DEGRADATION OF THE OXIRANE RING OF EPOXIDIZED VEGETABLE OILS IN LIQUID-LIQUID SYSTEMS: II. REACTIVITY WITH SOLVATED ACETIC AND PERACETIC ACIDS

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Abstract— **The impact of the main process variables (agitation, pH, temperature, concentration levels) on the degradation of the oxirane ring of epoxidized soybean oil (ESO) by attack by solvated acetic and peracetic acids in two-phase (polar-organic) systems when a homogeneous acid catalyst is used, is analyzed in detail. The first degradation reaction is first order with respect to the epoxide concentration and second order with respect to the solvated acetic acid [$k_{AA}(70^oC) = 4.27 \pm 0.12 \times 10^{-5}$ l^2 mol^{-2} min^{-1}; $Ea_{AA} = 12.9 \pm 0.64$ kcal mol^{-1}]. The degradation increases notoriusly the lower the pH of the reacting media is; the increase is directly proportional to the concentration of protons, as is usually found in homogeneous catalysis (for very low pHs the reaction is almost instantaneous). Likewise, the degradation reaction with peracetic acid is first order with respect to the epoxide [$k_{PAA}(70^oC) = 4.31 \times 10^{-4}$ l^2 mol^{-2} min^{-1}; $Ea_{PAA} = 10.6 \pm 0.38$ kcal mol^{-1}] and it also increases linearly with proton concentration. Although the *specific* attack on the ring by the peracid is almost 10 fold harsher, acetic acid is constantly being regenerated during the industrial process, so that its concentration is always far larger than that of peracetic acid. Thus, under process conditions the degradation of the oxirane ring is mostly caused by the carboxylic acid.**

Keywords— **Epoxidized soybean, degradation of oxiranes, solvated acetic acid, peracetic acid.**

I. INTRODUCTION

Epoxidized vegetable oils (EVO) are extensively used by industry, specially as plasticizers in PVC manufacture. Owing to the oxirane ring in the molecule, they also impart thermal and photo-stability to the polymer composite (Kirk and Othmer, 1984). Their main advantage is related to good performance combined with low production costs. Also, and most desirably, EVOs can be obtained from renewable sources.

The epoxidation of any given vegetable oil can be accomplished using organic peracids, either preformed or formed *in-situ*, by reacting a carboxylic acid with concentrated hydrogen peroxide to make a percarboxylic acid, which in turn donates an oxygen atom to the double bonds of the fatty acid carbon chain

of the oil (Reactions 1 and 2 in Fig. 1). Peracetic acid is customarily used in industrial practice, in which case homogeneous or heterogeneous acid catalysts (*viz.,* ion exchange resins) can be used. Together with the main oxygen-transfer reaction, several other, consecutive reactions are always present (Reactions 3-7, Fig. 1). They all imply process losses *via* ring-opening and must be minimized to achieve good yields and high peroxide values of the EVO.
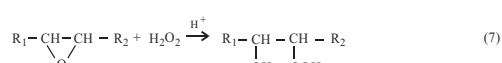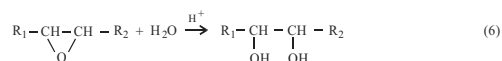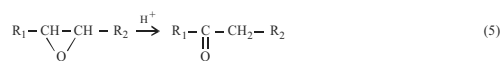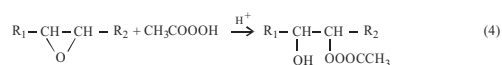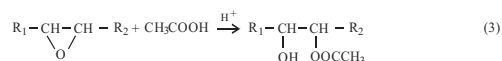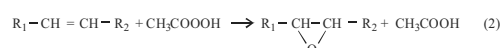

Figure 1: Epoxidation and ring opening reactions of the double bonds of vegetable oils (unsaturated triacylglycerides) in the conventional acetic acid-hydrogen peroxide process.

Until recently, the only oxirane ring opening reaction of oxiranes obtained from vegetable oils (VO) and/or fatty acid methyl esters (FAME) studied with some detail (amongst the set indicated in Fig. 1) was the attack by glacial acetic acid (*i.e.,* in a single organic phase) (Zaher *et al.*, 1989; Gan *et al.*, 1992, Pagès-Xatart-Parès *et al.*, 1999). In the first two works it was found that the reaction is first order with respect to the epoxide concentration and of second order with respect to acetic acid. Zaher *et al.* (1989), who studied the degradation of epoxidized soybean oil, found $k_{AA'} = 3.33 \times 10^{-5}$ l^2 mol^{-2} min^{-1} at 70 °C, with an activation energy of 15.84 kcal mol^{-1}. Gan *et al.* (1992) analyzed, instead, the ring opening of a mixture of epoxided FAME obtained from palm oil. Upon exposing the mixture to glacial acetic acid, they found similar values

of both the reaction rate constant ($k_{AA'} = 3.19 \times 10^{-5}$ l^2 mol^{-2} min^{-1}) and the activation energy ($Ea_{AA'} = 17.35$ kcal mol^{-1}) at aforementioned temperature.

