

# DEGRADATION OF THE OXIRANE RING OF EPOXIDIZED VEGETABLE OILS IN LIQUID-LIQUID SYSTEMS:

## I. HYDROLYSIS AND ATTACK BY H<sub>2</sub>O<sub>2</sub>

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**Abstract**— This work analyzes the impact of the main process variables (agitation, pH, temperature, volumetric ratio and concentration levels) on the degradation of the oxirane ring of epoxidized vegetable oils (VO) by hydrolysis and hydrogen peroxide in two-phase (polar-organic) systems, when a homogeneous acid catalyst is used.

Acid hydrolysis of epoxidized VO is a very slow reaction that proceeds at the liquid-liquid interphase, but only after an extended 'induction period' of several hours, during which enough *active* interfacial area is developed. The process is transport-controlled, as the influence of temperature was found to be almost negligible ( $E_a = 349.2 \pm 10.15 \text{ cal mol}^{-1}$ ).

On the contrary, the degradation of the oxirane ring with aqueous H<sub>2</sub>O<sub>2</sub> in acid media is fast and proceeds under a kinetic regime ( $E_a = 16.3 \pm 0.72 \text{ kcal mol}^{-1}$ ), without any observable induction times. If the concentration of H<sub>2</sub>O<sub>2</sub> is kept within moderate values the reaction order with respect to this reactant is two, the expected value.

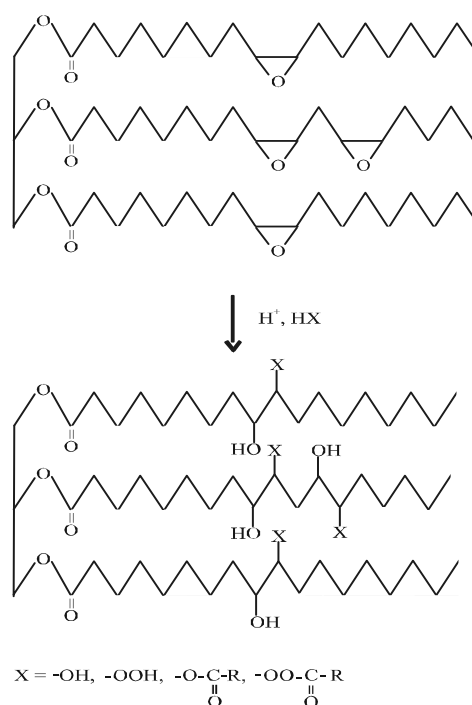
**Keywords**— Epoxidized vegetable oil, Oxiranes, Hydrolysis, Hydrogen peroxide.

### I. INTRODUCTION

The epoxidation of vegetable oils (VO) has been studied during the last decades owing to the commercial importance of these compounds as additives of polymers, lubricants and detergents (Wöhlers *et al.*, 1958; Rangarajan *et al.*, 1995; Sinadinović-Fišer *et al.*, 2001), as well as to the intrinsic interest of oxiranes as intermediates of synthesis that can be obtained from renewable resources.

For safety reasons, these epoxidations are usually carried out using peracids formed *in-situ*, by reacting a carboxylic acid with concentrated hydrogen peroxide. Homogeneous or heterogeneous acid catalysts (*viz.*, ion exchange resins) can be used, the latter being preferred for they allow an easy separation from the mixture. In both cases, though, besides the main reaction (the formation of the oxirane ring by reaction of unsaturated double bonds of the hydrocarbon chain of the VO with the peracid) several other, deleterious consecutive reactions occur. They all imply process losses *via* ring-opening and must be minimized (Fig. 1). Until now, the

only oxirane ring opening reaction which has been studied in detail is that of neat carboxylic acids (that is, in organic phase exclusively) with oxiranes from VO and/or fatty acid methyl esters (FAME) (Zaher *et al.*, 1989; Zaher and El-Shami, 1990; Gan *et al.*, 1992). However, under realistic process conditions an aqueous polar solution is always present, which raises questions about the true impact of hydrolysis on ring-opening in the solvated, acid media.



