

# Kinetics of Oxirane Cleavage In Epoxidized Soybean Oil

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The kinetics of oxirane ring cleavage in epoxidized soybean oil have been studied using glacial acetic acid at 60, 70, 80 and 90°C. It was shown that the reaction can be successfully modelled as first order with respect to the epoxide concentration and second order with respect to acetic acid. The reaction velocity constant at 70°C was found to be  $2 \times 10^{-3} \text{ l}^{-3} \text{ hr}^{-1} \text{ mol}^{-2}$ , the frequency factor,  $A$ , =  $2.321 \times 10^7 \text{ hr}^{-1}$  and the energy of activation,  $E_a$  = 15.84 k cal mol<sup>-1</sup>. The effects of the concentration of acetic acid and the temperature on the net yield of epoxides by *in situ* epoxidation were also studied on the basis of the predicted kinetic parameters of the reaction system.

Epoxidation, a chemical reaction that is restricted to unsaturated compounds, results in the formation of epoxides that have had practical importance for more than two decades as plasticizers and stabilizers for polyvinyl chloride (PVC) and even as components of epoxy resins<sup>(1)</sup>.

Since 1963, annual production of epoxidized esters as plasticizers has ranged from 60 to 150 million lb<sup>(2)</sup>. Epoxidized soybean oil (ESBO) accounted for 70-76% of the total epoxidized ester production (1963-1982)<sup>(3)</sup>.

In many epoxidation processes, yields are lowered because substantial amounts of epoxide products are converted to cleavage products<sup>(4)</sup>. A maximum yield of epoxides can be obtained by careful adjustment of the process conditions to minimize the rate of oxirane cleavage relative to formation. This requires a clear understanding of the effect of each process variable on the rate of both reactions. The effect of process variables on the rate of oxirane formation has been studied previously<sup>(5)</sup>.

The cleavage of the oxirane group has been studied with a wide variety of compounds containing the oxirane group and a broad range of electrophiles and nucleophiles<sup>(6,7)</sup>. However, only few studies have dealt with the cleavage kinetics of epoxides using glacial acetic acid. Moreover, these cleavage studies by acetic acid have used epoxides derived from classes of compounds other than fatty substances, such as propylene oxide<sup>(8-11)</sup>.

The present work was initiated to investigate the kinetics of cleavage of the oxirane group in epoxides of long chain fatty acids and hence to elucidate the role of the different process parameters on the reaction rate.

## MATERIALS AND METHODS

Commercial epoxidized soybean oil, ESBO, was used as a starting material for this study. The percentage oxirane oxygen was 6.4% which was equivalent to 0.4 mol oxirane in each 100 g of ESBO.

Analytical grade glacial acetic acid (120 g) in a three-necked reaction flask equipped with a reflux condenser was heated to the desired temperature using a thermostatically-controlled hot plate with magnetic stirrer. Forty g ESBO was then added to the acetic acid, and sampling started when the reaction mixture attained the desired temperature (within 3-5 min). Duplicate samples were withdrawn at half-hour intervals or less

(depending on the reaction temperature and hence the reaction speed). The samples were then tested for their content of residual oxirane mol by titration with 0.1 N HBr solution in acetic acid using crystal violet as indicator. These procedures have been conducted at three different temperatures, 60, 80 and 90°C. Under the conditions of these experiments, the reaction can be considered pseudo zero order with respect to acetic acid because the latter was used in excess compared to the oxirane content (about 2 mol acetic to 0.16 mol oxirane).

In another series of experiments, the same procedures as above were followed except that acetic acid was used at different concentration levels. The mol ratio of the reactants varied from 0.034, 0.24 and 0.721 mol oxirane/mol acetic acid. All reactions were conducted at 70°C and the withdrawn samples were tested, as above, for the residual oxirane content.

## RESULTS AND DISCUSSION

The results of the present work have been used to find the order of the ring opening reaction in both acetic acid and the epoxy acid, in addition to all other thermodynamic properties of the reaction system.

