Kinetic Parameters of a Two-Phase Model for *in situ* Epoxidation of Soybean Oil

Bharath Rangarajan[a], **Adam Havey**[a], **Eric A. Grulke**[b,*] **and P. Dean Culnan**[c]
[a]Department of Chemical Engineering, Michigan State University, East Lansing, Michigan 48824,
[b]Chemical and Materials Engineering Department, University of Kentucky, Lexington, Kentucky 40506
and [c]Process Development Corporation, Houston, Texas 77057

ABSTRACT: The process of *in situ* epoxidation consists of a two-phase system that involves reactions in both phases, mass transfer between phases, and thermodynamic driving forces for the mass transfer. In this paper, we present a model that treats the process as a two-phase system and uses local phase concentrations to calculate reaction and mass transfer rates. The process of *in situ* epoxidation has been broken down into a set of systematic steps, and rate constants for each step have been determined. A conventional stirred tank reactor, equipped with cooling coils, eliminated the heat and mass transfer limitations so that the true kinetics of *in situ* epoxidation were observed. It is shown that significantly larger rates (larger by factors of 2–10) are obtained when heat and mass transfer limitations are removed. The two-phase model adequately predicts the epoxidation kinetics over a wide range of temperatures (50–90°C). In addition, the model also correctly predicts the effect of adding an inert solvent.

JAOCS 72, 1161–1169 (1995).

KEY WORDS: Epoxidized soybean oil, hydrogen peroxide, *in situ* epoxidation, kinetics, mass transfer, model, reaction, soybean oil, two-phase.

Epoxidation is the formation of an oxirane group by the reaction of peroxy acids (peracid) with olefinic and aromatic double bonds. Epoxides are extremely valuable commercially because of the many reactions they undergo. Epoxidized soybean oil has a large and growing market (~70,000,000 kg/y) as a plasticizer for poly(vinylchloride). Epoxides of long-chain α-olefins are potentially useful as detergent precursors (1). Products based on limonene are flavor precursors. The pioneering work on epoxidation of a variety of unsaturated organic compounds, including soybean oil, was performed in the 1940s by Swern and co-workers (2) with preformed peracetic acid (PAA). A variety of other methods in which acetic and formic acid are used were soon developed (3,4). These processes can be separated into two major categories—one in which the peroxy acid is preformed and then used for epoxidation, and the other where the peracid is made *in situ* in the reaction vessel.

Process safety is a major problem in using peroxides and peracids because they can form detonable mixtures at high concentrations of active oxygen, and may explode on heating. It is generally accepted that the *in situ* process is safer than the preformed peracid processes (1). The *in situ* process results in a two-phase mixture of an aqueous and an oil phase and has low concentrations of peracid. The epoxidation reaction is highly exothermic, with a heat of reaction of about 250 kJ/mole (60 kcal/mole) (5). Heat removal is a problem and can limit process rates in conventional reactors. To prevent uncontrolled exothermic reaction, the peroxide or active oxygen (peracid) is added slowly (typically over 2 h) to the oil at moderate temperatures (50–65°C), and then the reaction is allowed to proceed for 10–12 h (1).

Reaction mechanism. The mechanism of *in situ* peracetic acid epoxidation is generally thought to involve the following steps: (i) formation of PAA in the aqueous phase, catalyzed by a mineral acid (H_2SO_4); (ii) transfer of the PAA from the aqueous phase to the oil phase; (iii) reaction of the peracid in the oil phase to form the epoxide and to release acetic acid; (iv) degradation of the epoxide in the oil phase, as well as at the oil–aqueous interface; (v) removal of the heat of reaction from the oil phase; and (vi) transfer of the AA from the oil phase to the aqueous phase.

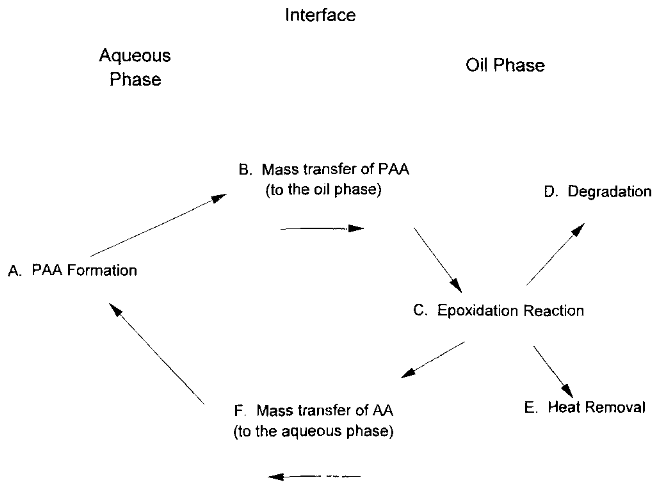
Hydrogen peroxide and the unsaturated oil alone do not react to any significant extent, and an organic peracid (usually AA or formic acid) is necessary to shuttle the active oxygen from the aqueous phase to the oil phase. Once in the oil phase, the peracid adds oxygen across the carbon–carbon double bond and regenerates the original acid. Scheme 1 illustrates the various process steps, and Table 1 lists some of the possible reactions involved in the process of *in situ* epoxidation.

Rate-limiting steps and process kinetics. A rough estimate of the importance of the various steps can be obtained by comparing the time scales of different epoxidation processes. Although a typical *in situ* PAA acid process takes about 12 h at 56°C (6), preformed PAA allows the reaction to be completed in about 4 h at 25°C (2), suggesting that step A in Scheme 1 is slow. If an organic solvent-based PAA is used (such as Peroxysolv I, PAA in ethyl acetate), the epoxidation reaction at 60°C takes place over a period of 3 h [which in-

---

*To whom correspondence should be addressed.