**Figure 1:** Oxirane ring opening of epoxidized vegetable oils (epoxidized triacylglycerides).

In the acid hydrolysis of propylene and isobutylene epoxides the mechanism of ring opening is attributed to nucleophilic substitution (Pocker *et al.*, 1998). These authors show that the type of substrate (as well as the nucleophile) and the pH have an impact of the type of substitution the system undergoes, S<sub>N</sub>1 or S<sub>N</sub>2. In a related paper by Johnson *et al.* (1996) the high relevance of the nature of the compound being hydrolyzed and the pH on the reaction mechanism are also emphasized.

More recently, several papers have specifically studied the deliberate hydrolysis of epoxides from VO and FAME with alumina or enzymes (Piazza *et al.*, 2003; Primožič *et al.*, 2003). These efforts, though, are not within the scope of our research program, which is focused on the systematic knowledge of the impact of the various consecutive reactions of oxirane ring opening on the yield of epoxidized VO manufacturing processes. Toward this goal, we present here the degradation by acid hydrolysis and H<sub>2</sub>O<sub>2</sub> attack, using a homogeneous acid catalyst (sulfuric acid).

## II. METHODS

### A. Preparation of epoxidized VO stocks

Well refined (*i.e.*, degummed, neutralized, bleached and deodorized) sunflower (Natura brand, from Aceitera General Deheza S.A., Córdoba, Arg.) and soybean oils (Oleaginosa Humboldt, Santa Fe, Arg.) were epoxidized in depth at low temperature (20-40 °C) with performic acid generated *in-situ*, using benzene as diluent of the organic phase, to minimize ring opening. The molar ratio of hydrogen peroxide/formic acid/VO unsaturation (double bonds) was 20/2/1. The VO, benzene and formic acid were jointly placed into a well-stirred, round-bottom glass reactor kept at 20 °C. Then, dilute (30 wt%) hydrogen peroxide was added (also at 20 °C), dropwise, after which the reactor temperature was slowly raised to 40 °C, to complete the reaction.

The whole procedure, which does not require adding any catalyst, demands about 20 h to achieve reaction completion. All reagents were acs analytical grade.

The theoretical maximal concentration of oxirane groups in epoxidized soybean oil is 5.5 wt%, which is equivalent to a contents of 0.34 mol of oxygen/100 g of epoxidized VO.

### B. Ring-opening studies

Epoxidized sunflower oil was used to study the opening of the oxirane ring by acid hydrolysis. Customarily, 15 ml of the epoxidized oil were placed in a 3-bore thermostated round-bottom flask, furnished with a reflux condenser and a mechanical stirrer. The system was heated to work temperature and H<sub>2</sub>SO<sub>4</sub>-acidified doubly distilled, deionized water (pre-equilibrated at the same temperature) was then added. Periodically, samples were taken from the reactor, thoroughly washed to eliminate acidity and dried using a rotary evaporator prior to their derivatization and analysis.

Epoxidized soybean oil was used to follow the degradation of the epoxide groups with hydrogen peroxide under homogeneous, acid catalysis. Reaction procedures, sample handling and analyses were similar to the ones described above. Concentrate sulfuric acid (98%) was acs grade.

In both studies, hydrolysis and hydrogen peroxide degradation of the oxirane ring, the experimental program included several conditions for stirring (1000, 1240, 1380, 1500 and 1680 rpm), pH (1, 1.5, 2, 3, 4 and 5) temperature (60, 70 and 80 °C) and aqueous phase-to-epoxidized oil volume ratios (20/20, 25/15 and 35/15), as indicated in Tables 1 and 2.

### C. Analytical

Iodine, oxirane and hydroxyl values of the stocks of epoxidized sunflower and soybean oils were analyzed using the Official and Recommended Practices of the American Oil Chemists' Society (1997).

The oxirane ring-opening reactions were followed by GLC, previously derivatizing the samples with sodium methoxide (Sales *et al.*, 2000). Standard deviations in regression analyses are given for a 95% confidence interval.

