

Effect of FA Composition on Epoxidation Kinetics of TAG

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ABSTRACT: The rate constants of epoxidation were determined by reacting formic acid with a number of oils, pure TAG, and pure FAME. These results showed that FA composition had a significant effect on the value of the rate constant. In TAG, the double bonds of oleic acid and linoleic acid were equally reactive, and the double bonds of linolenic acid were approximately three times more reactive than oleic and linoleic acids. For FAME, the rate constants of epoxidation increased as the level of unsaturation increased. Furthermore, the rate constants of epoxidation for the FAME were higher than their respective TAG. We conclude that steric and electronic effects caused FA with different levels of unsaturation to have different reactivities. These results were used to derive a model that predicts the epoxidation kinetics of oils from their FA composition. The predictions of the model closely match the experimentally determined rate constants.

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KEY WORDS: Epoxidation kinetics, epoxides, fatty acid methyl esters, ¹H NMR, partially epoxidized oils, triacylglycerols.

TAG in plant oils have been used to make a number of polymeric materials, such as coatings, and are also used as toughening agents for epoxy resins and other polymers (1). Recently, TAG have been used to create engineering composites (2,3) and pressure-sensitive adhesives (4). The properties of these TAG-based polymers have not been optimized. Genetic engineering offers a new way of optimizing the properties of TAG-based polymers by controlling the FA distribution. This allows us to change the composition of plant oils to control the structures that produce polymers with better properties. However, we do not know the effect of oil composition on the properties of the resulting polymer. We have been exploring the effect of TAG molecular structure on polymer properties and the reactions used to produce monomers and polymers. This paper presents results on the effect of FA composition on epoxidation reaction kinetics.

Epoxidation is among the most commonly used reactions to produce plant oil-based polymers. Other researchers have studied the epoxidation reaction (5–8). However, none of these researchers has looked at the effect of FA composition on the kinetics of the reaction. A detailed knowledge of the effects of FA composition on the epoxidation kinetics is necessary for the production of partially epoxidized oils for polymers or other applications.

The epoxidation reaction (Scheme 1) can be run using *in-situ* peracids or preformed peracids (8). The use of *in-situ* peracids is inappropriate for use in this study because the concentration

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of peracid changes as a function of time, making a kinetic analysis very difficult. Peracids of acetic acid and formic acid have been successfully used to epoxidize oils (6,8). Performic acid was used in this work because the rate of performic acid formation is much greater than that of peracetic acid (6,9). The problem with using a catalyst in a study like this one is that peracetic acid is only formed in high concentrations when a catalyst is used (6,9). Because the mass of catalyst added to the reaction is very small, random error in the catalyst mass is significant and can have a large effect on the peracid concentration. The formation of performic acid requires no catalyst and is therefore easier to produce with a specific concentration.

The kinetics of TAG epoxidation and the reaction mechanism (Scheme 2) are well known (10). The rate law is shown in Equation 1:

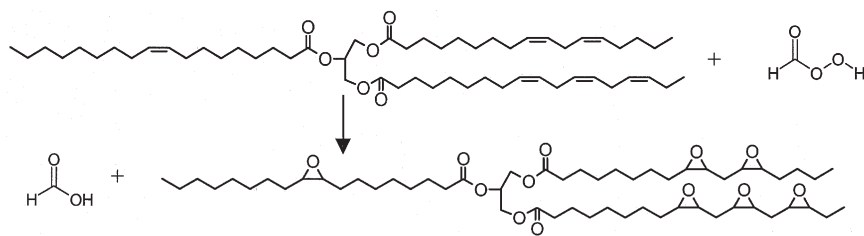
$$r = \frac{d[\text{DB}]}{dt} = k[\text{DB}][\text{PFA}] \quad [1]$$

where r is the rate of disappearance of carbon-carbon double bonds, [DB] is the concentration of double bonds, [PFA] is the concentration of performic acid, and k is the second-order rate constant. This rate law holds for all oils, TAG, and FAME. Thus, if TAG structure is going to have an effect on epoxidation reaction kinetics, the only parameter that can be affected is the rate constant. Therefore, the experiments were designed to determine the rate constants of various oils. We also examined the effect of double bond position and the unsaturation level of FA on the epoxidation rate constants of several plant oils, model TAG, and model FAME.