Copyright © 1995 by AOCS Press



SCHEME 1

cludes a two-hour reagent addition (7,8)], suggesting that mass and heat transfer limitations are important.

The study of epoxidation kinetics is difficult because heat and mass transfers limit the process rate. There are few reports in the literature regarding the kinetics of epoxidation. Chou and Chang (9) studied the epoxidation of oleic acid with H_2O_2 and AA. They conducted their experiments in a three-neck, glass, round-bottom flask and slowly added H_2O_2 to the system to maintain isothermal conditions. By varying the concentrations of various reactants, they concluded that the limiting step of the process was the rate of PAA formation and that the rate expression for PAA formation was

$$\text{rate (moles of PAA formed/L/min)} = k\, C_{AA} C_{H_2O_2} C_{H^+} \quad [1]$$

where k is 0.0298 L^2 mole^{-2} min^{-1} at 35°C; C_{AA} is moles AA per L of aqueous phase; $C_{H_2O_2}$, moles hydrogen peroxide per L of aqueous phase and C_{H^+}, moles hydrogen ion per L of aqueous phase. However, there are several problems with their study. First of all, the H_2O_2 was added slowly, at an unspecified rate, which limited the reaction. Later we will show that, with better heat removal, all of the H_2O_2 can be added at once, resulting in higher rates. Second, all concentrations in the rate expression are based on moles per total volume instead of individual phase volumes, and distribution of the compounds between phases is not considered. Third, the absence of baffles makes it difficult to estimate how well the system was mixed and what the interfacial area was. These factors, along with the incomplete information in their paper (9), make it extremely difficult to use their results. In a recent paper, Gan *et al.* (10) studied the epoxidation of palm olein methyl esters with *in situ* AA formic acid. They too concluded that the rate-limiting step of the epoxidation process was the rate of formation of PAA. Although their system did not have a heat transfer limitation due to the inherent dilution by the lower iodine number of the palm olein, their mixing is unspecified, and it is not known if their data are mass transfer-limited.

Side reactions. Degradation of the oxirane product has long been recognized as a serious problem in the epoxidation process. Findley *et al.* (2) claimed that the rate of ring opening of 9,10 epoxystearic acid was 1%/h at 25°C and 100% at 65–100°C in 1–4 h. They recommended that by-product formation could be minimized by operating at moderate temperatures with faster epoxidation, and by using a suitable solvent, such as heptane or toluene. The degradation reactions are catalyzed by sulfuric acid. Swern and co-workers (2) pointed out the need to neutralize the sulfuric acid present in the preformed PAA (2). The hypothesis that sulfuric acid stays in the

TABLE 1
***In situ* Peracetic Acid Epoxidation Reactions**[a]

Reaction number	Reaction	Description	Phase
1	$H_2O_2 + CH_3COOH \overset{H^+}{\longleftrightarrow} CH_3COOOH + H_2O$	Peracid formation	Aqueous
2	$R_1 - CH = CH - R_2 + CH_3COOOH \longrightarrow$ $R_1 - CHOCH - R_2 + CH_3COOH$	Epoxidation	Oil
3a	$R_1 - CHOCH - R_2 + CH_3COOH \overset{H^+}{\longrightarrow}$ $R_1 - CH(OH) - CH(OOCCH_3) - R_2$	Side reactions	Oil
3b	$R_1 - CHOCH - R_2 + H_2O \overset{H^+}{\longrightarrow}$ $R_1 - CH(OH) - CH(OH) - R_2$	Side reactions	Interface
3c	$R_1 - CHOCH - R_2 \overset{H^+}{\longrightarrow}$ $R_1 - CO - CH_2 - R_2$	Side reactions	Interface
3d	$R_1 - CHOCH - R_2 + CH_3COOH \overset{H^+}{\longrightarrow}$ $R_1 - CH(OH) - CH(OOOCCH_3) - R_2$	Side reactions	Oil
3e	$R_1 - CHOCH - R_2 + H_2O_2 \overset{H^+}{\longrightarrow}$ $R_1 - CH(OH) - CH(OOH) - R_2$	Side reactions	Interface

[a] Adapted from Lutz (Ref. 1).

aqueous phase and therefore reacts with the oxirane group in the form of an interfacial reaction (Reactions **3b** and **3c** of Table 1) was advanced by Wohlers *et al.* (11). Recently, Zaher *et al.* (12) studied the kinetics of degradation of epoxidized soybean oil (ESBO) by mixing ESBO with AA. They were able to obtain the following rate expression:

$$\text{rate of degradation (moles of ESBO/L/min)} = k_d C_{ESBO}(C_{AA})^2 \quad [2]$$

with a k_d of 0.12 $mol^{-2}min^{-1}$ L^2 at 70°C and an activation energy of 66.2 kJ/mole (15.84 kcal/mole). These studies were in a single phase (oil), and the rate expressions obtained are applicable to that phase. In a similar study, the same expression was obtained for the degradation of epoxidized methyl esters of palm olein with a k_d of 3.19×10^{-5} $mol^{-2}min^{-1}$ L^3 at 70°C, with an activation energy of 73.5 kJ/mole (17.58 kcal/mole). Neither study evaluated the effect of sulfuric acid catalyst concentration on the rate of degradation. Table 1 shows that acetolysis of the oxirane group is only one of several degradation reactions.

