The Effect of Fatty Acid Composition on the Acrylation Kinetics of Epoxidized Triacylglycerols

John La Scala and Richard P. Wool*

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

ABSTRACT: Epoxidized oils, epoxidized triacylglycerols, and epoxidized fatty acid methyl esters were made by reaction with performic acid formed *in situ*. The extent of epoxidation was *ca.* 95% for all of the epoxidized samples, as determined by ^{1}H nuclear magnetic resonance. The epoxidized samples were reacted with an excess of acrylic acid for different reaction times. The acrylation reaction was found to have a first-order dependence on the epoxide concentration for all oils, pure triacylglycerols, and fatty acid methyl esters. However, the rate constant of acrylation was found to depend on the composition of the epoxidized material. The acrylation rate constant for 9,10-epoxystearic acid was 96 $L^2/(mol^2 \cdot min)$. The rate constant of acrylation for the epoxides on 9,10,12,13-diepoxystearic acid was 60 $L^2/(mol^2 \cdot min)$. The acrylation rate constant for the epoxides on 9,10,12,13,15,16-triepoxystearic acid was 50 $L^2/(mol^2 \cdot min)$. Thus, the rate constant of acrylation increased as the number of epoxides per fatty acid decreased. Multiple epoxides per fatty acid decrease the reactivity of the epoxides because of steric hindrance effects, and the oxonium ion, formed as an intermediate during the epoxy-acrylic acid reaction, is stabilized by local epoxide groups. These results were used to derive an acrylation kinetic model that predicts rate constants from fatty acid distributions in the oil. The predictions of the model closely match the experimentally determined rate constants.

Paper no. J9869 in *JAOCS 79*, 59–63 (January 2002).

KEY WORDS: Acrylation kinetics, acrylation model, epoxides, highly epoxidized oils, ^{1}H NMR, triacylglycerols.

Acrylated soybean oil has been used as an additive to inks and coatings (1) and as the major component of a number of natural resins (2). Acrylated soybean oil is formed by reaction of acrylic acid with epoxidized soybean oil (Fig. 1) (3). A number of studies have examined the kinetics of oxirane cleavage. Zaher and co-workers have analyzed the kinetics of the reaction of acetic acid (4) and formic acid (5) with epoxidized oils. Bunker has examined the kinetics of acrylic acid with epoxidized methyl oleate (6). However, none of these researchers has looked at the effect of fatty acid composition on the epoxide–carboxylic acid reaction kinetics.

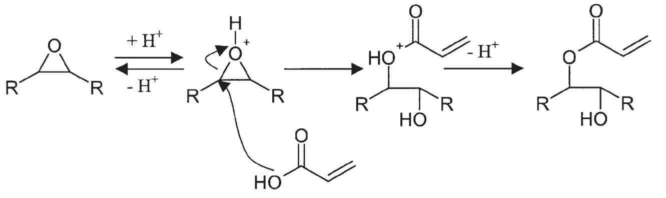

FIG. 1. Acid-catalyzed acrylation of epoxidized oils, epoxidized triacylglycerols, or epoxidized fatty acid methyl esters (Ref. 3).

The rate law for the acrylation of epoxidized triacylglycerols and fatty acid methyl esters has the following form (Eq. 1) (4–6):

$$r = -\frac{d[\mathrm{E}]}{dt} = k[\mathrm{E}]^{\alpha}[\mathrm{AA}]^{\beta} \qquad [1]$$

where *r* is the rate of reaction, *k* is the rate constant, *t* is the time, [E] is the epoxide concentration, [AA] is the acrylic acid concentration, α is the reaction order in epoxides, and β is the reaction order of acrylic acid. Bunker found the rate law to be second-order in acrylic acid (i.e., $\beta = 2$) (6). The reaction order in epoxides for reaction with a carboxylic acid has been found to be 1 or 2 depending on the acid (4–6). It is possible that the fatty acid content in epoxidized materials can affect the epoxide reaction order and/or rate constant of reaction. Thus, the experiments detailed herein are designed to determine any effects of fatty acid composition on the epoxide reaction order and rate constant.