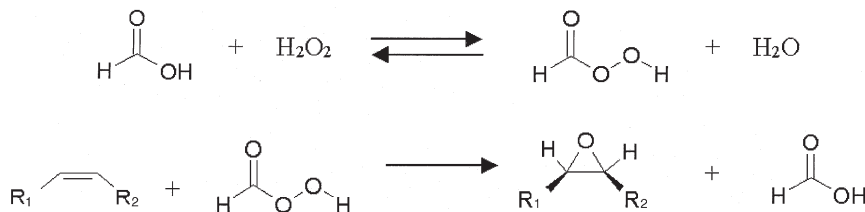
EXPERIMENTAL PROCEDURES

A number of oils (Sigma-Aldrich, St. Louis, MO; except high-oleic soybean oil provided by DuPont Corporation, Wilmington, DE), model TAG (Sigma-Aldrich, 99%) and FAME (Sigma-Aldrich, 99%) were used in this study. A performic acid solution was prepared by adding 40 g formic acid (Fluka, Buchs, Switzerland; 98%) to 30 g hydrogen peroxide (Fisher, Fairlawn, NJ; 30% aqueous solution). This ratio of reactants maximized the equilibrium concentration of performic acid (11,12). The reaction mixture was allowed 3 h to reach equilibrium.

A magnetic stir bar, 10.5 g of the performic acid solution, and 0.5 g of an oil were added to a screw-cap vial. The caps were tightened to prevent any mass loss to the surroundings. The sample was placed in a 19°C water bath and stirred continuously at 1150 rpm to homogenize the two-phase system. This was found to eliminate all heat and mass transfer limita-



SCHEME 1



SCHEME 2

tions, as discussed below, and thus enabled an analysis of the kinetic data. This procedure was repeated for a number of samples. The samples were run for reaction times between 0 and 30 min. Three runs were performed for each sample unless otherwise noted. At specific reaction times, an ether extraction was immediately performed on the sample. The purpose of the extraction was twofold. First, the extraction stopped further epoxidation of the oil. Second, the extraction allowed the recovery of a pure, partially epoxidized, oil product.

In the extraction, the sample was dissolved in about 25 mL diethyl ether and poured into a separatory funnel. An aqueous solution of saturated sodium bicarbonate was added, which was then shaken to ensure good mixing. The contents were allowed to separate into oil and water layers. The aqueous layer was discarded. Sodium bicarbonate washes were repeated until the pH of the water layer was neutral or alkaline, as determined by pH paper. In the next step, water was added to remove any residual salts produced by the neutralization reaction. The layers were allowed to separate, and the water layer was discarded. The ether solution was washed with saturated aqueous sodium chloride to remove water from the ether phase and dried over sodium sulfate. The ether was boiled away at a temperature of 40°C.

The level of epoxidation was measured with proton nuclear magnetic resonance (^1H NMR) spectroscopy using a Bruker AC250 spectrometer (250.13 MHz, spectral window of ± 2000 Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K). Figure 1 shows the NMR spectra of olive oil and partially epoxidized olive oil. The two sets of peaks from 4.0–4.4 ppm are produced by the four methylene protons on the glycerol center. The peak at 2.3 ppm is produced by six protons α to the carbonyl groups. The peak at 0.9 ppm is produced by the nine methyl protons. These internal standards were used to determine the number of double bonds (5.2–5.5 ppm) and epoxide groups per TAG (2.7–3.2 ppm). In all cases, the number of epoxides plus double bonds per TAG in the final product added to within the experimental error (3%) of the initial

number of double bonds per TAG. Thus, neither epoxides nor double bonds were lost during the ether removal step. Furthermore, NMR allowed us to detect the presence of hydroxyl or formate groups attached to the TAG. Hydroxyl or formate groups were not observed except during the epoxidation of linolenic acid methyl ester. In this case, the conversion vs. time data after hydroxylation were omitted from the analysis.