Although several parts of the epoxidation problem have been identified and investigated, there has been no attempt to model the entire process as a two-phase system. Chou and Chang (9) proposed a model that had the rate of PAA formation as the rate-limiting step, but they reported a rate constant while using concentrations based on total volume. No other paper that we are aware of presents a model or compares model predictions with experimental data.

Objectives. This paper analyzes *in situ* natural oil epoxidation as a two-phase process and models each step. Rate constants for the individual steps are obtained from the literature, or from experiments described here, or are estimated. The results from the model are compared to experimental data. The objectives of this study are to: (i) develop a two-phase engineering model of the epoxidation process; (ii) determine the model parameters, especially the true rate of *in situ* PAA epoxidation in the absence of heat transfer limitations; and (iii) compare the model predictions with experimental data.

MATERIALS AND METHODS

Mikado-brand soybean oil from PVO Foods Inc. (St. Louis, MO) with an iodine value of 130.6 (Wijs), Baker-analyzed H_2O_2 (31.3% w/w) from J.T. Baker (Phillipsburg, NJ), and reagent-grade H_2SO_4 and glacial acetic acid (>99.7%), both from EM Sciences (Gibbstown, NJ), were used in this study. Tests for iodine value and % oxirane were done according to International Union of Pure and Applied Chemists guidelines (13).

Partition coefficient measurements. Partition coefficients for AA between oil and water were measured by mixing different quantities of oil, water, and AA in a glass-stoppered Erlenmeyer flask. The Erlenmeyer was placed in a shaker bath, which had temperature control. Care was taken to ensure that the liquid level was at the lip of the Erlenmeyer to provide maximum mixing. After 3 h of mixing, the shaking was stopped, and the aqueous and oil phases were allowed to separate while still at the desired temperature. The water phase was carefully sampled, and 10 mL were withdrawn and titrated with NaOH and phenolphthalein indicator for AA. A variety of ratios of oil/water/acid (including typical *in situ* ratios) were used.

Reaction equipment. Epoxidation reactions were carried out in a 1-L fermentor (the reactor section was 76.5 mm diameter, 106.5 mm long), equipped with stainless-steel cooling coils (4 coils of 50-mm diameter, 3.1-mm tube o.d., or a total of 61 square cm heat transfer area), 4 baffles (8.8-mm wide and 63.8-mm long), and a magnetically driven agitator (53.4-mm in diameter). The impeller was a four-blade flat turbine (blade dimensions were 21.5-mm diameter and 9.6-mm height). The speed of the impeller could be set on the fermenter. All experiments reported here were carried out at 400 rpm. Cold anti-freeze was circulated at a constant rate through the cooling coils and provided constant cooling. Heating was provided with heating tape (~100 mm), mounted on the outside of the vessel, and was controlled by an on–off temperature controller. Temperature was effectively controlled to ±1°C and was monitored by means of a mercury thermometer with a least count of 1°C.

Single-phase epoxidations. Single-phase epoxidations were done to determine k^o_{+2}, the intrinsic rate constant for the epoxidation reaction (Reaction **2**, Table 1). To eliminate rate limitations due to PAA formation and mass transfer, preformed PAA made with acetic anhydride, H_2O_2 (31%), and H_2SO_4 was used (2). The solution, which consisted of about 11% (w/w) PAA and 87% AA, was miscible with the oil. The preformed PAA solution was mixed with a 40-molar excess of soybean oil. This large excess of oil allowed isothermal epoxidation at 40°C. Samples of the oil/acid mixture were periodically taken and washed with water to extract acids and peroxides. The mixture was centrifuged and analyzed for oxirane.

In situ *epoxidations.* The kinetics of *in situ* epoxidation were determined by using standard *in situ* compositions (6). In a typical experiment, about 200 g of oil and 23 g of glacial AA were mixed together and heated to the desired temperature. About 133 g of H_2O_2 (31.3%) and 3 g H_2SO_4 were mixed and heated to ~50°C in another beaker. Then, all of the H_2O_2 solution was added at once to the heated oil. After preselected time intervals, 5-mL samples were pipetted out of the reaction vessel and immediately poured into 50-mL Erlenmeyer flasks that contained about 30 mL of reverse-osmosis-purified water at room temperature. This procedure served to immediately quench the reaction, as well as to extract AA and PAA from the oil phase. The oil–water mixture was stirred with a Teflon spinbar for at least 20 min to allow extraction of the acids from the oil into the water. The oil–water mixture was then separated by centrifugation at 7500 rpm for 10 min in 50-mL centrifuge tubes. A small quantity of the oil phase was removed from the top, with a Pasteur pipette for analysis.

RESULTS AND DISCUSSION

Model development. This section develops a two-phase model that describes the process of epoxidation. The reaction mechanisms are assumed to follow Equation 1, Equation 2, or the stoichiometries given in Table 1. Because each reaction occurs in a particular phase, this model uses local phase concentrations, i.e., moles of a particular compound in a certain phase divided by the volume of that phase. Kinetic constants are, therefore, also based on local concentrations and individual phase volumes. This modeling approach should permit the rate equations to be applied to any mixture compositions of oil, acid, and peroxide.

Phase equilibria experiments verified that water, hydrogen peroxide, and sulfuric acid are essentially insoluble in the oil phase and *vice versa.* The concentrations of AA and PAA in the aqueous and oil phases are related by partition coefficients.