Formic and heptanoic acids have been used as well to find general traits about the attack of carboxylic acids on the epoxide ring of epoxidized VO and FAME in the organic phase (Zaher and El-Shami, 1990; Pagès-Xatart-Parès et al., 1999). The former authors, who used isobutanol to dilute the reacting system, found that the degradation of epoxidized soybean oil with formic acid was three orders of magnitude faster than with glacial acetic acid. Their data fitting indicated that in this case the reaction was of second order with respect to both reactants, but no explanation was given about such finding. Interestingly, the ring-opening rate using glacial acetic acid diluted with isobutanol was not significantly different from that encountered employing the neat carboxylic acid.

Industrial epoxidation is conducted, however, in two-phase polar (aqueous H_2O_2)-organic (VO) systems. Moreover, the aqueous solution of concentrated hydrogen peroxide used to generate the percarboxylic acid becomes progressively dilute the higher the extent of reaction is (Reaction 1, Fig. 1). In other words, under practical conditions the organic acids are always solvated, which raises questions about the true influence of solvation on ring-opening in the acid media.

We have set up a research program focused on the systematic knowledge of the impact of the various consecutive reactions of oxirane ring-opening on the yield of the EVO manufacturing process. Toward this goal, we report here the degradation of epoxided soybean oil with solvated acetic (AA) and peracetic (PAA) acids, using a homogeneous acidic catalyst (H_2SO_4). Ring-opening by acid hydrolysis and hydrogen peroxide attack has been reported elsewhere (Campanella and Baltanás, 2004).

II. METHODS

A. Preparation of an epoxidized soybean oil stock

Soybean oil, kindly provided by Oleaginosa Humboldt (Santa Fe, Arg.) was refined (i.e., degummed, neutralized, bleached and deodorized) in the laboratory and epoxidized in depth at low temperature (20-40 ºC) 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 ºC. Then, dilute (30 wt%) hydrogen peroxide was added (also at 20 °C) dropwise, after which the reactor temperature was slowly raised to 40 ºC, 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 content of 0.34 mol of oxygen/100 epoxidized VO.

B. Ring-opening studies

The stock of epoxidized soybean oil (ESO) was used to study the opening of the oxirane ring by either solvated acetic acid or an aqueous solution of peracetic acid ($AA/PAA/H_2O+H_2O_2 = 10.36/1.00/0.20$ mol). The latter was prepared following the method of Yadav and Satoskar (1997) and stabilized (equilibrated) at the reaction temperature. For each run, aliquots of the stock of ESO were placed in a 3-bore thermostatized round-bottom flask, furnished with a reflux condenser and a mechanical stirrer and then the system was heated to work temperature. Next, an appropriate volume of H_2SO_4-acidified acetic acid or peracetic acid solutions, diluted with doubly distilled, deionized water so as to get an initial concentration of AA in the reacting system, $C_{AA}°$, equal to 12 M, was previously thermostatized at the same temperature and added to the reactor. Periodically, samples were taken, thoroughly washed to eliminate acidity and dried using a rotary evaporator prior to their derivatization and analysis. Concentrate sulfuric acid (98%) was ACS grade.

In both studies, a molar excess of carboxylic acid with respect to the epoxide group was used (e.g., a molar ratio AA/oxirane = 20 was used in runs 1-6, Table 1). The experimental program included several levels of stirring (1000 and 1500 rpm), pH (3 to 5) and temperature (50 to 80 ºC), as indicated in Tables 1 and 2.

C. Analytical

Iodine, oxirane and hydroxyl values of the epoxidized soybean oil were analyzed using the Official and Recommended Practices of the American Oil Chemists' Society (1997). The oxirane ring-opening reactions were followed by GLC, derivatizing previously the samples with sodium methoxide (Sales et al., 2000). Standard deviations in regression analyses are given for a 95% confidence interval.

III. RESULTS AND DISCUSSION

A. Oxirane ring opening with solvated acetic acid

To fully take into account the impact of the main process variables on the degradation of the epoxide ring, said process variables were deliberately varied over a wide range of conditions, capable of including either extensive ring opening or minimal degradation (Table 1).