To determine if the measured rate conversion data were intrinsic values or mass transfer-limited, mass transfer studies and solubility studies were performed. In the mass transfer experiments, the organic phase mass and mixing speeds were varied to see their effect on the reaction kinetics.

To determine the effect of the organic phase mass on the reaction kinetics, samples containing 10.5 g of the performic acid solution and organic phase masses of 0.25, 0.5, 0.75, 1, and 2 g of oil were added to screw-cap vials. The samples were placed in a 19°C water bath and magnetically stirred on a VWR (Chicago, IL) Dylastir at 1150 rpm to homogenize the two-phase system. The samples were allowed to react for 30 min, and the conversion was measured using ^1H NMR.

To see if stirring speed affects the reaction kinetics, samples containing 0.5 g oil and 10.5 g of the performic acid solution were added to screw-cap vials. The samples were placed in a 19°C water bath and magnetically stirred with a VWR Dylastir at stirring speeds ranging from 400 to 1400 rpm. The samples were allowed to react for 30 min, and the conversion was measured using ^1H NMR.

Because we have a two-phase reaction mixture, different solubilities of performic acid in the organic phase can have a large effect on the kinetics. To see if this is the case, the solubilities of water in each of the oils, model TAG, and FAME used in this experiment were measured. Samples containing 10 mL oil and 10 mL deionized water were added to a vessel with a screw-cap lid. The vessel was placed in a temperature bath at 25°C. The oil and water were mixed well for 2 h. Then, the oil and water were allowed to phase-separate. Once the two phases separated, a sample of the organic phase was

