Kinetic Studies of Epoxidation and Oxirane Cleavage of Palm Olein Methyl Esters

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The kinetics for the epoxidation of methyl esters of palm olein (MEPOL) by peroxyformic acid and peroxyacetic acid generated *in situ* were studied. The rate-determining step was found to be the formation of peroxy acid. Epoxidized MEPOL (EpMEPOL), with almost complete conversion of the unsaturated carbon and negligible ring-opening, can be synthesized by the *in situ* technique described.

The kinetics of the oxirane cleavage of EpMEPOL by acetic acid were studied at various temperatures. The reaction was found to be first-order with respect to the epoxy concentration and second-order to the acetic acid concentration. The activation energy and the entropy of activation for the epoxidation of MEPOL were comparable to those for the oxirane cleavage of EpMEPOL by acetic acid, suggesting that the two reactions are competitive. The success of the epoxidation of MEPOL with only negligible oxirane cleavage is attributed to the heterogeneous nature of the system employed in the *in situ* technique.

KEY WORDS: **Epoxidation, kinetics, methyl ester, oxirane cleavage, palm olein.**

Epoxidized triglycerides and the esters derived from them have found important applications as plasticizers and additives for polyvinyl chloride (PVC) due to the excellent heat and light stability imparted by the oxirane groups. These epoxy esters have captured about 7% of the total plasticizer market. Epoxidized soybean oil accounted for about 70% of the total epoxidized esters production (1,2). Other epoxidized oils used as plasticizers are prepared from linseed, rapeseed (3,4), olive, corn (3) and cottonseed (3,5). However, there have been no reports on similar studies with palm oil as starting material, due primarily to the inherent low iodine value of the oil and to the fact that the resulting epoxidized product has low compatibility with PVC (unpublished results). In our current research effort to find new uses for palm oil in nonfood applications, we have extensively studied the epoxidation of a large variety of esters derived from palm oil. Some of these epoxy esters have been evaluated as plasticizers for PVC (6). The kinetic studies of the epoxidation of methyl esters of palm olein and the oxirane cleavage by acetic acid are presented in this study.

EXPERIMENTAL PROCEDURES

Materials. Methyl esters of palm olein (MEPOL) were synthesized *via* alcoholysis (6). Glacial acetic acid and formic acid (98%) from BDH (Poole, U.K.) and AR-grade benzene from Ajax (Sydney, Australia) were used without further purification. Hydrogen peroxide (∿30%) was obtained from Fluka (Buchs, Switzerland).

Kinetic studies of epoxidation of MEPOL. Epoxidations of MEPOL were carried out with peroxyacetic or peroxyformic acids generated *in situ.* The reaction compositions for the kinetic studies are shown in Table 1. A fixed volume of MEPOL (170 mL) was placed in a 500-mL round-bottom flask fitted with a reflux condenser and a magnetic stirrer. Sulfuric acid and benzene, when applicable, were added. The reaction flask was then immersed in a water bath with the desired temperature (20, 25, 40, 60 or 80°C) controlled to within 0.1°C for half an hour. Hydrogren peroxide (∿30%) (55 mL), which had been pre-equilibrated at the same temperature, was then added all at once. The stirring rate was controlled so that the oil in the mixture was finely dispersed. The reaction was followed by withdrawing 20 mL of the reaction mixture at various time intervals and placing them in a separatory funnel. The aqueous layer was drawn off, and the ester layer was washed with successive portions of warm water (40–50°C) until acid-free. The remaining traces of water and benzene were removed at 60–80°C under reduced pressure. The samples were analyzed for the iodine (7), hydroxyl (8) and oxirane (9) values according to AOCS methods.

Preparation of epoxy esters. Epoxy methyl esters of palm olein (EpMEPOL) were prepared with peroxyformic acid generated *in situ* at room temperature (26–27°C) in the presence of benzene in order to minimize oxirane

TABLE 1

Reaction Compositions in the Kinetic Studies of the Epoxidation of MEPOL[a]

	Acid (mL)					(Acid)$_0$ (mol/L)	
Experiment	HCOOH	CH_3COOH	% H_2SO_4 (mL)	Benzene (mL)	(H_2O_2) (mol/L)	$(HCOOH)_0$	$(CH_3COOH)_0$
(a)	4	—	—	—	2.178	0.454	—
(b)	4	—	—	40	1.854	0.386	—
(c)	—	10	1.5	—	2.109	—	0.735
(d)	—	10	1.5	40	1.804	—	0.629

[a] MEPOL (170 mL) and 30% H_2O_2 (55 mL) were added to each reaction mixture.

