

Effects of Epoxidation on the Thermal Oxidative Stabilities of Fatty Acid Esters Derived from Palm Olein

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ABSTRACT: A variety of esters from the reactions of monoalcohols with palm olein were prepared, epoxidized by *in situ* peroxyacid techniques, and some of their physical properties were compared. The thermal oxidative stabilities of these esters and bis(2-ethylhexyl) phthalate were studied. The esters were placed in an oven maintained at 120°C, and the loss of mass and acid, iodine, percent oxirane, hydroxyl, and peroxide values were monitored periodically. The epoxidized esters had higher densities and lower volatilities, and were more resistant toward oxidation than their unepoxidized counterparts. The stability of the oxirane was related to the initial acid value of the sample. Higher initial acid value resulted in a greater decrease in the oxirane content, indicating acid-catalyzed cleavage of the oxirane ring.

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Various industrial applications of fatty acid esters have been reviewed (1–4). The most widely used esters are methyl esters, which have become important intermediates for the synthesis of other oleochemicals. Methyl esters of fatty acids obtained by alcoholysis of vegetable oils and used frying oil have been investigated as fuel in diesel engines (5,6). Isopropyl esters may be used in ointments and creams (7), while other analogues are suitable for use in cosmetic and pharmaceutical products for the formulation of medicinal ointments, massage oils, etc. (3). The lubricant properties of fatty acid esters make them useful in metal processing, textiles, and the plastics industries (8). In our current research effort to find new uses for palm oil in nonfood applications, we have converted the oil to a variety of esters and epoxy esters. Some of these epoxy esters have been evaluated as plasticizers for polyvinyl chloride (9). Because some applications of these esters may be at relatively high temperatures, we have inves-

tigated their thermal oxidative stabilities and present the results here.

EXPERIMENTAL PROCEDURES

Materials. Alcohols were obtained from Fluka (Buchs, Switzerland) and TCI (Tokyo, Japan), and were AR- or high-purity grades. AR-grade methanol, ethanol, allyl alcohol, butanol, and 2-ethyl-1-hexanol were distilled from magnesium, activated with iodine, in a dry nitrogen atmosphere. Octanol, decanol, dodecanol, and oleyl alcohol were distilled under reduced pressure from magnesium activated with iodine.

A commercial-grade refined, bleached, and deodorized palm olein (POI) was employed. It consisted mainly of triglycerides with the following fatty acid composition (mol%) (9): lauric, 0.2; myristic, 1.1; palmitic, 39.8; palmitoleic, 0.2; stearic, 4.4; oleic, 42.5; linoleic, 11.2; linolenic, 0.4; and arachidic acid, 0.4. Trace amounts of water and volatile compounds present in the oil were removed under reduced pressure. Glacial acetic and formic acid (>98%) from BDH (Poole, United Kingdom) and AR-grade benzene from Ajax (Sydney, Australia) were used without further purification. Hydrogen peroxide (~30%) was obtained from Fluka.

Preparation of the fatty acid esters. A solvent-free and fast reaction method has been developed for the synthesis of various alkyl esters of palm olein with KOH as catalyst. Experimentally, ~2 wt% of KOH was dissolved in the alcohol at a temperature of 60–70°C. The alcoholic KOH solution was then poured into the oil, which had been preheated, and maintained at the same temperature with constant stirring. The reaction was essentially complete within few minutes after mixing. The progress of the reaction was monitored by thin-layer chromatography. The reactions were slightly slower for methanol and ethanol, which took more than 15 min to complete due to their poorer miscibilities with the oils. The esters formed from methanol and ethanol were separated from the glycerol layer and washed repeatedly with distilled water until neutral. Some esters remained in the glycerol layer and were extracted twice with petroleum ether (60–80°C), washed with water, and recovered after ether was removed by rotary evaporation.

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For alcohols where no separation of glycerol and esters occurred, the reaction mixture was poured into a 2-L separating funnel and washed three times with dilute HCl. This was followed by repeated washing with water until acid-free, and the sample was dried under reduced pressure.

The following abbreviations for the esters of POI are used herein after: methyl (MEPOI); ethyl (EtEPOI); butyl (BuEPOI); allyl (AlEPOI); 2-ethyl-1-hexyl (2-E-1-HEPOI); decyl (DeEPOI); dodecyl (DodeEPOI); benzyl (BzEPOI); and oleyl (OIEPOI).