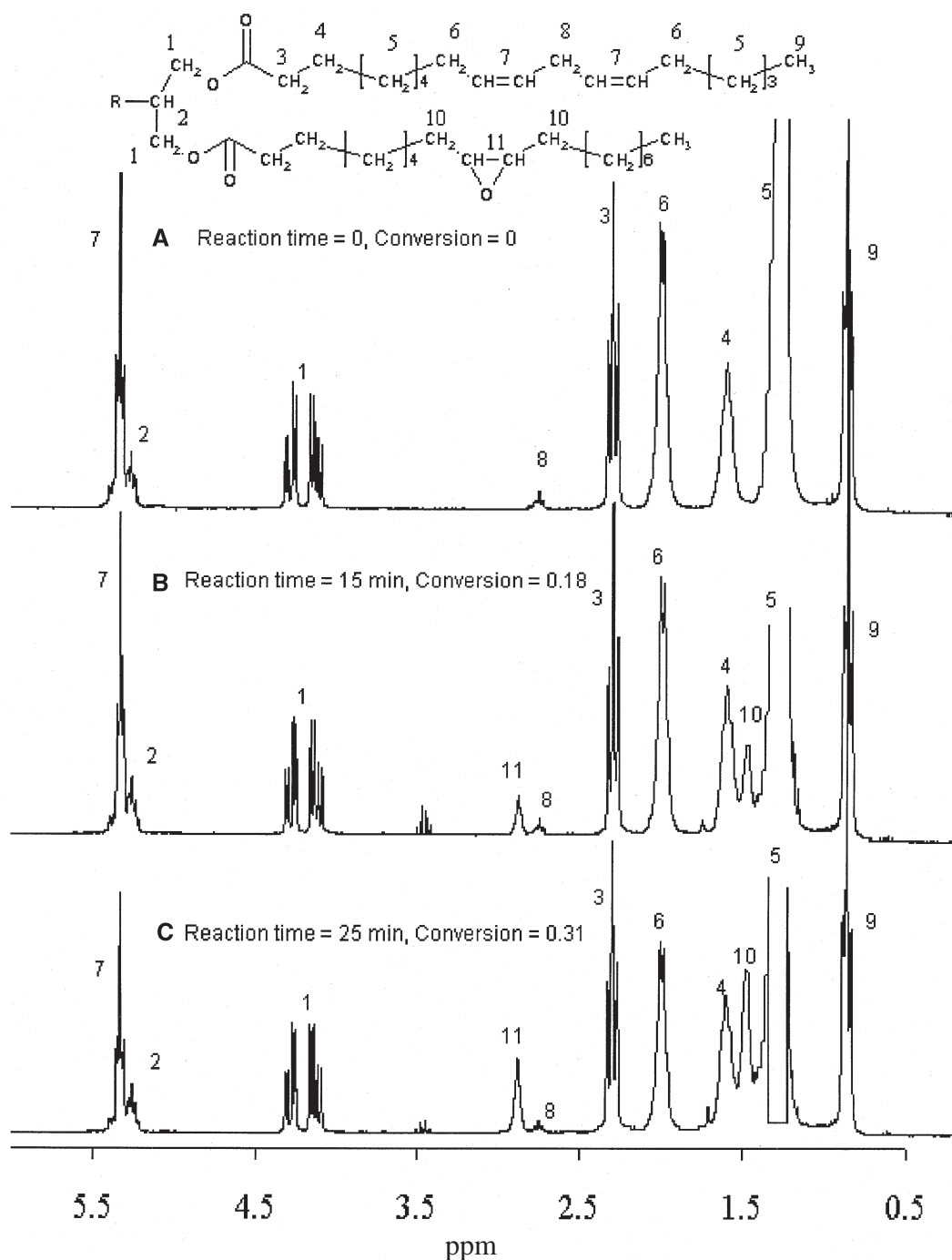


FIG. 1. ¹H NMR spectra of olive oil (A) and partially epoxidized olive oil (B, C).

taken from the vessel. The mass of the sample was measured and then injected into an MCI (Tokyo, Japan) Moisturemeter model CA-05, which measured the mass of water in the sample. All measurements were done in triplicate. With the measured sample mass and water mass in the sample, the concentration, in $\mu\text{g/g}$, of water in oil was calculated.

The solubility of formic acid in each of the oils was measured using a similar procedure as the oil–water solubility. However, after phase separation, 0.1 g of the organic phase was dissolved in 1 g deuterated chloroform. ¹H NMR was run

on these samples, as previously described, and the moles of formic acid (8 ppm) per TAG or FAME were measured.

RESULTS AND DISCUSSION

Mass transfer and solubility effects. An effect of oil mass on the reaction kinetics was observed. As the mass of the oil in the reaction mixture increased from 0.75 to 2 g, the extent of epoxidation decreased. However, as the oil mass increased from 0.25 to 0.75 g, the measured conversions were constant.

Therefore, mass transfer effects could be eliminated by using a mass of oil between 0.25 and 0.75 g. The oil mass of 0.5 g was chosen because it allows for a large enough sample size to minimize random error while being well within the acceptable mass transfer window.

Stirring speed also has an effect on the reaction kinetics. As the stirring speed increased from 400 to 900 rpm, the extent of epoxidation increased. However, as the stirring speed increased from 900 to 1400 rpm, no changes in extent of epoxidation were measured. To safely avoid mass transfer effects, a stirring speed of 1150 rpm was chosen.

The solubility of water was very similar for all of the oils, model TAG, and FAME. The solubility was $\sim 1200 \mu\text{g}$ water/g oil. All of the samples were within experimental error ($\pm 100 \mu\text{g/g}$).