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cleavage. In the experiment, 100 g of MEPOL was dissolved in 500 mL benzene, and 31 mL of formic acid was added. Hydrogen peroxide (~30%; 730 mL) was then added dropwise while the mixture was constantly stirred and maintained at 10–15°C. After addition of H_2O_2 was complete, the temperature was allowed to rise gradually to room temperature and the reaction was continued overnight. The reaction mixture was then washed repeatedly with water until acid-free. Benzene and water were removed under reduced pressure at 60°C. The product had an iodine value of 1.22, a hydroxyl value of 1.01, and 3.25% oxirane. The epoxidation was considered essentially complete because the iodine value of the starting material MEPOL was 59.88. The low hydroxyl value also indicated negligible oxirane cleavage. Almost complete epoxidation was further confirmed from C-13 nuclear magnetic resonance (NMR) spectra, which showed complete disappearance of the resonance signal at 127.6 ppm, due to the internal unsaturated carbon, and the emergence of the new signal at 56.5 ppm for the oxirane-ring carbons.

Kinetic study of oxirane cleavage. EpMEPOL, prepared as described above, was used for the kinetic study of oxirane cleavage by acetic acid. Glacial acetic acid (250 mL) in a long-necked, round-bottom flask, equipped with a reflux condenser and a magnetic stirrer, was equilibrated at a desired temperature (40, 60 or 80°C) in a thermostated bath, and 70 mL of EpMEPOL, pre-equilibrated at the same temperature, was added. Samples were withdrawn at various time intervals and titrated immediately for the oxirane content. Another series of experiments determined the order of reaction with respect to acetic acid by adding 40 mL of EpMEPOL to 20, 40 or 60 mL glacial acetic acid at 60°C or at 80°C.

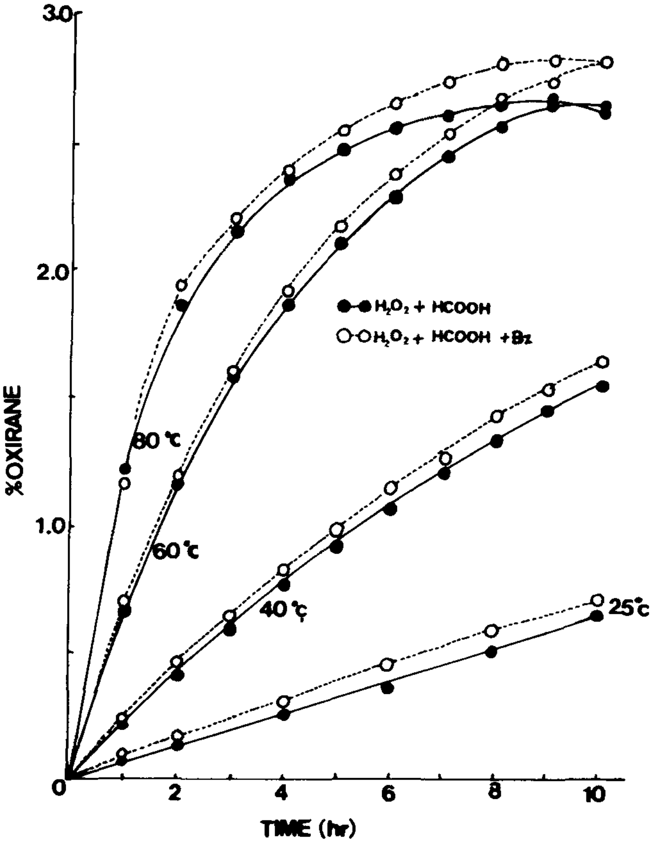
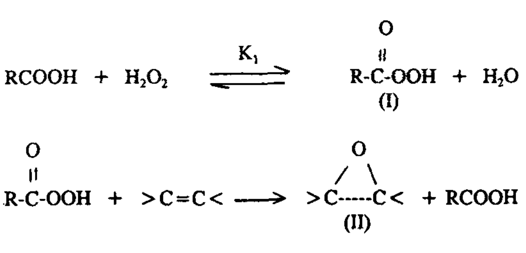


FIG. 1. Percent oxirane as a function of reaction time for the epoxidation of MEPOL by peroxyformic acid generated *in situ*.

