSO) by peracetic acid have been carried out in our laboratory (Aigbodion *et al*, 1999, 2000). These studies show that the *in situ* technique of epoxidising RSO can be modified advantageously for optimum yield of epoxide. Such modifications include use of acetic acid to oil mole ratio ≥ 0.40 and reaction temperature of about 333K resulting in minimum oxirane ring opening thereby yielding a product of high % oxirane suitable as plasticizer/stabilizer.

This paper extends the study of epoxidation of RSO by substituting formic acid for acetic acid as the organic acid for shuttling the active oxygen. There has been no report on the use of formic acid in the epoxidation of RSO to the best of the knowledge of these authors. The objective of this study was essentially to determine the efficiency of epoxidising RSO by performic acid generated *in situ* in comparison to the use of peracetic acid.

MATERIALS AND METHODS

Rubber seed oil (RSO) used in the study was obtained by solvent extraction from the seed using *n*-hexane (333-353K). The physicochemical properties of the oil determined according to IUPAC standard method (Paquot & Hauffenne 1987) are given in Table 1. The main saturated fatty acids are myristic (2.2%), palmitic (7.6%) and stearic (10.7%) and the main unsaturated fatty acids being oleic (20.0%), linoleic (36.0%) and linolenic (23.5%). Formic acid and 30% hydrogen peroxide were obtained from MERCK.

Epoxidation

A series of epoxidation reactions were carried out at 303, 323, 333 and 343K using performic acid generated *in situ* by the reaction of 30% hydrogen peroxide and formic acid. In each experiment, RSO (0.14 mole), formic acid (0.09 mole) and 30% hydrogen peroxide (0.44 mole) were used according to the method described previously (Aigbodion *et al.*, 1999). Calculated amounts of RSO and formic acid were placed in 500ml round bottom flask fitted with a reflux condenser, magnetic stirrer and thermometer. The required amount of 30% hydrogen peroxide was added

to the oil dropwise over a two-hour period with constant stirring at predetermined temperature. Progress of reaction was monitored by measurement of the oxirane content of the reaction medium as previously described (Aigbodion *et al.*, 1999).

Table 1. *Physico – chemical properties of rubber seed oil (RSO)*

Properties	RSO
Specific gravity (30°C)	0.912
Acid value (mg KOH/g)	9.03
Iodine value (g I_2/100g)	158.73
Saponification value (mg KOH/g)	198.6

RESULTS AND DISCUSSION

Effect of temperature on epoxidation of RSO with performic acid

Fig. 1 shows the plots of % oxirane versus reaction time for the epoxidation of RSO by performic acid at different temperatures. These plots illustrate that the reaction proceeds faster at higher temperature. At 303K, the reaction rate increases somewhat slowly with time. However, at temperature of 323K and above, the plots are linear at the early stages of the reaction (up to about 2h of reaction) when downward curvature is observed. This region is believed to mark the beginning of oxirane ring opening reaction that could lead to a decrease in the epoxide content of the reaction mixture. Percent oxirane of the reaction medium obtained at this region are compared to those obtained at similar region during the epoxidation of RSO with peracetic acid (Aigbodion *et al.*, 1999) in Table 2. Although there is no appreciable difference in the maximum % oxirane of the reaction medium when peracetic acid and performic acid are used in the epoxidation, however, there is marked difference in the reaction times. The time of attaining these maximum epoxide content decreases as the reaction temperature increases and are much shorter for epoxidation with performic acid thereby making epoxidation of RSO with performic acid more economical.

Table 2. *Estimated maximum extent of epoxidation (% oxirane) before oxirane cleavage during epoxidation of RSO with peracetic acid and performic acid*

Temperature of reaction (K)	Peracetic acid		Performic acid	
	% Oxirane	Time (h)	% Oxirane	Time (h)
323	3.0	4	3.0	2
333	3.8	2½	3.1	1½
343	3.7	1½	3.9	1

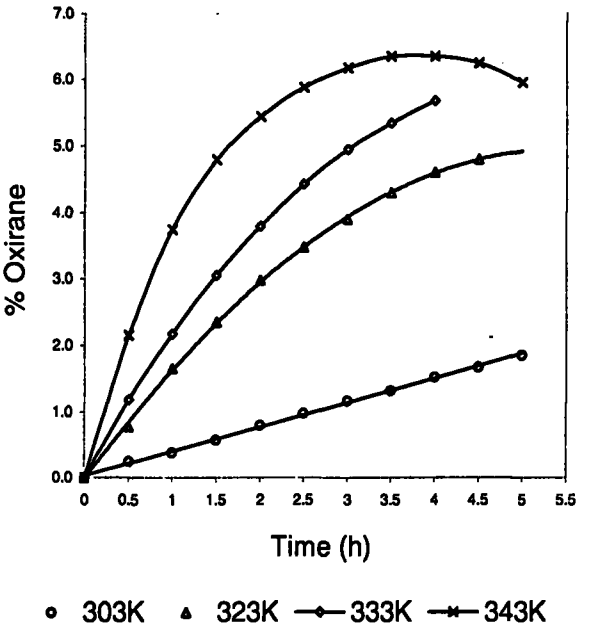

Fig. 1. Plots of % oxirane versus reaction time for epoxidation of RSO with performic acid generated *in situ* at different temperatures