**Table 1:** Reaction conditions and mass percent of residual epoxide groups in the organic phase (conversion) in the acid-catalyzed hydrolysis of epoxidized, refined sunflowerseed oil.

Run	H <sub>2</sub> O/epoxide volume ratio (v/v)	T (°C)	Stirring (rpm)	pH	Total duration (min)	% Residual epoxide groups (Conversion) (a)
1	25/15	70	1240	1	1650	6.02 (93.35)
2	25/15	70	1380	1	1650	3.50 (96.13)
3	25/15	70	1500	1	600	2.60 (97.13)
4	25/15	70	1680	1	600	2.69 (97.03)
5	35/15	70	1500	1	600	2.42 (97.33)
6	20/20	70	1500	1	600	2.66 (97.06)
7	25/15	70	1500	1.5	1530	16.83 (81.41)
8	25/15	70	1500	2	1620	65.15 (28.03)
9	25/15	70	1500	3	1560	86.12 (4.81)
10	25/15	70	1500	5	3300	90.52 (≅ 0)
11	25/15	60	1500	1	600	11.33 (87.84)
12	25/15	80	1500	1	600	1.37 (98.49)

(a) Initial mass percent of epoxide groups in the organic phase: 90.52. Homogeneous acid catalyst: H<sub>2</sub>SO<sub>4</sub>.

### III. RESULTS AND DISCUSSION

#### A. Oxirane ring opening *via* acid hydrolysis

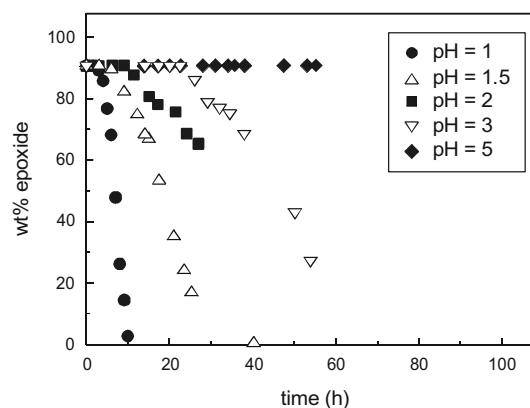
To fully take into account the impact of the main process variables on the acid hydrolysis of the epoxide ring, the experimental program deliberately included process conditions known to lead to extensive degradation of the oxirane ring, with glycol formation, namely: high temperature, low pH and high ratios of polar (aqueous) to nonpolar (epoxidized oil) phases, which causes the latter to be dispersed into tiny droplets.

As the hydrolysis reaction proceeds at the liquid-liquid interphase the degree of dispersion/mixing of the organic phase is highly relevant. During the time course of runs 1 to 4, where only the stirring rate was changed while keeping constant the rest of the process variables, in a demanding situation (pH= 1; T= 70 °C), the mass percent of remaining epoxide groups after 600 min was 45.99 (conversion = 49.19%) at 1240 rpm, decreasing to 25.83 (conversion = 71.46%) at 1380 rpm and, further, to just 2.60 (conversion = 97.13%) at 1500 rpm and 2.69 (conversion = 97.03%) at 1680 rpm (Table 1). In other words, under those last operating conditions the rate of hydrolysis was no longer controlled by the external mass transfer. Nevertheless, for stability reasons, stirring at 1500 rpm was chosen to further the study.

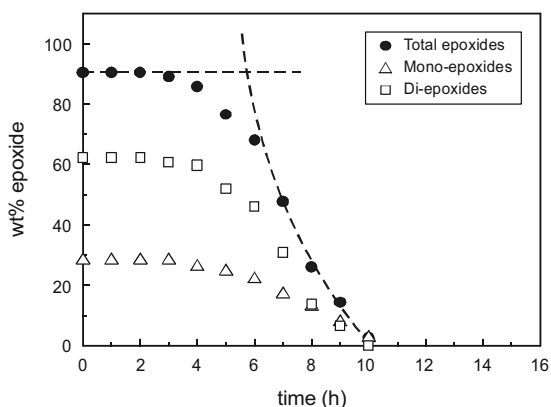
With respect to the possible effect of the volumetric ratio of the immiscible, water and epoxide phases, it is worth noticing that no significant differences were observed upon increasing the volume of the former (See runs 3, 5, and 6, Table 1), which implies that under the same operating conditions the dispersity of the organic phase (or the available interfacial area) reaches a plateau whenever the volume ratio is 1/1 or higher.