RESULTS AND DISCUSSION

The rates of epoxidation of MEPOL by peroxyformic and peroxyacetic acids, generated *in situ* at various temperatures, are shown in Figures 1 and 2, respectively. The presence of benzene appears to have some stabilizing effects on the oxirane formed. The effect becomes more apparent at higher temperatures, as exemplified by the reaction with peroxyacetic acid at 80°C, which clearly shows less destruction of oxirane in the presence of benzene.

The chemistry of *in situ* epoxidation can be explained by the following scheme (10,11):



$$\mathrm{RCOOH} + \mathrm{H_2O_2} \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\text{(I)}}{\mathrm{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OOH}} + \mathrm{H_2O}$$

$$\mathrm{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OOH} + \mathrm{>C{=}C<} \longrightarrow \underset{\text{(II)}}{\mathrm{>\overset{O}{\overset{/\ \backslash}{C\text{-----}C}}<}} + \mathrm{RCOOH}$$

If the rate-determining step is that of the formation of peroxy acid (I), and the concentration of this acid is essentially constant throughout the reaction, the following rate law applies:

$$d(\mathrm{II})/dt = k_1[(\mathrm{H_2O_2})_o - (\mathrm{II})](\mathrm{RCOOH})_o \qquad [1]$$

where the subscript o denotes the initial concentrations. Hence:

$$\ln[(\mathrm{H_2O_2})_o - (\mathrm{II})] = -k_1(\mathrm{RCOOH})_o t + \ln(\mathrm{H_2O_2})_o \qquad [2]$$

By assuming that the specific gravity of the MEPOL remained constant during the course of reaction, (II) was calculated from the experimentally determined oxirane content of aliquots. Plots of $\ln[(H_2O_2]_o - (II)]$ *vs.* reaction time yield straight lines for those reactions with negligible ring-opening of oxirane. For the reactions with substantial ring-opening, deviations from linearity were observed. In such cases, rate constants were obtained from the initial slopes (Figs. 3 and 4). The results are shown in Table 2. Good linear Arrhenius plots were obtained. Calculated values of activation energy, E_a, and entropy of activation, $\Delta S^\ddagger$ are shown in Table 3.

The rate constants obtained for *in situ* epoxidation of MEPOL by peroxyacetic acid in the presence of and without benzene were on the order of 10^{-6} dm^{3}mol^{-1}s^{-1}, in agreement with that reported for the formation of peroxyacetic acid (12). The activation parameters obtained were also in agreement with the values of E_a = 63.2 kJmol^{-1} and $\Delta S^\ddagger = -146$ Jmol^{-1}K^{-1} for the formation of peroxyacetic acid (12). On the other hand, the attack of the peroxyacetic acid on the double bond is about 100 times faster (k ≈ 10^{-4} dm^{3}mol^{-1}s^{-1}) and has a much larger negative value of $\Delta S^\ddagger$ (≈ −265 Jmol^{-1}K^{-1}) (13,14). Hence, the results show unequivocally that the rate-

TABLE 2

Rate Constants, k_1, for Epoxidation of MEPOL Under Different Reaction Conditions

	10^6k_1 ($dm^3mol^{-1}s^{-1}$) Temperature (°C)			
Reaction condition	20	25	40	60
(a) Peroxyformic	5.5 ± 0.2[a]	7.2 ± 0.2	21.3 ± 0.4	72 ± 3
(b) Peroxyformic + benzene	6.7 ± 0.2	10.2 ± 0.2	26.5 ± 0.6	86 ± 4
(c) Peroxyacetic	2.6 ± 0.1	4.0 ± 0.1	13.2 ± 0.1	55 ± 2
(d) Peroxyacetic + benzene	2.9 ± 0.1	4.6 ± 0.1	16.1 ± 0.4	65 ± 3

[a] All errors are least square errors.