EXPERIMENTAL PROCEDURES

Synthesis of epoxidized oils, epoxidized triacylglycerols, and epoxidized fatty acid methyl esters. Epoxidized samples were made by reacting the oils, triacylglycerols, and fatty acid methyl esters with a mixture of formic acid and hydrogen peroxide. Typically, formic acid is not used to make epoxidized material because it readily cleaves the oxirane ring (5,7). However, when used in low concentrations, formic acid does not cause significant oxirane cleavage. Formic acid is better suited for this work than acetic acid because, when reacted with hydrogen peroxide, performic acid forms at a much faster rate than peracetic acid (8,9).

Table 1 lists the starting materials for this study with their respective manufacturers, as well as the reactant masses used to produce the epoxidized material. In general, the amount of formic acid used was one-third the oil mass in order to have a low formic acid concentration. The amount of hydrogen peroxide used was twice the molar ratio needed to produce the

---

*To whom correspondence should be addressed at Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716.
E-mail: Wool@che.udel.edu

TABLE 1
Reactant Masses Used to Produce Highly Epoxidized Materials[a]

Sample (manufacturer)	Sample (g)	Hydrogen peroxide (g)	Formic acid (g)
Olive[b]	100.0	73.9	33.3
HOSO[c]	100.0	77.5	33.3
Cottonseed[b]	99.8	98.1	33.3
Canola[d]	100.3	102.2	33.4
Corn[b]	100.0	113.9	33.3
Soybean[d]	100.0	120.9	33.3
Safflower seed[d]	100.1	124.7	33.4
Triolein, 99%[b]	5.00	3.86	1.66
Trilinolein, 99%[b]	1.655	2.568	0.550
Methyl oleate, 99%[b]	20.84	16.47	11.04
Methyl linoleate, 99%[b]	1.77	2.73	0.59

[a] The oil, triacylglycerol, and fatty acid methyl ester manufacturers are also listed; HOSO, a genetically engineered high-oleic soybean oil.
[b] Sigma, St. Louis, Missouri.
[c] DuPont Corp., Wilmington, Delaware.
[d] Aldrich, Milwaukee, Wisconsin.

completely epoxidized sample. This amount of hydrogen peroxide was used to drive the epoxidation of oils to near completion.

The unsaturated starting materials were added to an Erlenmeyer flask, which contained a magnetic stir bar. The appropriate mass of hydrogen peroxide (Fisher Scientific, Pittsburgh, PA; 30% aqueous solution) was added, followed by the formic acid (Fluka, Ronkonkoma, NY; 98%). The performic acid was thus prepared *in situ*. Because only the end extent of epoxidation was important and not a kinetic analysis of the epoxidation, using *in-situ*-formed performic acid is appropriate. The flask was stoppered and placed on a magnetic stirrer to mix the contents. The reaction was run at room temperature. At the end of 16 h reaction time, the samples were ether-extracted to recover purified epoxidized oils. The samples were dissolved in ether and washed with aqueous sodium bicarbonate until the pH of the solution was slightly alkaline. The contents were allowed to phase-separate, and the aqueous layer was discarded. Finally, the solution was washed with aqueous sodium chloride and dried over sodium sulfate. The ether was removed by heating at a temperature of 40°C.

Epoxidized soybean oil (Witco, Greenwich, CT) was used for comparison to our synthesized epoxidized soybean oil. Epoxidized linseed oil (Elf Atochem, Philadelphia, PA) was used because we were unable to synthesize a highly epoxidized linseed oil.

Acrylation reaction. Epoxidized oils, epoxidized triacylglycerols, and epoxidized fatty acid methyl esters were reacted with acrylic acid to determine the epoxide reaction order and the effect of fatty acid composition on the rate constant. All samples were prepared in 20-mL screw-cap vials. Acrylic acid in the amount of 11.5 g was added to the vial. A mass of 0.03 g hydroquinone was added to the vial to inhibit polymerization of the acrylate groups. The epoxidized material was added to a separate vial. The acrylic acid vial, epoxidized sample vial, and silicon oil bath were heated to a temperature of 75°C. When the temperatures reached equilibrium, 3 g of the epoxidized material was added to the vial containing the acrylic acid. The cap was tightly screwed onto the reaction vial, and the vial was placed in the oil bath. For determination of the reaction order, the reaction was run for 3 h and samples were taken every 30 min. When examining the effect of fatty acid composition on the acrylation rate constant, the reaction was run for 1 h and samples were taken every 10 min. The reaction was stopped in these samples by quenching them in an ice-water bath. Then the samples were dissolved in deuterated chloroform and placed in a freezer at a temperature of –5°C.