The solubility of formic acid was also very similar for all of the oils, TAG, and FAME tested. The solubility was 0.1 g formic acid/g oil ± 0.01 g formic acid/g water. All of the samples were within experimental error of this solubility.

The solubility of PFA in the organic phase could not be accurately or reliably measured. Therefore, the PFA bulk solution concentration was used to calculate the rate constants. Because the epoxidation reaction takes place in the oil phase, the values of the rate constants reported in the paper need to be modified by the concentrations of PFA in the oil phase relative to the bulk. However, the solubility of PFA in the organic phase should be very similar for the different oils, TAG, and FAME because the solubilities of formic acid in the organic phase and water in the organic phase were similar. Therefore, the reaction rates observed in this experiment are intrinsic rates because mass transfer effects were eliminated and distribution effects (possible differences in solubility of performic acid in the organic phase) were not present.

Epoxidation rate constants. The equilibrium constant for the formation of performic acid at the reaction temperature was found to be 0.76 (11,12). With the equilibrium constant and the reactant masses listed above, it can be calculated that there are 23 moles of performic acid per mole of TAG. In addition, the equilibrium performic acid solution has relatively high concentrations of unreacted formic acid and hydrogen peroxide. Thus, as the performic acid reacts with unsaturation sites, more performic acid must be regenerated to maintain equilibrium. Although the rate of performic acid formation is not known, it can be estimated from the rate constant of peracid production. The rate constants given by Ogata and Sawaki (13) indicate that 500 L/(mol·min) would be a safe (low) estimate of the rate constant to produce performic acid. For the given reaction conditions, the rate of performic acid formation was calculated to be $1.5 \cdot 10^4$ mol/(L·min). The rate of epoxidation was overestimated by using an oil with nine unsaturation sites per TAG (the maximum used in this paper) and a rate constant of epoxidation of 0.1 L/(mol·min), which is higher than any calculated epoxidation rate constant found in this paper. By using this and the given reaction conditions, the rate of epoxidation was calculated to be 0.04 mol/(L·min). Thus, the rate of performic acid production is at least $4 \cdot 10^4$

faster than the rate of epoxidation. This means that whenever a performic acid molecule reacts, another performic acid molecule is generated before any further epoxidation occurs.

The performic acid concentration should change over the course of the reaction because the concentrations of formic acid and hydrogen peroxide decrease and the water concentration increases. Yet after three unsaturation sites per TAG have been epoxidized (the maximum extent of reaction used in this paper), equilibrium calculations show that the performic acid concentration only decreased from 1 to 0.96 mol/L.

Because the rate of formation of performic acid is much faster than the rate epoxidation, and the performic acid concentration is essentially constant throughout the reaction, the epoxidation reaction can be assumed to be pseudo-zero order in performic acid concentration. Thus, the epoxidation rate law (Eq. 1) simplifies to

$$-\frac{d[\text{DB}]}{dt} = k'[\text{DB}] \quad [2]$$

where k' is the pseudo-first-order rate constant:

$$k' = k[\text{PFA}] \quad [3]$$

Integrating Equation 2 results in

$$\ln\left(\frac{[\text{DB}]_0}{[\text{DB}]}\right) = k't \quad [4]$$

where $[\text{DB}]_0$ is the initial concentration of carbon-carbon double bonds. If $\ln([\text{DB}]_0/[\text{DB}])$ is plotted vs. time, a linear plot should result, with a slope equal to k' . Figure 2, the first-order plot of triolein and linseed oil, is representative of such plots. By using Equations 3 and 4 and the calculated performic acid concentration, the second-order rate constants