The impact of the acid catalysis was studied in the 1 to 5 pH range. Typical results at 70 °C are shown in Fig. 2. At pH= 5 there is no observable ring opening but lowering the the pH may lead to considerable (pH= 3) to severe (pH= 1) hydrolysis. Figure 2 also shows the presence of an 'induction time' in every case, which decreases noticeably the lower the pH is set. This induction period seems to be related to the need of enough *active* area-to-volume ratio in the system, after which a 'break-up' point is reached, thus allowing the hydrolysis of the oxirane ring to proceed as a pseudo-homogeneous reaction. The two broken lines in Fig. 3 strongly suggest this, but also indicate that the sigmoidal evolution of the concentration of residual epoxide groups is an artifact where both phenomena are convoluted. The exponential decay in the percent of remaining epoxide only becomes appreciable after the interfacial area is entirely developed. Our data show, then, that the pH has a double influence of the hydrolysis rate: onset of the 'break-up point' (due to a decrease on the surface tension once enough glycols are formed?) and attack on the oxirane ring proper.

Three different temperatures (60, 70 and 80 °C) were employed to evaluate the energetics of the reaction, only



**Figure 2:** Effect of pH in acid hydrolysis of the oxirane groups of epoxidized sunflowerseed oil (70 °C; 1500 rpm; water/epoxide volume ratio= 25/15).



**Figure 3:** Reactivity of di- and mono-epoxides of sunflowerseed oil in the (acid) oxirane ring hydrolysis at pH= 1 (70 °C; 1500 rpm; water/epoxidized oil volume ratio= 25/15). The dashed lines intersect the 'break-up' point and the evolution of the chemical reaction proper.

at pH= 1 to avoid excessively long runs (See entries 3, 11 and 12 in Table 1). After 8 h, the percent of remaining epoxide at the lowest temperature was 47.1 (corresponding to 47.9% conversion), while at 70 °C it was 26.1 (conversion = 71.4%) and just 17.0 (conversion = 81.2) at 80 °C. Sigmoidal curves were always found, similar to those observed while studying the effect of pH, with induction periods decreasing the higher the reaction temperature was: 4 h at 60 °C, 2 h at 70 °C and 1 h at 80 °C. The interpretation of these data is not straightforward, as changes in both transport (viscosity and diffusivities) and physicochemical (*e.g.*, surface tension) parameters may be involved. Yet, the apparent activation energy resulting from analyzing the exponential part of the process was  $349.2 \pm 10.15$  cal mol<sup>-1</sup>, which very strongly indicates that the homogeneously (acid) catalyzed hydrolysis of the epoxidized oil is mass-transport controlled.

Another relevant information coming from our data is that the relative reactivity of the di-epoxides *vs.* the mono-epoxides towards the hydrolytic rupture of the ring is similar (their concentration ratio was constant,

**Table 2:** Reaction conditions and mass percent of residual epoxide groups in the organic phase (conversion) in the acid-catalyzed degradation of the oxirane ring by H<sub>2</sub>O<sub>2</sub>(aq.) of epoxidized, refined soybean oil.

Run	H <sub>2</sub> O <sub>2</sub> aq./epoxide volume ratio	T	Stirring	pH	[H <sub>2</sub> O <sub>2</sub> ] <sub>aq.</sub>	Total duration	% Residual epoxide groups (Conversion)
	(v/v)	(°C)	(rpm)		(wt %)	(min)	(a)
1	25/15	70	1000	1	30	50	18.38 (80.60)
2	25/15	70	1300	1	30	50	1.70 (98.21)
3	25/15	70	1500	1	30	50	1.61 (98.30)
4	25/15	70	1600	1	30	50	1.65 (98.26)
5	35/15	70	1500	1	30	50	1.70 (98.21)
6	20/20	70	1500	1	30	50	1.68 (98.23)
7	25/15	70	1500	2	30	330	23.14 (75.57)
8	25/15	70	1500	3	30	600	20.18 (78.70)
9	25/15	70	1500	4	30	600	62.25 (34.28)
10	25/15	60	1500	1	30	50	55.21 (40.97)
11	25/15	80	1500	1	30	30	1.20 (98.73)
12	25/15	70	1500	1	48	15	1.54 (98.37)
13	25/15	70	1500	1	40	25	1.25 (98.68)
14	25/15	70	1500	1	20	50	44.87 (52.26)
15	25/15	70	1500	1	15	50	66.45 (29.84)