In this paper, the symbol C will be used to refer to concentration, with the subscript indicating the component and a superscript indicating the phase. The letters o and w refer to the oil and aqueous phases, respectively. The rate constants k for the various reactions also have the superscripts o and w to refer to the phase. The subscripts on the rate constants refer to the reaction number from Table 1, with the + and − subscripts referring to the forward and reverse reaction. For example, the symbol k^w_{-l} refers to the reverse reaction 1 in Table 1, i.e., the dissociation of PAA in the aqueous phase. Table 2 gives a list of symbols used in developing the model and explicitly shows the components that are soluble only in one phase.

Component material balances in each phase are based on the reactions given in Table 1 and the transport and equilibrium processes shown in Scheme 1. The assumptions for the material balances are: (i) that the reaction mechanism of the epoxidation reaction (Reaction **2** of Table 1) is represented by the stoichiometry (14); (ii) that the epoxidation reaction (Reaction **2**) is irreversible; (iii) that the system is isothermal and well mixed; (iv) that no reactions take place at the interface; (v) that the oxirane degradation is not affected by H_2SO_4; and (vi) that degradation of the oxirane group by AA as modeled by Equation 2 is the sole mechanism for degradation. We will show that the degradation is more complex than that predicted by Equation 2, but that it gives a reasonable representation of our data in the absence of detailed degradation product analyses.

TABLE 2
List of Concentration Nomenclature

Component	Phase[a]		Symbol
	Oil	Aqueous	
Water	—	$C^w_{H_2O}$	H_2O
Hydrogen peroxide	—	$C^w_{H_2O_2}$	H_2O_2
Hydrogen ion	—	$C^w_{H^+}$	H^+
Acetic acid	C^o_{AA}	C^w_{AA}	AA
Peracetic acid	C^o_{PAA}	C^w_{PAA}	PAA
C=C group	$C^o_{C=C}$	—	C=C
Oxirane group	C^o_{COC}	—	COC

[a] C, concentration; o, w, oil and aqueous phases, respectively; PAA, peracetic acid; AA, acetic acid.

Mass balances in the aqueous phase. Mass balances for H_2O_2, PAA, AA, and water in the aqueous phase are written in Equations 3–6. Whereas hydrogen peroxide and water stay only in the aqueous phase, PAA, and AA partition between the two phases. Therefore, a mass transfer term is included to account for the transfer of the two components (AA, PAA) between the aqueous and oil phases.

Hydrogen peroxide:

$$-\frac{dC^w_{H_2O_2}V^w}{dt} = k^w_{+1}C^w_{AA}C^w_{H_2O_2}C^w_{H+}V^w - k^w_{-1}C^w_{PAA}C^w_{H_2O}C^w_{H+}V^w \qquad [3]$$

PAA:

$$-\frac{dC^w_{PAA}V^w}{dt} = -k^w_{+1}C^w_{AA}C^w_{H_2O_2}C^w_{H+}V^w + k^w_{-1}C^w_{PAA}C^w_{H_2O}C^w_{H+}V^w + k_{l,PAA}a(K_{PAA}C^w_{PAA} - C^o_{PAA})V^o \qquad [4]$$

AA:

$$-\frac{d\,C^w_{AA}V^w}{dt} = k^w_{+1}C^w_{AA}C^w_{H_2O_2}C^w_{H+}V^w - k^w_{-1}C^w_{PAA}C^w_{H_2O}C^w_{H+}V^w - k_{l,AA}a(C^o_{AA} - K_{AA}C^w_{AA})V^o \qquad [5]$$

water:

$$C^w_{H_2O}V^w = (C^w_{H_2O_i} + C^w_{H_2O_{2i}})V^w_i - C^w_{H_2O_2}V^w \qquad [6]$$

The hydrogen peroxide balance includes terms for the forward and reverse steps of Reaction **1**, Table 1. The PAA balance includes these terms and an interfacial mass transfer coefficient that describes the flux of this acid from the aqueous to the oil phase. This mass transfer coefficient is defined to give the total transfer of the component based on the surface area per unit volume of the oil phase. AA is consumed in the aqueous phase and there is a flux of regenerated AA from the oil phase into the aqueous phase. The water balance is simple and describes the slow increase in the water phase volume as hydrogen peroxide is converted to water during the reaction. Because the volume of the system need not be constant, the balances have been written on an absolute molar basis (moles/time) rather than on a concentration basis (moles/volume/time).

Mass balances in the oil phase. The components in the oil phase are the unsaturated group, oxirane group, PAA, and AA. The first two stay only in the oil phase, and the latter two are coupled with the aqueous phase through thermodynamic and mass transfer terms.

Unsaturated (C=C) group (k^o_{-2} is zero):

$$-\frac{d\,C^o_{C=C}V^o}{dt} = k^o_{+2}C^o_{C=C}C^o_{PAA}V^o \qquad [7]$$

where $C^o_{c=c}$ is the moles C=C group per L of oil phase. Oxirane group (k^o_{-3} is zero):

$$-\frac{d\,C^o_{COC}V^o}{dt} = -k^o_{+2}C^o_{C=C}C^o_{PAA}V^o + k^o_{+3a}C^o_{COC}(C^o_{AA})^2\,V^o \qquad [8]$$

where C^o_{COC} is moles oxirane group per L of oil phase. PAA balance:

$$-\frac{d\,C^o_{PAA}V^o}{dt} = -k_{l,PAA}\,a(K_{PAA}C^w_{PAA} - C^o_{PAA})V^o + k^o_{+2}C^o_{C=C}C^o_{PAA}V^o \qquad [9]$$