^{1}H nuclear magnetic resonance (NMR) analysis. Samples were prepared for ^{1}H NMR spectroscopy to determine the extent of epoxidation or acrylation by adding *ca.* 0.1 g functionalized oil to 1 g deuterated chloroform. A Bruker (Billerica, MA) AC250 spectrometer (250.13 MHz, spectral window of ± 2000 Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) was used to analyze every sample. Figure 2 shows the ^{1}H NMR spectrum of acrylated epoxidized soybean oil. The two sets of peaks from 4.0 to 4.4 ppm are produced by the four methylene hydrogen atoms attached to the glycerol center. The peak at 2.3 ppm is produced by the six methylene hydrogen atoms alpha to the carbonyl groups. The peak at 0.9 ppm is produced by the nine methyl hydrogen atoms. The peak areas of these internal standards were used to determine the number of double bonds (5.2–5.5 ppm), epoxides (2.8– 3.25 ppm), and acrylates per triacylglycerol (5.7–6.6 ppm). In all cases, the sum of the double bonds, epoxides, and twice the number of acrylates per triacylglycerol on the final product was equal to the initial number of double bonds per triacylglycerol, within experimental error.

RESULTS AND DISCUSSION

Reaction order in epoxides. Table 2 lists the extent of epoxidation of all of the oils, pure triacylglycerols, and fatty acid

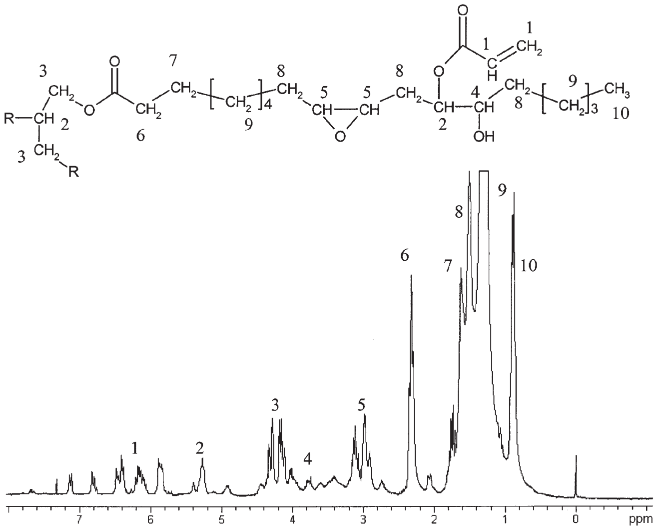

FIG. 2. The ^{1}H nuclear magnetic resonance spectrum of acrylated epoxidized soybean oil. The methylene peak (9) is cut off to allow a better view of the other peaks.

TABLE 2
The Extent of Epoxidation for the Oils, Triacylglycerols, and Fatty Acid Methyl Esters Used in This Experiment, as Measured with ^{1}H Nuclear Magnetic Resonance

Oil	Epoxides/ molecule	Extent of epoxidation (%)
Methyl oleate	0.93	93
Methyl linoleate	1.8	93
Olive oil	2.6	92
High-oleic soybean oil	2.8	93
Triolein	2.8	93
Cottonseed oil	3.5	95
Canola oil	3.8	97
Corn oil	4.3	98
Soybean oil	4.4	96
Soybean oil[a]	4.5	98
Safflower seed oil	4.5	94
Trilinolein	5.8	97
Linseed oil[b]	6.2	97

[a] Greenwich, Connecticut.
[b] Elf Atochem, Philadelphia, Pennsylvania.

methyl esters used in this experiment. The extent of epoxidation is similar for all samples and is *ca.* 95%. This extent of epoxidation is similar to that of the industrially prepared epoxidized soybean and linseed oils. This proves that performic acid can be used to produce highly epoxidized materials with up to five epoxide groups per triacylglycerol.