(a) Initial mass percent of epoxide groups in the organic phase: 94.72. Homogeneous acid catalyst: H<sub>2</sub>SO<sub>4</sub>.

equal to the initial one, until almost total disappearance of both), as neatly shown in Fig. 3. This means that the hydrolysis reaction proceeds at about the same rate regardless of the type or source of epoxidized vegetable oil (be it from olive oil -highly oleic- or from linseed oil -highly linolenic-).

We compared our results with those of Zaher *et al.* (1989), who studied the degradation of the oxirane ring of epoxidized soybean oil with glacial acetic acid (14.38 M), with no catalyst added. After 3 h at 70 °C, for example, they reported a 75% ring-opening whereas, even under the harsher hydrolysis conditions used here (pH= 1, run 3 in Table 1), just about 1% of the epoxide reacted with the acidified water after the same elapsed time. Set over against the attack from the carboxylic acid, hence, the hydrolysis reaction of the oxirane ring is negligible.

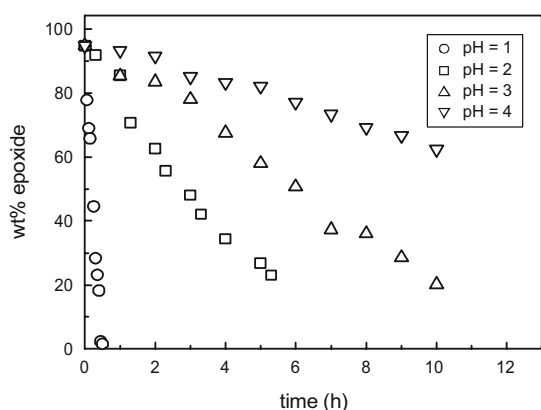
What is perhaps more relevant is the following: The total reaction time in the epoxidation process of vegetable oils at the usual, moderate process temperatures used to minimize ring opening (*e.g.*, 60 °C) is about 4 h (Chou and Chang, 1986; Gan *et al.*, 1992; Rangarajan *et al.*, 1995), which practically coincides with the observed induction time prior to any hydrolytic rupture. By no means, then, process losses could be ascribed to this reaction in practice (*i.e.*, under industrial conditions).

#### A. Oxirane ring opening via hydrogen peroxide attack

Like for the hydrolysis reaction, the experimental program was designed to include working conditions which would presumably maximize ring opening (high temperature, low pH, high H<sub>2</sub>O<sub>2</sub>(aq.)-to-epoxidized oil volume ratios, etc.), but keeping 'realistic'

concentrations of hydrogen peroxide in the reacting system. Also, an excess of hydrogen peroxide was always used (*e.g.*, the H<sub>2</sub>O<sub>2</sub>/oxirane groups mol ratio in runs 1-4 and 7-4 is 4.7) (Table 2). The detailed analysis of those runs where the stirring rate was purposely varied (runs 1-4, Table 2) showed similar performances between 1300 and 1600 rpm. As perfect mixing was also observed within said agitation range, 1500 rpm was chosen for the remaining runs. No significant differences in reactivity were perceived either when the volumetric ratio of the H<sub>2</sub>O<sub>2</sub>(aq.)-to-epoxidized oil phases was changed *and* the latter phase was kept dispersed (runs 3, 5 and 6, Table 2). This indicates that the effective interfacial area (a result of competing dispersion and coalescence processes of the organic phase) no longer changed upon adding further volume of the polar phase into the reactor, just as it was also observed in the hydrolysis case.