Preparation of epoxy esters. Epoxy esters of POI were prepared with peroxyformic acid generated *in situ* as described previously (10). A prefix, Ep, is used in the abbreviation for epoxidized esters of POI. Hence, EpMEPOI represents epoxidized methyl esters of palm olein.

Specific gravity and refractive index. Specific gravities of samples were determined at 30°C in a pycnometer. Refractive indices were determined at 30°C with an Abbe refractometer.

Thermal oxidative stability. Esters (300 mL) in a 500-mL beaker were placed in an oven maintained at $120 \pm 2^\circ\text{C}$. Samples were withdrawn at different time intervals and analyzed for acid (11), iodine (12), percent oxirane (13), hydroxyl (14), and peroxide (15) values according to American Oil Chemists' Society methods. Another 100 mL of each ester was placed in the same oven at the same temperature for the determination of loss of mass. *Bis*(2-ethylhexyl) phthalate (DOP) was also included in the study for comparison.

RESULTS AND DISCUSSION

A total of seventeen esters of POI from monoalcohols, including the epoxidized analogues, were synthesized. The densi-

ties, refractive indices, percent oxirane, and the acid, iodine, hydroxyl and peroxide values of these esters are shown in Table 1. Epoxidations of all esters by the peroxyformic acid method were effective, as indicated from the iodine values of the esters and the corresponding epoxidized analogues. Epoxidations were almost complete for esters with internal unsaturations. For AlEPOI, the terminal double bond was not epoxidized under the experimental condition employed, as shown by the ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) analysis described previously (16). The totally unreacted allyl group of these esters has been exploited in our polymerization studies (16). In our previous kinetic studies of epoxidation and oxirane cleavage of methyl esters of POI, we have attributed the success of the *in situ* epoxidation by peroxyacetic and peroxyformic acids with negligible ring opening to the heterogeneity of the reaction mixture (10). Undoubtedly, this is due to inaccessibility of the H^+ ion to the hydrophobic oil. The presence of acetic or formic acid improves miscibility, thus it facilitates the ring opening of the oxirane. Hence, to obtain high percent oxirane in the peroxyacid *in situ* epoxidation, only small amounts of the organic acid should be employed, so that the ring-opening reaction can be minimized. Oxirane cleavage was also reduced if the epoxidation reaction was carried out in the presence of benzene, especially at higher temperatures. A comparison of the hydroxyl value, resulting from the oxirane cleavage, for the *in situ* epoxidation by peroxyacetic and peroxyformic acids with and without benzene are shown in Figure 1. At temperatures below 40°C , there was virtually no oxirane cleavage and almost no advantage for the addition of benzene. Only at higher temperatures, where considerable cleavage occurs, is the effect of benzene in retarding oxirane cleavage significant.

TABLE 1
Some Physical and Chemical Properties of Various Esters and Epoxy Esters of Palm Olein and Their Rates of Mass Loss and Increase in Acid Value (AV) at 120°C

No.	Esters of palm olein ^a	Density (g/cm ³) at 30°C	Refractive index at 30°C	AV	Iodine value	% Oxirane	Hydroxyl value	Hydroperoxide value	Rate of mass loss (mg/cm ² /d)	Rate of increase in acid value (ΔAV/d)
1	MEPOI	0.8645	1.4442	0.24	59.88			79.8	15.6	0.65
2	EpMEPOI	0.8956	1.4459	0.31	1.22	3.25	1.01	58.8	12.5	0.28
3	EtEPOI	0.8654	1.4449	2.19	58.03			64.5	14.6	0.60
4	EpEtEPOI	0.9048	1.4479	1.99	1.37	3.61	1.22	57.7	6.6	0.11
5	BuEPOI	0.8571	1.4430	1.24	41.89			73.2	10.8	0.32
6	EpBuEPOI	0.8771	1.4501	1.02	1.46	2.56	1.24	57.1	4.1	0.22
7	AlEPOI	0.8691	1.4503	2.14	129.06			127.7	8.3	0.32
8	EpAlEPOI	0.8968	1.4518	1.08	81.24	2.37	1.32	49.6	4.2	0.26
9	2-E-1-HEPOI	0.8708	1.4489	0.17	31.44			77.3	8.4	0.32
10	Ep-2-E-1-HEPOI	0.8821	1.4562	0.14	2.31	1.91	1.25	56.5	3.7	0.15
11	DeEPOI	0.8610	1.4508	2.03	39.50			79.3	8.1	0.18
12	EpDeEPOI	0.8763	1.4522	1.11	2.40	1.74	1.21	33.3	3.5	0.17
13	DodeEPOI	0.8624	1.4500	2.01	39.40			73.6	8.1	0.19
14	EpDodeEPOI	0.8771	1.4521	1.22	2.47	1.71	1.36	28.3	3.3	0.16
15	BzEPOI	0.9402	1.4767	1.07	50.63			61.2	8.9	0.19
16	EpBzEPOI	0.9671	1.4776	0.98	2.87	2.29	1.00	51.8	6.1	0.18
17	OIEPOI	0.8694	1.4598	1.42	88.19			113.4	0.57	0.10
18	DOP								5.9	0.26