In all experiments, there was a large excess of acrylic acid. Specifically, there was a 50:1 molar ratio of acrylic acid to triacylglycerol. Therefore, the reaction can be assumed to be pseudo zero order in acrylic acid. The rate law of Equation 1 then simplifies to Equation 2:

$$r = -\frac{d[\mathrm{E}]}{dt} = k'[\mathrm{E}]^{\alpha} \qquad [2]$$

where k' is defined in Equation 3 (6):

$$k' = k[\mathrm{AA}]^2 \qquad [3]$$

The reaction order was determined by using the derivative and integral methods. Results of the integral method show that first order in epoxide concentration fits the conversion results better than second order (Fig. 3). For the derivative method, we first must take the natural logarithm of Equation 2 (Eq. 4):

$$\mathrm{Ln}\left(-\frac{d[\mathrm{E}]}{dt}\right) = \mathrm{Ln}(k') + \alpha \cdot \mathrm{Ln}[\mathrm{E}] \qquad [4]$$

The plot of the logarithm of $-d[\mathrm{E}]/dt$ vs. Ln[E] should be linear with slope α. Figure 4 is a plot of the derivative method for three samples used in this experiment. The slope of each line is *ca.* 1 for the two triglyceride-based oils (Fig. 4A) and the fatty acid methyl ester (Fig. 4B). The integral and derivative methods can both be used to determine the pseudo rate constant, k', and should be in good agreement. The pseudo rate constants determined from the first-order integral method (Fig. 3) match those determined from the derivative method (Fig. 4). Thus, we conclude that the acrylation of epoxidized triacylglycerols and fatty acid methyl esters is first order in epoxide concentration. The rate law for the acrylation of epoxidized oils is, by Equation 5,

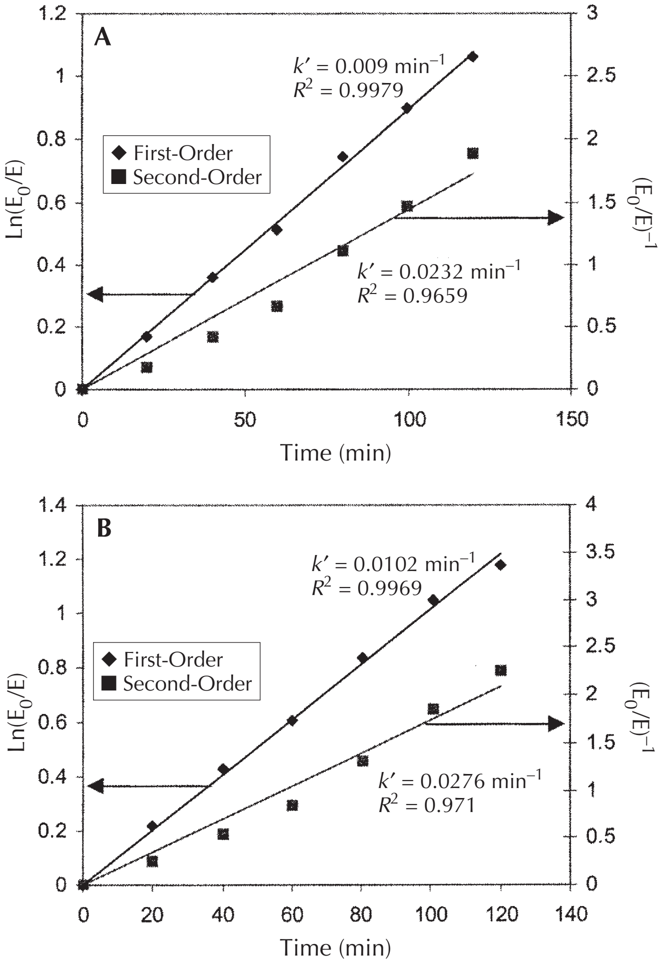

FIG. 3. Integral method for determining the epoxide reaction order for (A) high-oleic soybean oil and (B) methyl oleate.

$$r = k[\mathrm{E}][\mathrm{AA}]^2 \qquad [5]$$

Therefore, fatty acid composition and the bulkiness of triacylglycerols (relative to fatty acid methyl esters) have no effect on the epoxide reaction order. If these factors are to alter acrylation kinetics, these effects must be manifested in the rate constant, *k*.