AA balance:

$$-\frac{d\,C^o_{AA}V^o}{dt} = k_{l,AA}\,a(C^o_{AA} - K_{AA}C^w_{AA})V^o - k^o_{+2}C^o_{C=C}C^o_{PAA}V^o + k^o_{+3a}C^o_{COC}(C^o_{AA})^2\frac{V^0}{Y_{AA}} \qquad [10]$$

Unsaturated groups are lost from the oil phase by irreversible reaction with the peracid. Epoxide groups are formed by Reaction **2**, but can be lost by a variety of side reactions (Reactions **3a**–**3e**). As a first step toward modeling the side reactions, we have used the degradation mechanism of Equation **3a** to describe all oxirane losses. We will show that Equation **3a** approximates the oxirane degradation rate reasonably well, but gives a higher loss of AA than occurs in the system. An empirical yield coefficient (Y_{AA}) is used in the AA balance (Eq. 10) to account for the loss of AA. The PAA and AA balances include terms for their transfer between the phases.

Equations 3–10 are a set of eight simultaneous ordinary differential equations that can be integrated if the starting compositions of the different components in each phase are known. The model contains the following parameters—the forward and reverse rate constants of Reaction **1** (k^w_{+1} and k^w_{-1}), the forward rate constant of Reaction **2** (k^o_{+2}), the degradation rate constant of Equation 2 (k_d or k^o_{+3a}), the mass transfer coefficients between the oil and aqueous phases for AA and PAA ($k_{l,AA}a = k_{l,PAA}a$), and the partition coefficients of AA and PAA, (K_{AA} and K_{PAA}). These parameters have been determined as described in the next section.

Partition coefficients. Measured partition coefficients for AA between soybean oil and water (K_{AA}) are presented in Table 3. The values are based on the molar concentration of AA in each phase ($K_{AA} = C^o_{AA}/C^w_{AA}$). There is some dependence of K_{AA} on mixture composition as well as on temperature. Compositions 1 and 4 are nearest to those used in the *in situ* process, and a value of about 0.04 near operating temperature (50 and 70°C) may be used. Because PAA has a greater preference for the oil phase, its partition coefficient is higher, and a value of 0.1 is used. A value of 0.47 was reported for PAA at 20°C between ether and water (15).

TABLE 3
Partition Coefficients for Acetic Acid Between Oil and Water[a]

Temperature (°C)	Soybean oil (g)	Water (g)	Acetic acid (g)	$K_{AA} = C^o_{AA}/C^w_{AA}$
40	100.1	28.5	9.8755	0.0671
40	100	50.1	49.7438	0.098
40	24	40	40.0969	0.075
60	101.4	28.2	9.9067	0.036
60	50	26.5	24.7	0.028
60	24	40.3	40.0553	0.023

[a]See Table 2 for abbreviations.

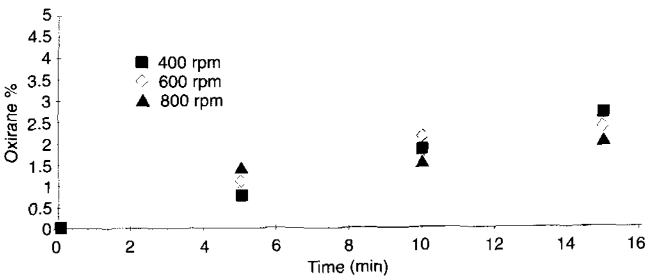


FIG. 1. *The effect of stirring speed on the initial rate of in situ epoxidation.*

Mass transfer coefficients. The mass transfer coefficients of PAA and AA were assumed to be similar. These coefficients often scale with the inverse of the square root of the molecular weight and are expected to differ only by 12% on this basis. One method for determining the effects of mass transfer on the reaction process is to perform experiments with a range of agitation speeds. Mass transfer limitations might be observed if the initial epoxidation rate varied with agitation. Figure 1 shows that the initial epoxidation rate (as defined by the slope of the % oxirane vs. time curve) does not vary for agitation rates of 400, 600, and 800 rpm. The specific reaction conditions for this test (performed at 90°C) are such that the process rate is highest of the data presented, demonstrating that mass transfer rates do not limit the process rate for these data.

Reaction rate constants. Four reaction rate constants are needed: the forward (k^w_{+1})and reverse (k^w_{-1}) rate constants for PAA formation, the irreversible epoxidation rate constant (k^o_{+2}), and the oxirane degradation rate constant (k^o_{+3a}). Although optimization packages could be used to estimate these values from the data, it is preferable to design experiments to measure the constants independently.

Intrinsic epoxidation rate constant. Single-phase epoxidations were performed to get the intrinsic rate constant for the epoxidation reaction (k^o_{+2}) in the absence of rate limitations due to PAA formation, mass transfer between the phases, and heat removal from the mixture. Preformed PAA, made with acetic anhydride, H_2O_2 and H_2SO_4 (2), was mixed with 40-molar excess soybean oil at 40°C. The large excess of soybean oil and the low reaction temperature allowed complete removal of the heat of reaction. The resulting mixture was a single-phase oil/acid mixture. The PAA solution used was analyzed for percent PAA and hydrogen peroxide prior to use.