The inspection of runs 1 and 2 in Table 1, where only the stirring rate was changed while keeping unchanged the rest of the process variables, shows that either 1000 or 1500 rpm gave almost identical results, which implies that under these operating conditions the observable rate is not controlled by external mass transfer. In our former study of ring opening via hydrolysis (Campanella and Baltanás, 2004) we found some differences in activity when the stirring rate was lower than 1300 rpm, though. Because acetic acid is

Table 1: Reaction conditions and mass percent of residual epoxide groups in the organic phase (conversion) in the acid-catalyzed degradation of epoxidized, refined soybean oil with solvated acetic acid.

Run	C_{AA}^o (M) (a)	T (°C)	Stirring (rpm)	pH (b)	Volume ratio (v/v) (c)	Total duration (min)	% Residual epoxide groups (Conversion) (d)
1	12	70	1000	5	75/15	180	30.15 (67.47)
2	12	70	1500	5	75/15	180	30.24 (67.37)
3	12	60	1500	5	75/15	180	46.03 (50.34)
4	12	80	1500	5	75/15	180	13.86 (85.05)
5	12	70	1500	3.4	75/15	180	17.28 (81.35)
6	12	70	1500	3	75/15	120	4.85 (94.77)
7	14	70	1500	5	81/15	180	15.02 (83.80)
8	8	70	1500	5	55/15	180	42.49 (54.16)
9	4	70	1500	5	35/15	180	73.64 (20.55)

(a) Initial molarity of acetic acid (AA). C_{AA}^o = mol AA l^{-1} of *total* volume of the reacting system.

(b) By addition of H_2SO_4(aq.) as homogeneous catalyst.

(c) Volume ratio of the aqueous AA solution to the organic (ESO) phase.

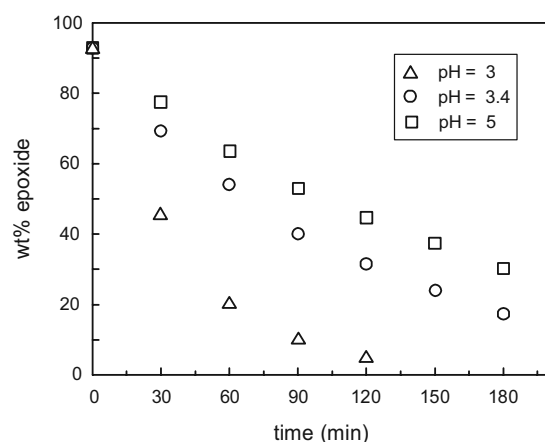*(d)* Initial mass percent of epoxide groups in the organic phase: 92.69.

soluble in both the aqueous and the organic phase (as is the reaction product of the ring opening), and the surface tension of aqueous solutions of AA is lower than that of pure water, it is most likely that these combined facts are enough to grant a good dispersion of the ESO even at 1000 rpm. Anyhow, for stability reasons, stirring at 1500 rpm was chosen to further the study.

A (pseudohomogeneous) kinetic rate expression suitable for describing the oxirane ring opening is given by:

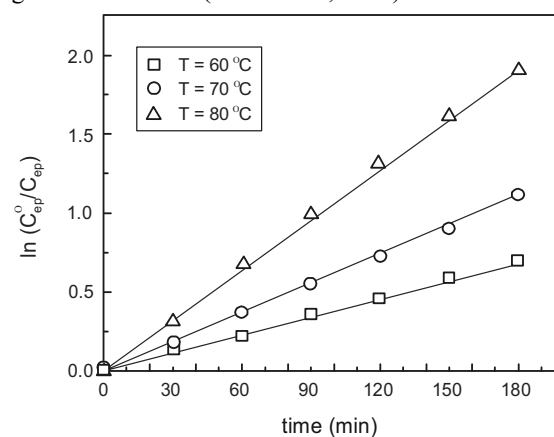$$v = k_{AA} \, C_{AA}^{\alpha} \, C_{ep}^{\beta}, \qquad (1)$$

where

$$k_{obs(AA)} = k_{AA} \, (C_{AA}^o)^{\alpha}, \qquad (2)$$

when an excess of acetic acid is used. Ring opening was found to be first order with respect to the concentration of epoxide groups, in agreement with the findings of Zaher *et al.* (1989) using neat acetic acid.

The impact of the acidity of the media on the reaction rate was evaluated for three different levels of pH (See entries 2, 5 and 6 in Table 1 and Fig. 2). The analysis of the reaction data gave a linear relationship between k_{AA} and proton concentration (*i.e.*, $k_{AA} = k_n + k_{H^+} C_{H^+}$), with a correlation coefficient of 0.9989, which is typical of homogenous catalysis.