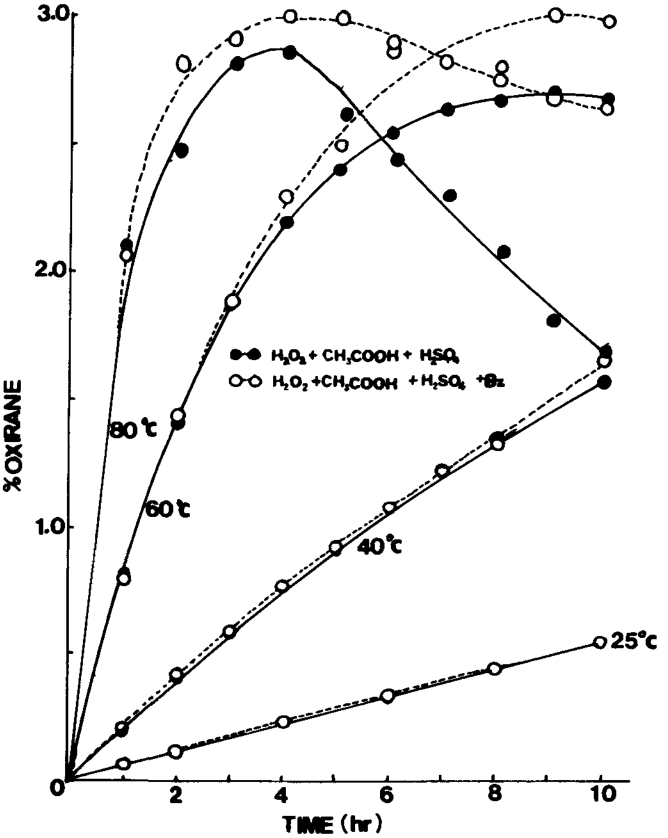


FIG. 2. Percent oxirane as a function of reaction time for the epoxidation of MEPOL by peroxyacetic acid generated *in situ*.

TABLE 3

Activation Energy, E_a, and Entropy of Activation, $\Delta S^‡$, for the Epoxidation of MEPOL

Reaction condition	E_a($kJmol^{-1}$)	$\Delta S^‡$ ($Jmol^{-1}K^{-1}$)
(a)	53 ± 2	−165 ± 7
(b)	51 ± 1	−169 ± 4
(c)	62 ± 1	−141 ± 2
(d)	63 ± 2	−136 ± 6

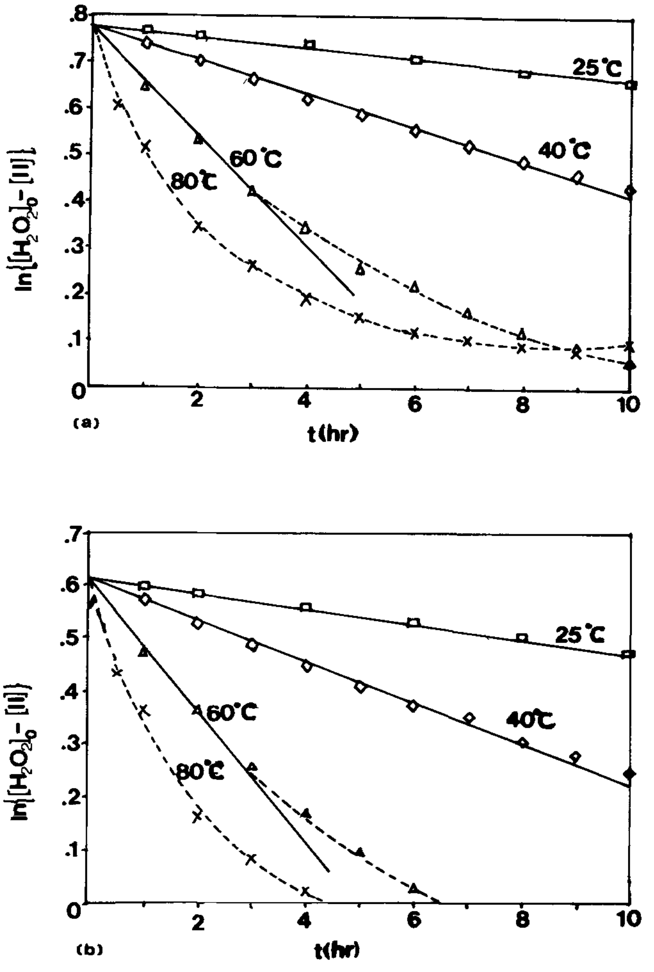


FIG. 3. Plots of $ln[(H_2O_2)_0 - (II)]$ *vs.* reaction time for the epoxidation of MEPOL by peroxyformic acid (a) without benzene and (b) in the presence of benzene.