Because the reaction took place in one phase, only Equations 7–10 need to be considered. Because the system is dilute and has a low concentration of active oxygen, the reaction volume is nearly constant and can be canceled from each side of the equations. In addition, because this system is in a single phase, there is no transfer of PAA from the oil phase, and Equation 9 is not needed. Although oxirane groups can be lost by degradation mechanisms, the rate of degradation should be low in a diluted system as it is sensitive to the square of the AA concentration. Therefore, Equation 7 can be used to analyze the kinetic data, which were evaluated by the following expression:

$$\frac{d(C^o_{C=C})}{dt} = k^o_{+2} C^o_{C=C} C^o_{PAA} \qquad [11]$$

and the stoichiometry:

$$C^o_{C=C} = C^o_{C=C,_{initial}} - C^o_{COC} \qquad [12]$$

$$C^o_{PAA} = C^o_{PAA,_{initial}} - C^o_{COC} \qquad [13]$$

Figure 2 shows the kinetics of a typical single-phase epoxidation, as well as the model. Substantial conversion (>75%) was achieved in 20 s. Because the sampling process itself takes time, it was not possible to get much better data. Fortunately, the rate of epoxidation is about two orders of magnitude higher (10) than the rate of PAA formation, and only a rough estimate of the epoxidation rate is needed. The rate constant for epoxidation, in the oil phase, was calculated to be 3.4 L min^{-1} $mole^{-1}$ at 40°C. Almost all of the active oxygen in the system was converted into oxirane. The fact that essentially all of the oxygen was accounted for validates the assumption of minimal degradation. The activation energy for the epoxidation reaction is 76.5 kJ/mole (18,300 cal/mole) (12).

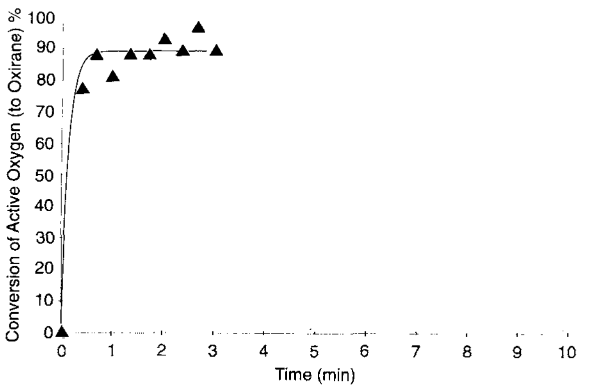


FIG. 2. The kinetics of epoxidation, at ~40°C, for a single-phase reaction with preformed peracetic acid. The solid line is a fit to the data.

Peracid and oxirane rate constants: in situ *epoxidations.* The kinetics of *in situ* epoxidation were used to determine the forward (k^w_{+1}) and reverse (k^w_{-1}) rate constants for Reaction **1**, at three different temperatures (Fig. 3). Table 4 gives the starting compositions for these runs. All of the runs discussed here were done at 400 rpm. The model was fit to the initial data (conversions less than the maximum) by using the partition coefficients and intrinsic epoxidation rate coefficients found previously, and by assuming that the process was not mass transfer-limited. A look at Figure 3 shows an Arrhenius type of dependence of reaction rate on temperature. A plot of ln k vs. 1/T gave an activation energy of 74 kJ/mole (17,800 cal/mole). With such a high number, mass transfer cannot be the rate-limiting step. As mentioned before, experiments performed at different rpm (400, 600, and 800 rpm) showed no differences in the initial rates (although there are differences later), confirming that the process was not limited by the rate of mass transfer of PAA.

The following experimental procedures have been used to simplify the solution of the model: (i) all of the peroxide was added at once, and (ii) typical *in situ* recipes were used so that

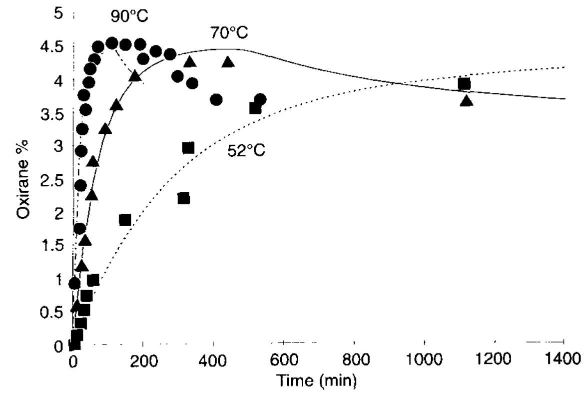


FIG. 3. Epoxidation of soybean oil with acetic acid and H_2O_2 (~31%). The lines are computer model calculations.

TABLE 4
Starting Compositions for *in situ* Epoxidations

Temperature (°C)	Soybean oil (g)	Acetic acid (g)	H_2O_2 31.3% (g)	H_2SO_4 (g)	rpm
52	200.2	23.0	134.8	2.70	400
70	203.2	22.9	133.3	2.85	400
90	201.9	23.7	133.0	3.00	400
90	200.2	23.7	134.7	3.25	600
90	200.3	24.1	134.6	2.90	800

the volumes of each phase did not change significantly with time. We have assumed that the mass transfer coefficient is the same for both AA and PAA, the partition coefficients for AA and PAA do not change with time (as compositions change), and that water and hydrogen peroxide are immiscible with oil. These differential equations were solved simultaneously, by Euler's method, by using the starting compositions of each phase as initial conditions. These calculations took on the order of 1–5 min on a PC (386 with co-processor/486–33 MHz).