Rate constants of acrylation. Because acrylic acid was used in excess in these experiments, Equation 5 simplifies to Equation 6,

$$-\frac{d[\mathrm{E}]}{dt} = k'[\mathrm{E}] \qquad [6]$$

and k' is defined by Equation 3. Integrating Equation 6 gives Equation 7:

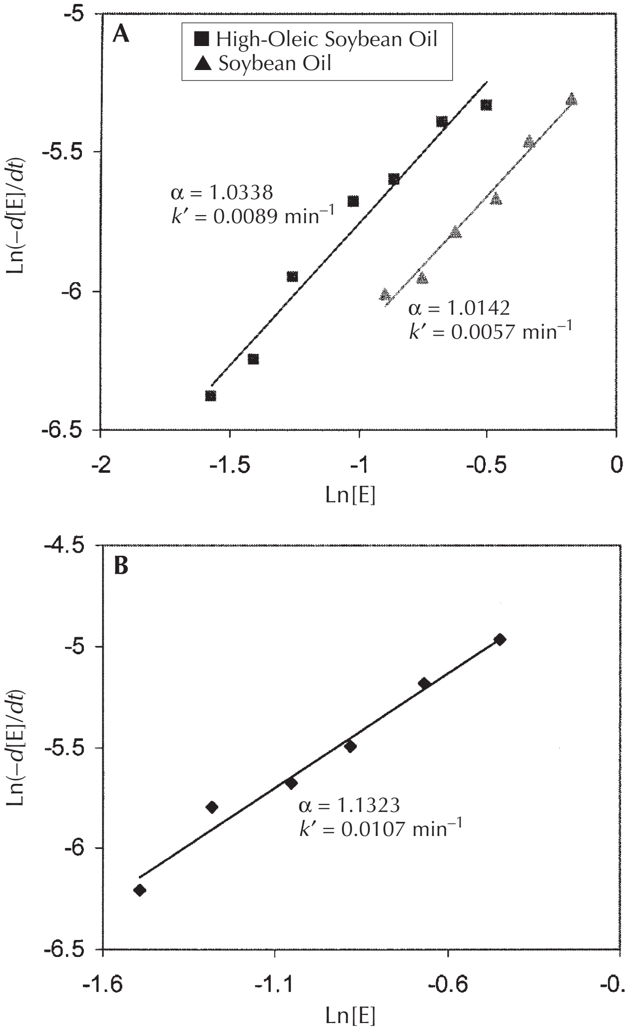

FIG. 4. Derivative method to determine the epoxide reaction order for (A) high-oleic soybean oil and soybean oil and (B) methyl oleate.

TABLE 3
The Acrylation Rate Constants and the Percentages of Oleic, Linoleic, and Linolenic Acids Contained Within the Pre-epoxidized Materials[a]

Sample	k $L^2/(mol^2 \cdot min)$	Oleic acid	Linoleic acid	Linolenic acid
Triolein	97	100	0	0
Methyl oleate	93	100	0	0
Olive oil	91	71.1	10	0.6
HOSO	90	82.6	2.3	3.7
Canola oil	80	64.1	18.7	9.2
Methyl linoleate	69	0	100	0
Cottonseed oil	68	17.6	53.3	0.3
Corn oil	66	27.5	57	0.9
Soybean oil	66	23.4	53.2	7.8
Safflower seed oil	65	13.1	77.7	0
Trilinolein	60	0	100	0
Linseed oil	56	19.1	15.3	54

[a]See Table 1 for abbreviation.

$$\mathrm{Ln}\frac{[\mathrm{E}]_0}{[\mathrm{E}]} = k't \qquad [7]$$

where $[E]_0$ is the initial epoxide concentration. If $\mathrm{Ln}([E]_0/[E])$ is plotted vs. time, a linear plot should result, with slope equal to k'. Table 3 lists the acrylation rate constants and the percentages of oleic, linoleic, and linolenic acids contained within the pre-epoxidized samples. Only these acids are important because they contain >99% of the double bonds, and hence epoxide groups, in the samples. The table shows that different epoxidized materials do have different rate constants, which indicates that fatty acid composition does have an effect on acrylation kinetics. Furthermore, it seems that oils with higher oleic acid content have higher rate constants.