Kinetic analysis

The rate expression for the epoxidation of vegetable oils has been given as (Gran *et al.*, 1992);

$$ln\,([H_2O_2]_o - [\%\ oxirane]) = -\,k\,[HCOOH]_o\,t + ln\,[H_2O_2]_o \qquad \text{------ (1)}$$

where $[H_2O_2]_o$ and $[HCOOH]_o$ are the initial concentrations of hydrogen peroxide and formic acid respectively, k is the rate constant, and t is the time of reaction. From equation 1 plots of $ln\,([H_2O_2]_o - [\%\ oxirane])$ versus t is expected to be linear and the gradient equals $-\,k\,[HCOOH]_o$. Fig. 2 shows the plots of equation 1 for the epoxidation of RSO by formic acid at different temperatures. It can be seen in fig. 2 that these plots are not linear throughout the course of reaction except for the epoxidation at 303K. Only the initial portions of these plots are linear. The curved portion of these plots corresponding to the later stages of the reaction also tend to support the claims of simultaneous occurrence of epoxidation and oxirane ring opening reaction at the later period of reaction.

The values of the rate constant, k calculated for the linear portion of the plots in fig. 2 are also compared with those obtained for the epoxidation of RSO with peracetic acid in Table 3. The values of k range from 1.20×10^{-5} at 303K to 14.62

$x10^{-5}$ L mol^{-1} s^{-1} at 343K. These values represent five fold, seven fold and fourteen fold increase in reaction rate when epoxidation was carried out at 323, 333 and 343K respectively. While the magnitude of the rate constant is of the order of 10^{-5} L mol^{-1} s^{-1} for the epoxidation of RSO by performic acid, it is of the order of 10^{-6} L mol^{-1} s^{-1} for the epoxidation with peracetic acid. These larger *k* values for the epoxidation of RSO with performic acid can be attributed to the stronger acidic nature of formic acid which makes it more effective than acetic acid in shuttling the active oxygen from aqueous phase to the oil phase, the main centre of epoxidation.

Table 3. *Values of the rate constant, k, calculated for the epoxidation of RSO by both peractic acid and performic acid generated in situ at different temperatures*

Temp. of reaction (K)	Rate constant	
	Peractic acid $k \times 10^6$ (L mol^{-1} s^{-1})	Performic acid $k \times 10^5$ (L mol^{-1} s^{-1})
303	0.20	1.20
323	1.34	5.13
333	3.32	7.00
343	5.01	14.62

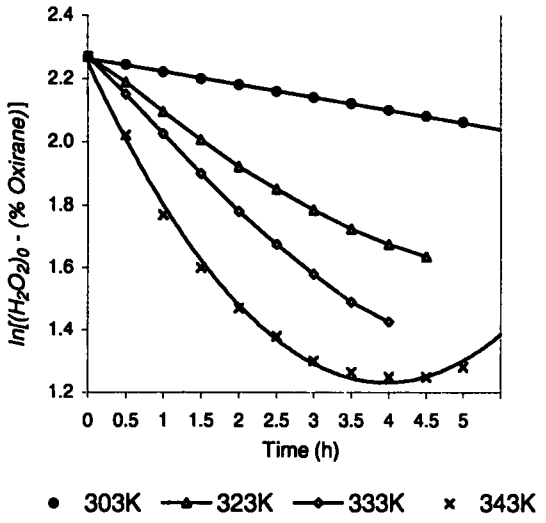

Fig. 2. Plots of *ln* $[(H_2O)_0 - (\%$ oxirane$)]$ versus reaction time for epoxidation of RSO with performic acid generated *in situ* at different temperatures

Thermodynamics

The activation energy (E_a) and the enthalpy of activation (ΔH) of epoxidation of RSO with performic acid are respectively 57 KJ mol^{-1} and 54.3 KJ mol^{-1}. These values are lower than $E_a \simeq 65.8$ KJ mol^{-1} and $\Delta H \simeq 63.3$ KJ mol^{-1} reported earlier for the epoxidation of RSO with peracetic acid (Aigbodion *et al.*, 1999). Similarly, $\Delta G \simeq 26.7$ KJ mol^{-1} and $\Delta S \simeq 84.8$ J mol^{-1} K^{-1} were obtained in this study compared to $\Delta G \simeq 36.2$ KJ mol^{-1} and ΔS 83.2 J mol^{-1} K^{-1} for the epoxidation of RSO with peracetic acid. These thermodynamic parameters tend to indicate that it is energetically more feasible to epoxidise RSO with perforrmic acid than with peracetic acid.

CONCLUSION

A study of the epoxidation of RSO by performic acid generated *in situ* by the reaction of 30% hydrogen peroxide with formic acid was carried out. The reaction is favoured by high temperature but epoxidation is accompanied by oxirane cleavage reaction. *In situ* epoxidation of RSO by performic acid is faster and yields product of higher % oxirane than epoxidation with peracetic acid.

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