The rate of PAA formation in the aqueous phase was obtained from fitting the early data of the kinetic experiments. Changing the rate constant for the epoxidation/degradation reactions did not affect the fit to the early data, suggesting that, during the early stage, the process is limited by the formation of PAA. The rate constant for the degradation reaction was obtained by fitting the data taken during the later stage of the kinetic experiments. Zaher *et al.* (12) obtained a rate constant for the degradation reaction of the oxirane group in the absence of the sulfuric acid catalyst. Because their data were obtained in the absence of sulfuric acid, the value of the rate constant was low. It is known that H_2SO_4 catalyzes the degradation reactions (2,11,16). In addition, some of the degradation occurs at the interface and is due to the presence of H_2O and H_2O_2. Neither of these facts is incorporated in our model. In the absence of data and kinetic information about the various degradation mechanisms, it was assumed that the overall rate of degradation was represented by Equation 2 (which represents Reaction **3a**). However, only a part of the total degradation is due to Reaction **3a**, which results in the consumption of AA (in the oil phase). Because only a fraction of the actual degradation consumes AA, the yield coefficient Y_{AA} of 1.65 was obtained from an empirical fit to the data. This gives reasonable agreement with the experimental data over a wide range of temperatures.

Table 5 summarizes the rate constants for the different reactions. This study was performed in a stirred tank reactor, with well-controlled and well-defined mixing conditions. The specific interfacial area would change if a different stirring speed was used and could result in different amounts of epoxidation and degradation. Further work needs to be done to correlate the specific interfacial area and droplet size with the extent of stirring and to relate these factors to the various rates of reactions. Additionally, to enable meaningful comparisons with other two-phase experimental data, mixing conditions (geometry, speed, etc.) should always be reported.

To extend the use of this model to higher H_2O_2 concentrations, the following factors need to be considered. The equilibrium constant for the peracetic acid formation reaction:

$$K_1^w = k_{+1}^w / k_{-1}^w = C_{PAA}^w C_{H_2O}^w / (C_{AA}^w C_{H_2O_2}^w) \qquad [14]$$

depends on the concentration of H_2O_2 used. Commercially available PAA, made from 70% H_2O_2, has a K_I^w of 5, whereas PAA made from 30 and 50% H_2O_2 have K_I^w values of around 0.7–1 and 2, respectively. K_I^w also depends on a number of factors, such as temperature, amount of mineral acid used, and molar ratio of AA to H_2O_2. A similar dependence has been reported for the manufacture of mineral acid-free PAA by the use of a cation exchange resin (15). Because the K_I^w used here was defined as k_{+I}^w/k_{-I}^w, the nonlinear effect of using higher H_2O_2 concentrations may be lumped into the k_{+I}^w term. Therefore, if one uses 50 or 70% H_2O_2, the forward rate constant should be increased by a factor of 2 or 5, respectively. Preliminary experiments with 50% H_2O_2 show that the model adequately predicts the rate of *in situ* epoxidation if k_{+I}^w is enhanced by a factor of 2.

TABLE 5
A Summary of Rate Constants Used in the Two-Phase Epoxidation Model[a]

Reaction	Symbol used	$k = A \exp^{(\frac{-E_a}{RT})}$	T (K)	E_a (cal/mole)	A
Peracetic acid (PAA) formation	k_{+1}^w (aqueous)	0.00332 ($L^2/mol^2/min$)	333	18620	5.53×10^9
	k_{-1}^w (aqueous)	0.00453 $L^2/mol^2/min$	333	18620	7.55×10^9
Epoxidation	k_{+2}^o (oil)	20.2 L/mol/min	333	18300[b]	2.07×10^{13}
Degradation	k_{+3a}^{o}[a] (oil)	0.28 $L^2/mol^2/min$	333	15840[b]	6.9×10^9
Mass transfer	$k_{l,AA}a = k_{l,PAA}a$	A suitably large value 20 min^{-1}	Not mass transfer-limited		
Partition coefficient for acetic acid (AA)	K_{AA}	0.04	333		
Partition coefficient for PAA	K_{PAA}	0.1[c]	333		

[a] Yield coefficient YAA = 1.65.
[b] Zaher *et al.* (Ref. 12).
[c] Estimated.

TABLE 6
A Comparison of the Rate of Reaction with Other Work from the Literature

Temperature (°C)	Source	Conditions	Reported rate (moles/min)	Predicted rate (moles/min)	Enhancement factor (predict./exp.)
Chou and Chang (Ref. 9)					
35	Figure 2–ii	$AcOH/H_2O_2 = 0.25$	0.00149	0.01237	8.3
35	Figure 2–iii	$AcOH/H_2O_2 = 0.5$	0.00298	0.01814	6.1
35	Figure 2–iv	$AcOH/H_2O_2 = 1.0$	0.00596	0.02071	3.5
Gan *et al.* (Ref. 10)					
20	Figure 2	No benzene	6.22×10^{-5}	7.95×10^{-5}	1.3
25	Figure 2	No benzene	9.57×10^{-5}	1.36×10^{-4}	1.4
40	Figure 2	No benzene	3.16×10^{-4}	6.13×10^{-4}	1.9
60	Figure 2	No benzene	1.315×10^{-3}	3.70×10^{-3}	2.8
20	Figure 2	Benzene	5.93×10^{-5}	7.82×10^{-5}	1.3
25	Figure 2	Benzene	9.41×10^{-5}	1.34×10^{-4}	1.4
40	Figure 2	Benzene	3.29×10^{-4}	6.04×10^{-4}	1.8
60	Figure 2	Benzene	1.33×10^{-3}	3.65×10^{-3}	2.7