*The Reaction Order in Acetic Acid and the Oxirane Mole.* The general form of the rate equation for oxirane ring cleavage by acetic acid can be written as:

$$-\frac{d(\text{Ep})}{dt} = k (\text{Ep})^{n_1} (\text{Ac})^{n_2} \quad [1]$$

where—  $\frac{d(\text{Ep})}{dt}$  is rate of oxirane ring opening, mol hr<sup>-1</sup>;

(Ep) and (Ac) are the molar concentrations of the epoxy component and the acetic acid, respectively, mole liter<sup>-1</sup>;  $n_1$  and  $n_2$  are the reaction order with respect to the epoxy component and acetic acid, respectively, and  $k$  is velocity or rate constant.

If acetic acid is used in large excess as compared to the moles of oxirane, the reaction can be considered pseudo zero order in acetic acid. Thus, the rate equation can be written as:

$$-\frac{d(\text{Ep})}{dt} = k' (\text{Ep})^{n_1} \quad [2]$$

Where  $k'$  is the pseudo rate constant and is equal to  $k (\text{Ac})^{n_2}$ .

Based on the above considerations, the rate data from the cleavage reaction between 120 g acetic acid and 40 g ESBO (about 2 mol acid and 0.16 mol oxirane) would fit with equation [2]. The results of this reaction at 60, 80 and 90°C are represented in Figure 1. It can be seen from these results that the cleavage reaction is first order in the epoxy concentration; a result which is in agreement with those reported by Szakacs<sup>(8)</sup>, Isaacs<sup>(9,10)</sup> and Schmitt<sup>(11)</sup>, who studied the cleavage of the oxirane ring in propylene oxide. The slope of each straight line in Figure 1 equals  $k'$  where  $k'$  is the pseudo first order rate constant. The determined pseudo rate constants at 60, 80 and 90°C were calculated as 0.1303, 0.4467 and 0.9663, respec-

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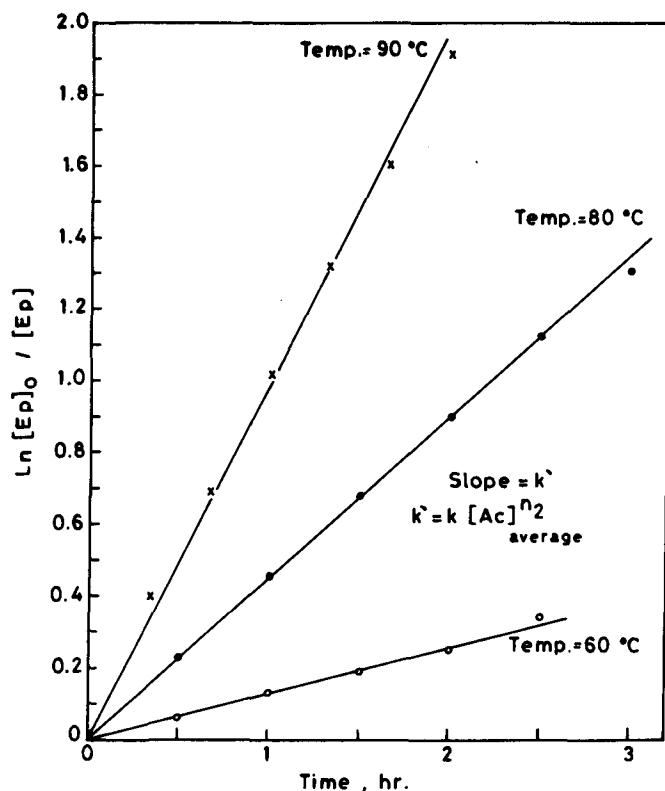


Fig. 1. Determination of the reaction order in the epoxy concentration.

tively, at an average acetic concentration of 12.345, 12.094 and 12.05 molar.