^aAbbreviations for the esters of palm olein: methyl (MEPOI), ethyl (EtEPOI), butyl (BuEPOI), allyl (AlEPOI), 2-ethyl-1-hexyl (2-E-1-HEPOI), decyl (DeEPOI), dodecyl (DodeEPOI), benzyl (BzEPOI), and oleyl (OIEPOI); epoxy esters are prefixed with Ep; and *bis*(2-ethylhexyl)phthalate (DOP).

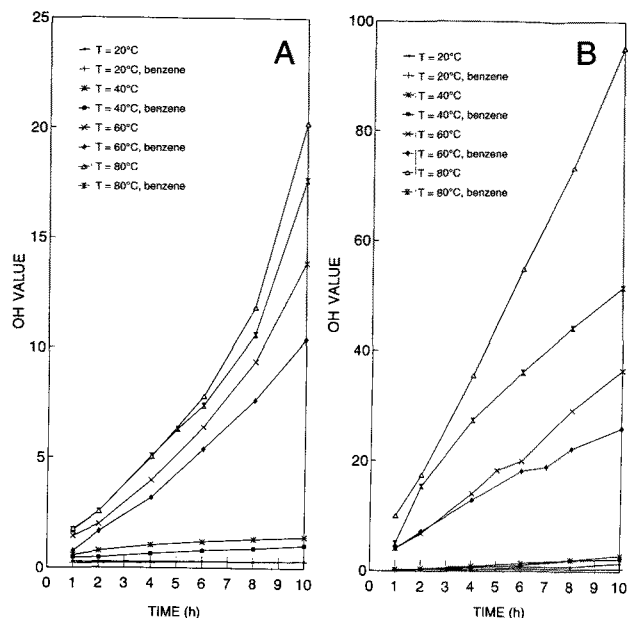


FIG. 1. Hydroxyl value as a function of reaction time for the *in situ* epoxidation of ester of palm olein, methyl (MEPOL) by (a) peroxyformic acid: MEPOI (170 mL), H_2O_2 (55 mL), formic acid (4 mL) and (b) peroxyacetic acid: MEPOI (170 mL), H_2O_2 (55 mL), acetic acid (10 mL), 10% H_2SO_4 (1.5 mL) with and without 40 mL of benzene.

Epoxidation increases the densities of all esters studied.

Thermal oxidative stabilities of the esters and DOP were compared, and changes in various physical and chemical properties were observed. Both the mass loss and increase in acid value were fairly linear with time. The rates of these changes are presented in Table 1. The rate of mass loss for both the ester and epoxy ester series decreased with increasing chainlength of the alkyl group. MEPOI was most volatile, with a mass loss of $15.6 \text{ mg/cm}^2/\text{d}$, while the least mass loss was recorded for OIEPOI, with a value of $0.57 \text{ mg/cm}^2/\text{d}$. As for the epoxy ester series, the rate of mass loss decreased from a high of $12.5 \text{ mg/cm}^2/\text{d}$ for EpMEPOI to a low of $3.28 \text{ mg/cm}^2/\text{d}$ for EpDodeEPOI. All epoxy esters were consistently less volatile than their corresponding unepoxidized counterparts. A similar trend was observed for the increase in acid value (Table 1). Epoxidation increased thermal oxidative stabilities and reduced the rate of increase in acid value. Several epoxy esters (i.e., EpDe-POI, EpDodeEPOI, and EpBzEPOI) were less volatile and thermally more stable than DOP. Generally, the iodine values of the unepoxidized esters decreased gradually with time, indicating that some of the double bonds were destroyed in the oxidative process. For the allyl and epoxidized allyl esters, which contained terminal double bonds, large decreases in iodine value were observed as the oxidative process initiated polymerization of the allyl group. EpAIEPOI became very viscous after 18 d at 120°C . The refractive index also increased from 1.4519 to 1.4762. Figure 2 shows the results of the change of percent oxirane, which appears to be related to the initial acid value of the sample. Greater changes in percent oxirane were generally observed for samples with higher initial acid values, suggest-