Using the integral method for data analysis, the degradation reaction of the oxirane ring with hydrogen peroxide was found to be of order zero with respect to the epoxide groups. In other words, a linear concentration *vs.* time behavior was usually the best fit (See Figs. 4, 5), which suggests that the concentration of epoxide groups in the external film of the organic droplets is always high. Wöhlens *et al.* (1958) also found zero order with respect to the epoxide groups in their study of oxirane ring opening with either pre-formed peracetic acid or with percarboxylic acid prepared *in-situ* (without specifying the attacking reagent, though), concluding that 'such behavior is typical of heterogeneous reactions'. Yet, for very low pH or highly concentrated H<sub>2</sub>O<sub>2</sub> (> 40 wt%), the zero order kinetics no longer holds at high conversion (Fig. 5.a).



**Figure 4:** Effect of pH in the degradation of the oxirane groups of epoxidized soybean oil with aqueous  $\text{H}_2\text{O}_2$  in acid media ( $70^\circ\text{C}$ ;  $1500\text{ rpm}$ ;  $\text{H}_2\text{O}_2(\text{aq.})/\text{epoxide}$  volume ratio=  $25/15$ ;  $30\text{ wt}\%$   $\text{H}_2\text{O}_2$ ).

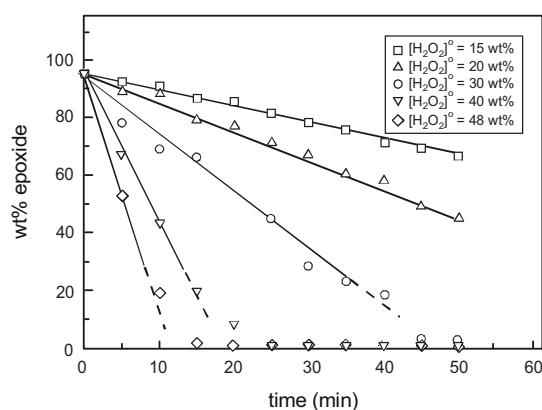
The degradation of the epoxidized oil with  $\text{H}_2\text{O}_2(\text{aq.})$  is strongly dependent on pH, but it does not show any appreciable induction time, even at  $\text{pH}=4$  (Fig. 4). This indicates that, unlike ring opening via hydrolysis, the development of enough interfacial area is fast. Yet, even though there is a notorious intensification in the degradation rate with acidity, such increase was not found to be directly proportional to pH (*i.e.* the reaction order with respect to  $[\text{H}^+]$  is not unit), as it usually happens in conventional homogeneous catalysis.

Raising the reaction temperature (runs 3, 10 and 11, Table 2) may also lead to severe degradation: At  $60^\circ\text{C}$  the calculated value of the reaction rate constant (pseudohomogeneous, normalized by total organic phase volume only) was  $k_{\text{obs}} = 0.79 \pm 0.07\text{ l mol}^{-1}\text{ min}^{-1}$ , whereas at  $80^\circ\text{C}$ , instead, said value was  $3.23 \pm 0.23\text{ l mol}^{-1}\text{ min}^{-1}$ . The activation energy was  $16.3 \pm 0.72\text{ kcal mol}^{-1}$  (Fig. 5.b), a value quite similar to the one found by Zaher *et al.* (1989) in their homogeneous single-phase organic system.

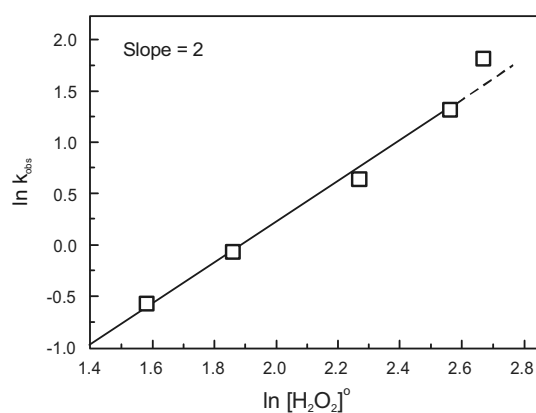
The relative reactivity of di- and mono-epoxide groups towards the attack by aqueous hydrogen peroxide was the same, and their initial ratio did not change throughout the process. This was also found in the hydrolysis case, as already discussed above.