Acrylation model. The third-order rate constant of acrylation for a triacylglycerol can be written in terms of the rate constants of the fatty acids that make up the triacylglycerol (Eq. 8):

$$k = k_1\left(\frac{[\mathrm{E}_1]}{[\mathrm{E}]}\right)_0 + k_2\left(\frac{[\mathrm{E}_2]}{[\mathrm{E}]}\right)_0 + k_3\left(\frac{[\mathrm{E}_3]}{[\mathrm{E}]}\right)_0 \qquad [8]$$

where k_y is the rate constant for epoxides on fatty acids with y epoxides (e.g., k_2 is the rate constant of both epoxides on 9,10,12,13-diepoxystearic acid) and $([E_y]/[E])_0$ is the initial fraction of epoxides on fatty acids with y epoxides. Equation 8 is the acrylation kinetic model.

To determine the three unknown parameters (k_1, k_2, and k_3), an epoxidation kinetic study was performed on three model compounds. The first model sample used was epoxidized triolein. Nearly all the fatty acids in epoxidized triolein are 9,10-epoxystearic acid. Therefore, the second and third terms on the right side in Equation 8 are zero, and k_1 is equal to the rate constant for the epoxidation of epoxidized triolein, which was found to be 96 ± 2 $L^2/(mol^2 \cdot min)$. The second model sample was epoxidized trilinolein. 9,10,12,13-Diepoxystearic acid makes up nearly all of the fatty acids in this compound. Thus, the first and third terms on the right side of Equation 7 are zero. So, k_2 is equal to the rate constant for epoxidized trilinolein, which was determined to be 60 ± 2 $L^2/(mol^2 \cdot min)$. The third model sample used was epoxidized linseed oil. This oil was used because it contains greater than 50% 9,10,12,13,15,16-triepoxystearic acid. Using the values of k_1 and k_2 and an analysis similar to that shown above, as well as the fatty acid distribution of linseed oil, k_3 was calculated to be 50 ± 3 $L^2/(mol^2 \cdot min)$. This model shows that the reactivities of the epoxide groups decrease as the number of epoxide groups per fatty acid increases.

To confirm the accuracy of this model, the rate constants for several oils were calculated. $(E_y/E)_0$ are known from the fatty acid composition, and k_1, k_2, k_3 were calculated above. Table 4 lists the predictions of the model along with the experimentally determined values of the rate constants. The table shows that there is good agreement between model and experiment. The experimental and model rate constants are within ±4 $L^2/(mol^2 \cdot min)$. Thus, the acrylation kinetic model accurately describes the effect of fatty acid content on epoxidation kinetics. Results have shown that the different fatty acid types do not epoxidize to equal extents, (La Scala, J., and R.P. Wool, unpublished results). Therefore, the unsaturated fatty

TABLE 4
The Third-Order Rate Constants of Acrylation as Determined by Experiment and the Acrylation Kinetic Model[a]

Oil	k (Experiment) $L^2/(mol^2 \cdot min)$	k (Model) $L^2/(mol^2 \cdot min)$
Olive oil	91	88
HOSO	90	88
Canola oil	80	76
Cottonseed oil	68	65
Corn oil	66	67
Soybean oil	66	64
Safflower seed oil	65	63

[a] See Table 1 for abbreviation.

acid distribution is not equal to the epoxidized fatty acid distribution. Some of the error in the model is attributed to this. The remaining error is attributed to the determination of model parameters k_1, k_2, and k_3.