determining step was the formation of the peroxyacetic acid. The same conclusion can be reached for the *in situ* epoxidation by peroxyformic acid. The values of rate constant, activation energy and entropy of activation obtained were almost identical to those obtained for the epoxidation of natural rubber reported earlier (11). The presence of benzene did not have much effect on the formation of the peroxy acids, as indicated from the values of E_a and $\Delta S^‡$, even though the rate constants were consistently slightly higher.

Oxirane cleavage. The general rate law for the oxirane ring cleavage by acetic acid can be written as:

$$-d(Ep)/dt = k(Ep)^a(Ac)^b \qquad [3]$$

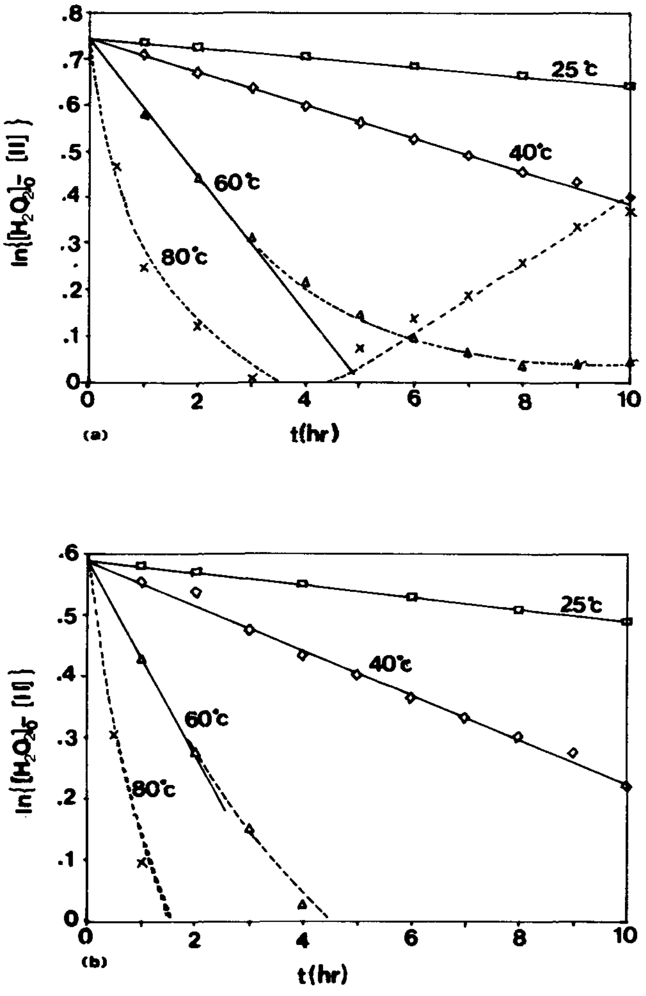


FIG. 4. Plots of $\ln[(H_2O_2)_o - (II)]$ *vs.* reaction time for the epoxidation of MEPOL by peroxyacetic acid (a) without benzene and (b) in the presence of benzene.

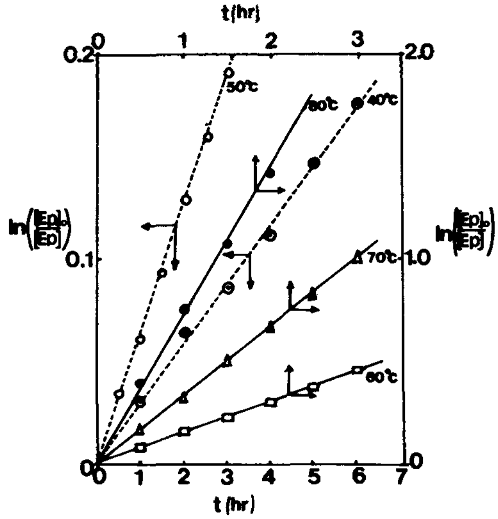


FIG. 5. Plots of ln [(Ep)$_o$/(Ep)] *vs.* reaction time for the oxirane cleavage of EpMEPOL by acetic acid at various temperatures.