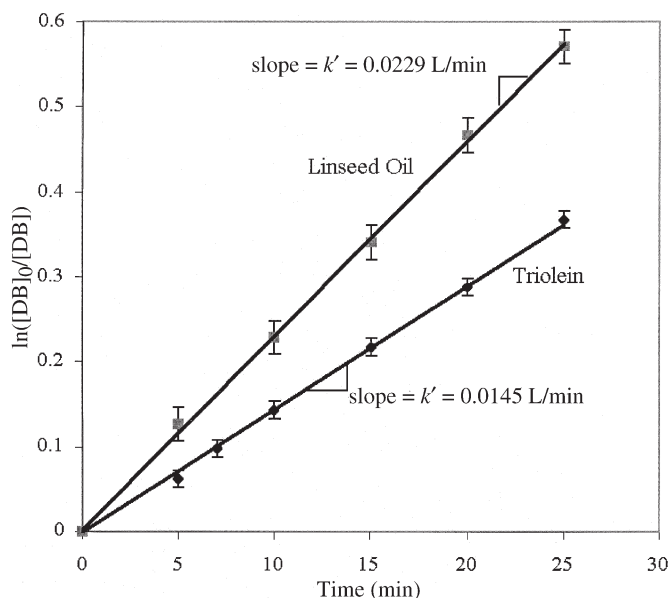


FIG. 2. First-order plot of the conversion vs. time data for the epoxidation of triolein and linseed oil. The epoxidation rate constant for linseed oil is larger than that for triolein.

were calculated for every oil. Table 1 lists the second-order rate constants and the percentages of oleic acid, linoleic acid, and linolenic acid contained within the oils. Only these acids are important because they contain greater than 99% of the unsaturation sites in the oil. From the results of Table 1, it is clear that FA composition affects the epoxidation rate constant. Specifically, oils with higher contents of linolenic acid have higher epoxidation rate constants.

Epoxidation model. The effect of FA composition on epoxidation kinetics was modeled. In assuming that each double bond reacts independently of the others, Equation 1 can be rewritten as:

$$r = k[\text{DB}][\text{PFA}] = (k_{\text{oleic}}[\text{DB}_{\text{oleic}}] + k_{\text{linoleic}}[\text{DB}_{\text{linoleic}}] + k_{\text{linolenic}}[\text{DB}_{\text{linolenic}}]) \cdot [\text{PFA}] \quad [5]$$

where k_y is the rate constant of FA type y and $[\text{DB}_y]$ is the concentration of double bonds on FA of type y . Solving for k , we obtain:

$$k = (k_{\text{oleic}}[\text{DB}_{\text{oleic}}] + k_{\text{linoleic}}[\text{DB}_{\text{linoleic}}] + k_{\text{linolenic}}[\text{DB}_{\text{linolenic}}]) / [\text{DB}] \quad [6]$$

At low conversions, the ratio of the double bond concentration on a given FA to the total concentration of double bonds is approximately constant, so these values can be assumed to be their initial quantities. We make this assumption so we do not have to measure the FA compositions as a function of reaction time. In these experiments, the conversion was low for all samples in order to meet this criterion. With this assumption, we can write the epoxidation kinetic model as:

$$k = k_{\text{oleic}} \left(\frac{[\text{DB}_{\text{oleic}}]}{[\text{DB}]} \right)_0 + k_{\text{linoleic}} \left(\frac{[\text{DB}_{\text{linoleic}}]}{[\text{DB}]} \right)_0 + k_{\text{linolenic}} \left(\frac{[\text{DB}_{\text{linolenic}}]}{[\text{DB}]} \right)_0 \quad [7]$$

where the concentrations of double bonds (i.e., $[\text{DB}]_{\text{oleic}}$, etc.) are initial quantities.

TABLE 1
Second-Order Rate Constants and the Percentages of Oleic Acid, Linoleic Acid, and Linolenic Acid for the Different Oils Used in This Experiment

Oil	k L/(mol·min)	Oleic acid	Linoleic acid	Linolenic acid
Triolein	0.0145	99	0	0
Trilinolein	0.0145	0	99	0
Safflower seed	0.0145	21.5	66.0	0
Cottonseed oil	0.0145	23.0	50.0	0.3
Corn oil	0.0146	27.5	57.0	0.9
Olive oil	0.0148	71.1	10.0	0.6
HOSO ^a	0.0156	82.6	2.3	3.7
Soybean oil	0.0158	25.0	53.2	6.0
Canola oil	0.0166	64.1	18.7	9.2
50% Linseed, 50% olive ^b	0.0185	45.1	12.7	28.6
Linseed oil	0.0229	19.1	15.3	56.6

^aHOSO, high-oleic soybean oil.