In order to predict the reaction order with respect to acetic acid, the value of  $k'$  at 70°C was determined at three different concentration levels of acetic acid (Fig. 2). The value of this constant was found to be 0.4022, 0.1508 and 0.04082 at an average concentration of acetic acid of 14.381, 7.893 and 3.98 M, respectively. Because  $k'$  is defined as  $k(\text{Ac})^{n_2}$ , then:

$$\ln k' = \ln k + n_2 \ln (\text{Ac}) \quad [3]$$

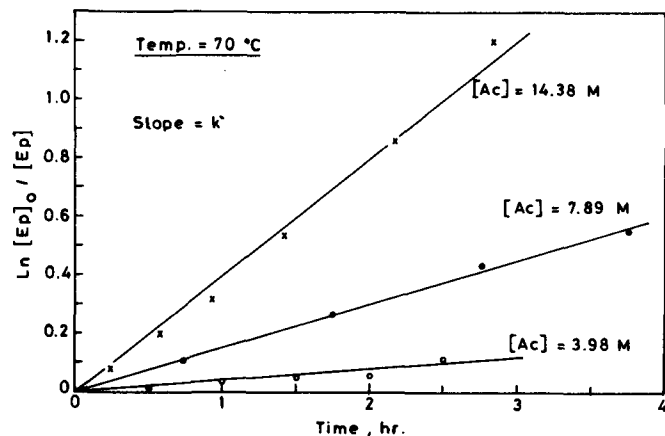


Fig. 2. Determination of the pseudo rate constant,  $k'$  at different concentrations of acetic acid.

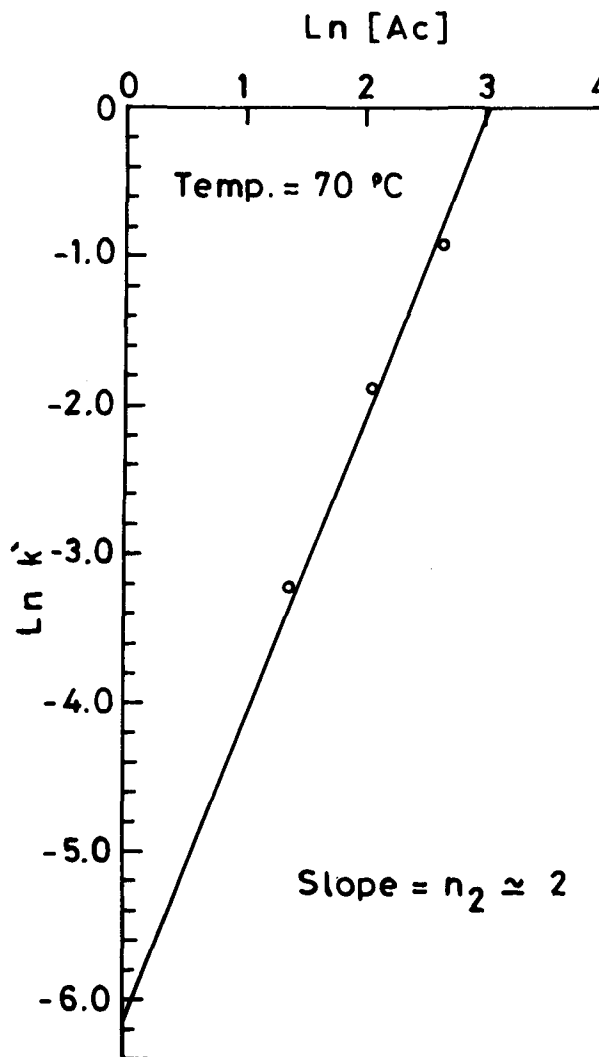


Fig. 3. Determination of the reaction order in acetic acid.

According to this equation, and using the results presented in Figure 3, the cleavage reaction was found to be second order in acetic acid ( $n_2 = 2$ ). This result can be used to understand the effect of acetic acid concentration on the net yield of epoxides by in situ epoxidation.

The formation of peracetic acid from acetic acid and hydrogen peroxide is a reversible reaction ( $\text{RCO}_2\text{H} + \text{H}_2\text{O}_2 \rightleftharpoons \text{RCO}_3\text{H} + \text{H}_2\text{O}$ ). Hence, the increase of acetic concentration will increase the equilibrium concentration of the peracid in the reaction medium, and consequently, it will increase the rate of oxirane formation, which is first order in the peracid (4). However, the expected increase in the rate of oxirane formation, which is first order in the peracid<sup>(4)</sup>, will be much less than that of oxirane cleavage whose order in acetic acid is second. Thus, the use of a higher concentration of acetic acid during in situ epoxidation will, definitely, reduce the net yield of epoxides.