TABLE 4

Values of k′ for the Oxirane Cleavage of EpMEPOL by Various Concentrations of CH_3COOH at 60°C and 80°C

$[CH_3COOH]$ (mol/L)	10^5 k′ (dm^3 $mol^{-1}s^{-1}$)	
	60°C	80°C
5.823	1.056	4.016
8.734	2.216	9.550
10.481	3.240	12.201

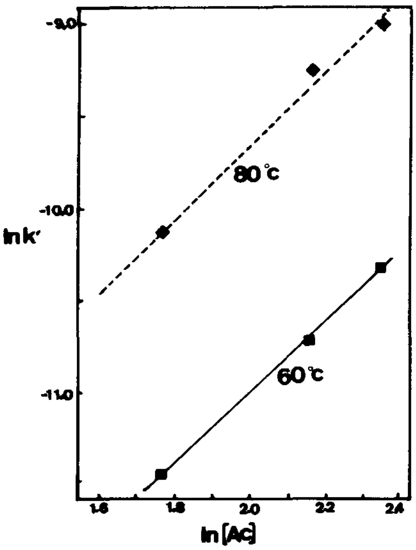


FIG. 6. Plots of ln k′ *vs.* ln(Ac) for the oxirane cleavage of EpMEPOL by acetic acid at 60 and 80°C.

where (Ep) and (Ac) are the molar concentrations of epoxy component and acetic acid, respectively.

Under the experimental condition where the acetic acid is used in excess, the rate equation becomes:

$$-d(Ep)/dt = k' (Ep)^a \qquad [4]$$

where $k' = k(Ac)^b$.

Plots of ln[(Ep)$_o$/(Ep)] *vs.* reaction time at various temperatures were linear in all cases (Fig. 5), with the slopes giving the values of k′. Thus, the cleavage is first-order with respect to oxirane concentration, in agreement with other works reported earlier (15–17).

For the determination of the reaction order with respect to acetic acid, the values of k′ were obtained at three different concentrations of acetic acid at 60 and 80°C (Table 4). Since $k' = k(Ac)^b$,

$$\ln k' = \ln k + b \ln(Ac) \qquad [5]$$

Hence, by plotting ln k′ *vs.* ln(Ac), b can be obtained from the slope. A value of b = 2 was obtained at both temperatures (Fig. 6). Hence, the overall rate law for the oxirane cleavage of EpMEPOL is

$$-d(Ep)/dt = k(Ep)(Ac)^2 \qquad [6]$$

Based on this rate law, the calculated rate constants, k, are presented in Table 5 at various temperatures. Activation energy $E_a = 73.5$ kJmol^{-1} and entropy of activation $\Delta S^{\ddagger} = -151$ Jmol^{-1}K^{-1} were obtained. These values are similar to those reported for the oxirane cleavage of expoxidized soybean oil by acetic acid (17). The observed reaction order of 2 with respect to the acetic acid, obtained from this study and as found also for acetolysis of epoxidized soybean oil (17), is at variance with the partial order of 2.6 reported for the simple model compound propylene oxide at higher molar ratio of acetic acid over oxirane (16).

TABLE 5

Rate Constants for Oxirane Cleavage of EpMEPOL by Acetic Acid

T (K)	k (dm^{6}mol^{-2}s^{-1})
313.15	4.52×10^{-8}
323.15	1.00×10^{-7}
333.15	2.43×10^{-7}
343.15	5.31×10^{-7}
353.15	1.07×10^{-6}

It should be pointed out that the reaction condition for the oxirane cleavage study was quite different from that in which epoxidation was carried out by the *in situ* technique. Hence, information derived from the cleavage study should be viewed with care for the assessment of the relative rates between the epoxidation and the subsequent ring-opening during the epoxidation process. The values of the activation energy and the entropy of activation for the epoxidation and the oxirane cleavage obtained in these separate studies indicate that these two reactions are competitive. The reason that almost complete epoxidation can be achieved by the *in situ* technique is attributed to the heterogeniety of the reaction mixture in this process. Under such conditions, only a small amount of the acid was present in the oil phase, hence the rate of ring-opening was greatly reduced.

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