Finally, the impact of hydrogen peroxide concentration was analyzed in detail, at  $70^\circ\text{C}$  (Runs 3, 12-15 in Table 1). Figure 5.a shows that the higher the concentration of  $\text{H}_2\text{O}_2(\text{aq.})$  is, the faster the attack of the oxirane ring results. Moreover, since the experimental program was purposely designed to have a high molar ratio  $\text{H}_2\text{O}_2/\text{epoxide}$  groups in the reacting system, the (pseudohomogeneous)  $k_{\text{obs}}$  readily gives a measurement of said impact in quantitative terms. The log-log plot of  $k_{\text{obs}}$  vs. the initial concentration of hydrogen peroxide,  $[\text{H}_2\text{O}_2]^0$ , shows (Fig. 5.b) that the reaction order for hydrogen peroxide is 2 (actually,  $2.03 \pm 0.27$ ) whenever  $[\text{H}_2\text{O}_2]^0 < 40\text{ wt}\%$ .

More concentrated solutions lead to a higher (apparent) reaction order. In this concentration range,



(a)



(b)

**Figure 5:** (a) Effect of the concentration of  $\text{H}_2\text{O}_2(\text{aq.})$  in the degradation of the oxirane groups of epoxidized soybean oil with aqueous  $\text{H}_2\text{O}_2$  ( $\text{pH}=1$ ;  $70^\circ\text{C}$ ;  $1500\text{ rpm}$ ;  $\text{H}_2\text{O}_2(\text{aq.})/\text{epoxidized oil}$  volume ratio=  $25/15$ ); (b) Order of reaction with respect to the initial concentration of  $\text{H}_2\text{O}_2(\text{aq.})$ , for same process conditions.

though, the reaction is no longer zero order with respect to the epoxide groups either. Further analysis calls for a heterogeneous model, instead (in progress), with a complete description of the concentration field inside the organic droplets.

One of the most consequential, albeit indirect conclusion of our study is that the degradation of the oxirane ring by hydrogen peroxide in the conventional manufacture of epoxidized oils, using peracetic acid prepared *in-situ* (usually at  $60^\circ\text{C}$ , with molar ratio of double bonds/ $\text{H}_2\text{O}_2/\text{acetic acid} = 1/1.1/0.5$ ), is minimal. In said process aqueous hydrogen peroxide is added stepwise, which quickly reacts with acetic acid to give peracetic acid so that there is never an appreciable amount of  $\text{H}_2\text{O}_2$  inside the reactor.

#### IV. CONCLUSIONS

The hydrolysis of epoxides of long chain fatty acids triacylglycerols is an extremely slow reaction, which requires an acid catalyst to proceed at an appreciable rate. The reaction proceeds at the liquid-liquid

interphase, but only after an extended 'induction period' during which enough *active* interfacial area is developed, said active interfacial area being most likely related to a preferential accumulation of glycols at the polar-non polar interface. The induction period is also a strong function of pH. The process is transport-controlled, though, since the impact of temperature is almost nil (*ca* 349 cal mol<sup>-1</sup>).

On the contrary, the degradation of the oxirane ring with aqueous hydrogen peroxide in acid media is quite fast, proceeding under a kinetic regime ( $E_a = 16.3 \pm 0.72$  kcal mol<sup>-1</sup>) and in the absence of observable induction times. Even though there is a notorious intensification in the degradation rate with acidity, such increase is was not directly proportional to pH as it is usually encountered in conventional homogeneous catalysis. If the concentration of H<sub>2</sub>O<sub>2</sub> is kept within moderate values, the reaction order of the ring opening with respect to this reactant is two, the expected value. Otherwise, the attack on the oxirane groups is seriously enhanced whenever exceedingly high oxidizing conditions are found in the media.

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