^bThis mixture was 50% linseed oil and 50% olive oil by mole fraction.

To determine the three unknown parameters (k_{oleic} , k_{linoleic} , and $k_{\text{linolenic}}$), an epoxidation kinetic study was performed on three model compounds. The first model oil used was triolein. Triolein is composed entirely of oleic acid, which is 18 carbon atoms long and has one carbon double bond, which is located in the n-9 position. Because triolein is composed entirely of oleic acid, the second and third terms on the right side of Equation 7 are zero. Therefore, k_{oleic} is equal to the rate constant for the epoxidation of triolein, which was found to be 0.0145 ± 0.0002 L/(mol·min). The second model oil was trilinolein. This compound is composed entirely of linoleic acid, which is 18 carbon atoms long and has two double bonds: one at the n-9 position and the other at the n-12 position. Therefore, the first and third terms on the right side of Equation 7 are zero, so k_{linoleic} is equal to the rate constant for trilinolein, which was determined to be 0.0145 ± 0.0002 L/(mol·min). The third model oil used was linseed oil. This oil was used because it contains greater than 50% linolenic acid. This acid is 18 carbon atoms long and has three double bonds. The double bonds are located at the n-9, n-12, and n-15 positions. By using an analysis similar to that shown above, $k_{\text{linolenic}}$ was calculated to be equal to 0.0254 ± 0.0005 L/(mol·min). The model oil trilinolenin was also used to determine $k_{\text{linolenic}}$. Trilinolenin is composed entirely of linolenic acid. With this oil, $k_{\text{linolenic}}$ was determined to be 0.0240 ± 0.0015 L/(mol·min), which is within experimental error of that determined using linseed oil. Because of the high cost of trilinolenin, triplicate runs were not done. Thus, there is higher error associated with its results, which would lead to lower confidence in the model's predictions. Therefore, $k_{\text{linolenic}}$ determined from linseed oil was used in the model instead of $k_{\text{linolenic}}$ determined from trilinolenin.

To test the accuracy of this model, the rate constants for several oils were calculated based on their FA compositions. Table 2 lists the predictions of the model along with the experimentally determined values. The table shows that there is excellent agreement between model and experiment. Thus, the epoxidation kinetic model accurately describes the effect of FA composition on epoxidation kinetics.

Steric and electronic effects on epoxidation kinetics. The TAG used in this experiment vary only in the number of

TABLE 2
Model's Predictions of the Second-Order Rate Constant of Epoxidation Compared with the Experimentally Determined Rate Constants^a

Oil	k (experiment), L/(mol·min)	k (model), L/(mol·min)
Safflower seed oil	0.0145	0.0145
Cottonseed oil	0.0145	0.0146
Corn oil	0.0146	0.0147
Olive oil	0.0148	0.0147
HOSO	0.0156	0.0157
Soybean oil	0.0158	0.0158
Canola oil	0.0166	0.0168
50% Linseed oil, 50% olive oil	0.0185	0.0187

^aFor abbreviation see Table 1.

TABLE 3
Comparison of Rate Constants of Epoxidation for Specific FA
Between TAG and Their Respective FAME

FA	k of FAME [L/(mol·min)]	k of TAG [L/(mol·min)]
Oleic acid	0.0273	0.0145
Linoleic acid	0.0433	0.0145
Linolenic acid	0.0712	0.0254

double bonds. Thus, there are three possible causes for the variation in epoxidation rate constants with FA composition. The first possibility involves steric factors, such that double bonds further from the glycerol center are more reactive than double bonds near the glycerol center. The second possibility is that double bonds on different FA have different reactivities because of electronic effects. The third possibility is a combination of the steric and electronic effects. To separate these possibilities, we performed kinetic experiments on FAME.