It is recommended, therefore, to use acetic acid and the olefinic substrate at a low molar ratio of the former to the latter whenever the epoxy derivative is the desired product. On the other hand, when the process objective is to prepare hydroxylated (cleavage product) rather than

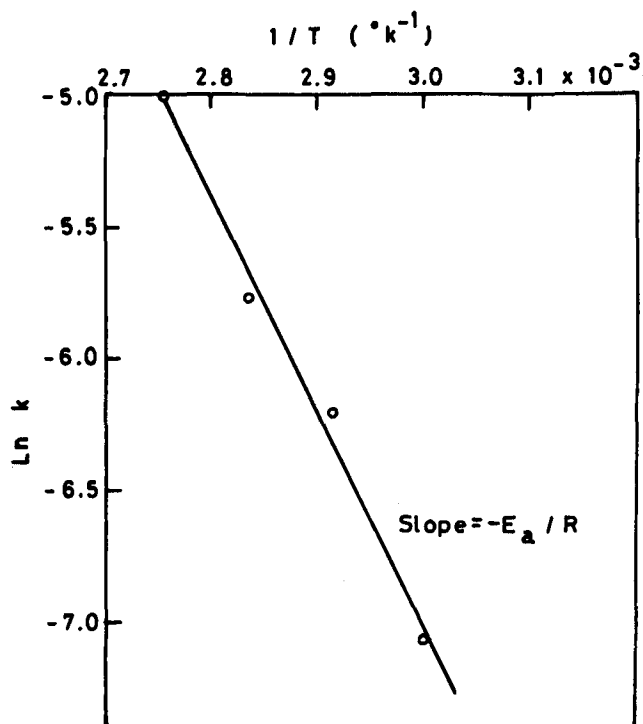


Fig. 4. Determination of the energy of activation,  $E_a$ .

the epoxidized product, a high molar ratio of acetic acid to the olefinic substrate should be used.

**Thermodynamic properties of the reaction system.** The activation energy of the cleavage reaction,  $E_a$ , the frequency factor,  $A$ , the enthalpy of activation,  $\Delta H$ , the free energy of activation,  $\Delta F$ , and the entropy of activation,  $\Delta S$ , were determined as in Frost and Pearson<sup>(12)</sup>.

Using the ring opening data presented in Figure 4, the activation energy was found to be  $15.84 \text{ k cal mol}^{-1}$  and the frequency factor,  $A$ , equals  $2.321 \times 10^7 \text{ hr}^{-1}$ . According to Chalabiev et al.<sup>(13)</sup>, the activation energy of soybean oil epoxidation is  $18.3 \text{ k cal mol}^{-1}$ , which is higher than that for the decomposition of ESBO due to oxirane cleavage ( $=15.84 \text{ k cal mol}^{-1}$ ). On the basis of these results, it may be

suggested that the increase in the process temperature during the production of commercial ESBO will increase the rate of oxirane formation as compared to cleavage. Hence, the net yield of epoxides may increase. However, in a previous paper by the authors (5), it has been shown that the equilibrium concentration of peracetic acid decreases as the temperature increases; hence, the rate of formation of the oxirane group will be reduced. Thus, the net yield of epoxides can be maximized if the process of in situ epoxidation is carried out at an optimum temperature which depends on the type of catalyst used in such process.

The enthalpy of activation,  $\Delta H$ , was calculated using the equation;  $\Delta H = E_a - RT$ , and found to be  $15.161 \text{ k cal mol}^{-1}$  at  $70^\circ\text{C}$ . The free energy of activation,  $\Delta F$ , and the entropy of activation,  $\Delta S$ , were also calculated at the same temperature and found to be  $30.076 \text{ k cal mol}^{-1}$  and  $-43.485 \text{ cal mol}^{-1} \text{ k}^{-1}$ , respectively.

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