A comparison of the kinetics of *in situ* epoxidation, as predicted by the two-phase model and experimental data in the literature, is possible if one looks at the total rate of epoxidation (moles/time) instead of comparing reaction rate constants. (A direct comparison of reaction rate constants would be meaningless because the system is a two-phase system and other authors have reported rate constants while treating the system as one phase.) The two-phase model was used to predict the rates of epoxidation in the experiments of Chou and Chang (9) and of Gan *et al.* (10). Our model was solved by using individual phase compositions, which were calculated from the stated reaction mixtures of these authors. The predicted reaction rates are compared with their experimental data in Table 6. The two-phase model predicts reaction rates 3–8 times greater than those observed by Chou and Chang (9). This difference is attributed to the fact that the model calculations were performed for the instantaneous addition of H_2O_2, whereas Chou and Chang (9) slowly added H_2O_2 to heat demand. The model also predicts epoxidation rates 1.3–2.8 times larger than those reported by Gan *et al.* These differences are attributed to improved mixing and mass transfer in our system and model. Although Gan and co-workers (10) were able to overcome heat transfer limitations and add all of the peroxide at once (due to the inherent dilution present in a lower iodine number oil), it is unlikely that they were able to overcome mass transfer limitations. These researchers used a round-bottom flask with a magnetic stirrer. The vessel did not contain any baffles, and the rate of stirring was not measured. A conventional stirred tank reactor would certainly have better mixing than a round-bottom flask.

Another interesting feature of this model is its prediction of the effect of an inert solvent. Because all of the benzene (solvent) stays in the oil phase, the rate of *in situ* epoxidation, which is limited by the rate of PAA formation in the aqueous phase, should be almost unaffected by the addition of benzene. (A slight difference will occur due to the different partitioning of AA.) However, the degradation reaction is significantly slowed down because the AA and epoxy concentrations in the oil phase are diluted. This prediction is backed up by the observations of Gan *et al.* (10), who show that the initial rate of *in situ* epoxidation is almost the same, with or without benzene, and that degradation of the oxirane is slowed down in the presence of benzene.

The importance and necessity of using a two-phase model is illustrated by the following example. Consider a typical reaction mixture with a total volume of V. The lumped single-phase rate of epoxidation (with PA formation as rate-limiting) in moles/time is $k[H^+][AA][H_2O_2]V$, where the square brackets represent molar concentrations (moles/total volume). Therefore, for this mixture, the rate would be (moles H^+)(moles AA)(moles H_2O_2)/V^2. If this system is diluted with an equal volume of benzene, then the rate as predicted by the lumped single-phase models would be reduced by a factor of 4, because the number of moles of the reactive species remains the same and the total volume is increased by a factor of two. This is clearly not the case. If a two-phase model is used, then no significant change is predicted because the controlling reaction takes place in the aqueous phase, which is undiluted.

Further work needs to be done to measure the rate of *in situ* epoxidation with 50 and 70% H_2O_2. Better characterization of the degradation reaction rates, as well as relating the effects of droplet size and distribution to reactions at the interface, will help refine this model and improve our understanding of the process of epoxidation.

ACKNOWLEDGMENTS

Support for this work was provided by the Center for Crop and Food Bioprocessing at Michigan State University. The authors would also like to thank Rodney Andrews and Ronald Egres, Jr. for their help with this project. Finally, the authors are indebted to Solvay Interox, (Houston, TX) for valuable information on hydrogen peroxide and epoxidation.

REFERENCES

1. Lutz, J.T., in *Encyclopedia of Chemical Technology,* 3rd edn., edited by J.G. Wallace, John Wiley & Sons, Vol. 9, 1978, pp. 251–266.
2. Findley, T.W., D. Swern and J.T. Scanlan, *J. Am. Chem. Soc. 67*:412 (1945).
3. Terry, D.E., and D.H. Wheeler, U.S. Patent 2,458,484 (1949).
4. Greenspan, F.P., U.S. Patent 2,490,800 (1949).
5. Swern, D., in *Organic Peroxides Volume II,* edited by D. Swern, Wiley-Interscience (John Wiley), New York, 1971, pp. 337–533.
6. French, W.H., U.S. Patent 3,360,531 (1971).
7. Solvay Interox, *Epoxidation,* A1.1.4.UK-2C-989 (1989).
8. Solvay Interox, *Considerations for the Safe Design of Processes Using H_2O_2 and Organics,* Houston, 1989.
9. Chou, T.C., and J.Y. Chang, *Chem. Eng. Commun. 41*:253 (1986).
10. Gan, L.H., S.H. Goh and K.S. Ooi, *J. Am. Oil Chem. Soc. 69*:347 (1992).
11. Wohlers, H.C., M. Sack and H.P. LeVan, *Ind. Eng. Chem. 50*:1685 (1958).
12. Zaher, F.A., M.H. El-Mallah and M.M. El-Hefnawy, *J. Am. Oil Chem. Soc. 66*:698 (1989).
13. Paquot, C., in *Standard Methods for the Analysis of Oils, Fats and Derivatives, Part 1,* 6th edn., IUPAC, Pergamon Press, New York, 1979.
14. Abraham, M.E., and R.F. Benenati, *AIChE J. 18*:807 (1972).
15. Swern, D., in *Organic Peroxides, Volume I,* edited by D. Swern, Wiley-Interscience (John Wiley), New York, 1970.
16. Sack, M., and H.C. Wohlers, *J. Am. Oil Chem. Soc. 36*:623 (1959).

[Received November 29, 1994; accepted June 8, 1995]