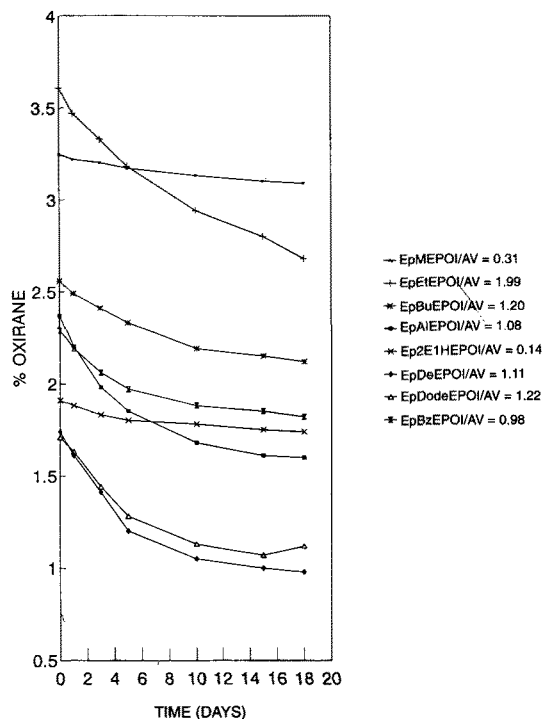


FIG. 2. Change in percent oxirane of various epoxidized esters of palm olein at 120°C , AV, initial acid value; Ep, epoxidized; and abbreviations for the esters of palm olein (POI): methyl (MEPOI); ethyl (EtEPOI);

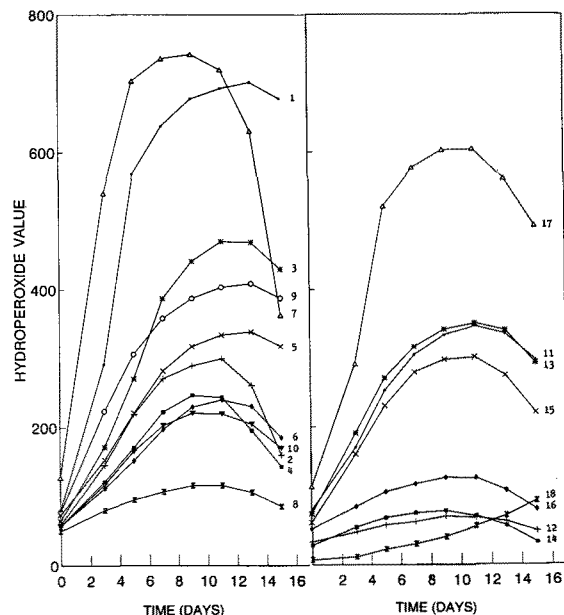


FIG. 3. Development of hydroperoxide of various esters and epoxidized esters of palm olein at 120°C . Abbreviations as in Figure 2. 1, MEPOI; 2, EpMEPOI; 3, EtEPOI; 4, EpEtEPOI; 5, BuEPOI; 6, EpBuEPOI; 7, AIEPOI; 8, EpAIEPOI; 9, 2-E-1-HEPOI; 10, ep-2-E-1-HEPOI; 11, DeEPOI; 12, EpDeEPOI; 13, DodeEPOI; 14, EpDodeEPOI; 15, BzEPOI; 16, EpBzEPOI; 17, OIEPOI; 18, DOP [*bis*(2-ethylhexy)phthalate].

ing that the free fatty acids present in the sample were able to catalyze the oxirane cleavage. For example, EpEtEPOI gave greater reduction in percent oxirane than EpMEPOI due to its

higher initial acid value of 1.99, compared to 0.31 for EpME-POI. Hydroperoxide formation, as expected, was related to the degree of unsaturation in the sample (Fig. 3). The labile nature of the allylic hydrogen, leading to its susceptibility for oxidation, is well known (17). AIEPOI thus showed the greatest increase in hydroperoxide value due to its high degree of unsaturation (internal and terminal double bonds). On the other hand, with their unsaturation removed through epoxidation, the epoxy esters produced less hydroperoxides and were thermally more stable.

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