Table 3 lists the measured rate constants for the different FAME. It is clear that the FAME with a higher degree of unsaturation have a higher rate constant of epoxidation. An explanation for this occurrence is that as the number of double bonds increases, the electron density increases, which causes an increase in the rate constant. Table 3 also shows that the double bonds on the FAME were more reactive than the double bonds of the respective FA of TAG. Thus, steric factors inherent in the TAG structure reduce the reactivity of the unsaturated sites. This indicates that double bonds located at the end of the FA chain (i.e., n-15) will be less sterically hindered. Therefore, steric and electronic effects cause the variation in epoxidation kinetics from oil to oil.

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REFERENCES

1. Kirschenbauer, H.G., *Fats and Oils: An Outline of Their Chemistry and Technology*, Reinhold Publishing, New York, 1960, pp. 146–156.
2. Wool, R.P., S.H. Kusefoglu, G.R. Palmese, R. Zhao, and S.N. Khot, High Modulus Polymers and Composites from Plant Oils, U.S. Patent 6,121,398 (2001).
3. Khot, S.N., J.J. La Scala, E. Can, S.S. Morye, G.I. Williams, G.R. Palmese, S.H. Kusefoglu, and R.P. Wool, Development and Application of Triglyceride-Based Polymers and Composites, *J. Appl. Polym. Sci.* 82:703–723.
4. Bunker, S.P., and R.P. Wool, Synthesis and Characterization of Monomers and Polymers for Adhesives from Methyl Oleate, *J. Polym. Sci. Part A, Polym. Chem.* 40:451–458 (2002).
5. King, G., The Mechanism of the Oxidation of Oleic and Elaidic Acids and Their Methyl Esters by Hydrogen Peroxide in Acetic Acid. Further Observations on the Configurations of the 9,10-Dihydroxystearic Acids, *J. Chem. Soc. (London)*:37–38 (1943).
6. Findley, T.W., D. Swern, and J.T. Scanlan, Epoxidation of Unsaturated Fatty Materials with Peracetic Acid in Glacial Acetic Acid Solution, *J. Am. Chem. Soc.* 67:412–414 (1945).
7. Rangarajan, B., A. Havey, E.A. Grulke, and P.D. Culnan, Kinetic Parameters of a Two-Phase Model for *in situ* Epoxidation of Soybean Oil, *J. Am. Oil Chem. Soc.* 72:1161–1169 (1995).
8. Gnecco, S., A. Pooley, and M. Krause, Epoxidation of Low Molecular Weight *Euphorbia lactiflua* Natural Rubber with *in situ* Formed Performic Acid, *Polym. Bull.* 37:609–615 (1996).
9. Greenspan, F.P., The Convenient Preparation of Per-acids, *J. Am. Chem. Soc.* 68:907 (1946).
10. Swern, D., G.N. Billen, T.W. Findley, and J.T. Scanlan, Hydroxylation of Monounsaturated Fatty Materials with Hydrogen Peroxide, *Ibid.* 67:1786–1789 (1945).
11. Monger, J.M., and O. Redlich, Peroxysulfuric Acid and Peroxyformic acid. Equilibrium and Formation Rate, *J. Phys. Chem.* 60:797–799 (1956).
12. Hatcher, W.H., and G.W. Holden, *Trans. Roy. Soc. Canada* 21:237 (1927).
13. Ogata, Y., and Y. Sawaki, Kinetics of the Acid-Catalyzed Formation of Aliphatic Peracids from Hydrogen Peroxide and Aliphatic Acids in Dioxan, *Tetrahedron* 21:3381 (1965).

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