Steric and electronic effects on acrylation kinetics. There are a number of possible causes for the variation in acrylation kinetics. The first possibility is that multiple epoxide groups on the same fatty acid sterically hinder each other from reacting. Another possibility is that epoxides on different fatty acids have different reactivities because of electronic effects. Lastly, a combination of these steric and electronic effects can cause the observed effect on the acrylation rate constants. The triacylglycerols used in this experiment only vary in the number of epoxides per fatty acid. Therefore, other factors that are not varied, such as fatty acid chain length, do not affect the acrylation rate constants observed in these experiments. Because the extent of acrylation was low, steric factors caused by the addition of acrylic acid to the fatty acid should have only a minimal effect on the observed results.

To help separate these possibilities, we performed kinetic experiments on epoxidized fatty acid methyl esters. The rate constants of acrylation for epoxidized methyl oleate and methyl linoleate were 93 ± 2 $L^2/(mol^2 \cdot min)$ and 69 ± 2 $L^2/(mol^2 \cdot min)$, respectively. These are very similar to the rate constants for their respective triacylglycerols. Therefore, steric factors inherent in triacylglycerol structure (i.e., steric factors associated with three fatty acids attached at a glycerol center, not including steric factors associated with fatty acid structure itself) do not affect the reactivity of the epoxides.

The acrylation rate constants decreased as the number of methylene-interrupted epoxide groups per fatty acid increased for both triacylglycerols and fatty acid methyl esters. Therefore, multiple methylene-interrupted epoxides per fatty acid either stabilize the epoxides or increase the steric hindrance of their reaction with acrylic acid. The acid-catalyzed reaction of epoxides involves the formation of an oxonium ion (10). Another epoxide group in close proximity (i.e., on the same fatty acid) could stabilize this oxonium ion by allowing the oxonium proton to be shared among the epoxide groups. This would reduce the rate of epoxide disappearance as the number of epoxide groups per fatty acid increased. However, additional epoxide groups may still sterically hinder the reaction of other epoxide groups on the same fatty acid. Therefore, we conclude that steric and electronic factors reduce the reactivity of epoxides as the number of methylene-interrupted epoxide groups per fatty acid increases.

ACKNOWLEDGMENTS

This work was supported in part by research grants from the United Soybean Board, the National Science Foundation, and the DuPont Corporation.

REFERENCES

1. Borden, G.W., and O.W. Smith, Union Carbide Corp., Acrylated Epoxidized Soybean Oil Urethane Derivatives, U.S. Patent 4,025,477 (1977).
2. Khot, S.N., Rigid Thermoset Polymers from Acrylated Epoxidized Triglycerides, M.S. Thesis, University of Delaware, Newark, 1998.
3. Solomons, T.W.G., *Organic Chemistry*, 5th edn., John Wiley & Sons, New York, 1992, pp. 432–434.
4. Zaher, F.A., M.H. El-Mallah, and M.M. El-Hefnawy, Kinetics of Oxirane Cleavage in Epoxidized Soybean Oil, *J. Am. Oil Chem. Soc. 66*:698–700 (1989).
5. Zaher, F.A., and S.M. El-Shami, Oxirane Ring Opening by Formic Acid, *Res. Ind. 36*:191–194 (1991).
6. Bunker, S.P., The Synthesis and Characterization of Linear Polymers from a Fatty Acid Methyl Ester, M.S. Thesis, University of Delaware, Newark, 2000.
7. Swern, D., G.N. Billen, T.W. Findley, and J.T. Scanlan, Hydroxylation of Monounsaturated Fatty Materials with Hydrogen Peroxide, *J. Am. Chem. Soc. 67*:1786–1789 (1945).
8. Findley, T.W., D. Swern, and J.T. Scanlan, Epoxidation of Unsaturated Fatty Materials with Peracetic Acid in Glacial Acetic Acid Solution, *Ibid. 67*:412–414 (1945).
9. Greenspan, F.P., The Convenient Preparation of Per-acids, *Ibid. 68*:907 (1946).
10. Carey, F.A. *Organic Chemistry*, 2nd edn., McGraw-Hill, New York, 1992, pp. 652–654.

[Received January 16, 2001; accepted October 29, 2001]