The effect of temperature was studied at 60, 70 and 80 °C (Runs 2-4 of Table 1 and Fig. 3). At 70 °C $k_{obs(AA)}$ = 6.15 ± 0.17 × 10^{-3} min^{-1}, while the calculated activation energy was 12.9 ± 0.64 kcal mol^{-1}, quite close to the value found for oxirane ring destruction using glacial acetic acid (Zaher *et al.*, 1989).

Figure 2: Effect of pH in the oxirane ring opening of epoxidized soybean oil with solvated acetic acid (70 °C; 1500 rpm; C_{AA}^o = 12 M).

Figure 3: Effect of temperature in the oxirane ring opening of epoxidized soybean oil with solvated acetic acid (pH = 5; 1500 rpm; C_{AA}^o = 12 M).

The degradation of the ring using solvated acid is somewhat faster, though. Under similar reference conditions (150 min; 60 ºC; pH = 5; C_{AA}^o = 12 M) we had a 44.01% conversion of epoxide groups, while in their case the conversion was 25.91% instead.

As for the concentration of acetic acid, a monotonic increase of the reaction rate *vs.* C_{AA}^o was consistently found (runs 2, 7-9 in Table 1, and Fig. 4.a). To predict the order of reaction with respect to the carboxylic acid, the values of $k_{obs(AA)}$ at 70 ºC (corresponding to the initial concentrations of 4, 8, 12 and 14 M) were obtained from Fig. 4.a and used in the linearized form of Eq. 2:

$$\ln (k_{obs(AA)}) = \ln (k_{AA}) + \alpha \ln (C_{AA}^o). \qquad (3)$$

Figure 4.b shows that, indeed, the order of reaction with respect to solvated AA is two, in close agreement with the experimental information on epoxide ring opening
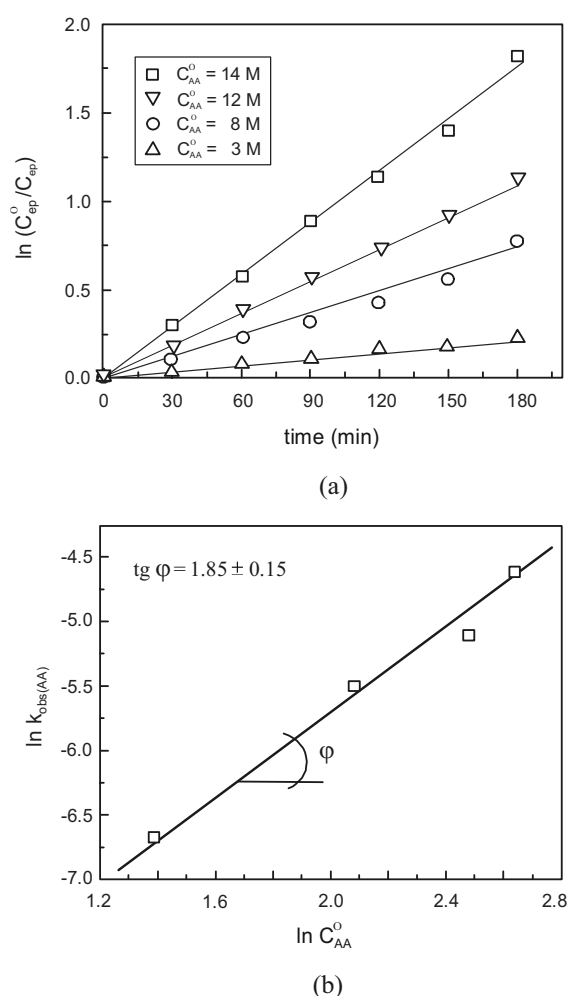

(a)

(b)

Figure 4: Effect of the initial concentration of acetic acid (AA) in the degradation of the oxirane groups of epoxidized soybean oil with solvated AA in acid media (70 ºC; pH = 5; 1500 rpm). (a) Order of reaction with respect to the oxirane group; (b) Order of reaction with respect to the *initial* concentration of solvated AA, C_{AA}^o.

of long-chain unsaturated olefins upon attack with formic acid and/or glacial acetic acid (Zaher *et al.*, 1989; Zaher and El-Shami, 1990).

B. Oxirane ring opening with solvated peracetic acid

Like in the previous case, diferent levels of stirring, temperature and pH were used to evaluate their impact on the degradation of the ESO upon exposing the oxirane rings to an appreciable concentration of peracetic acid (Table 2). It is worthwhile to emphasize at this point that in every run, as for solvated acetic acid, the reacting media was a two-phase liquid-liquid system where the ESO was the disperse phase.

The stabilized aqueous solution of preformed peracetic acid, prepared as indicated in the experimental section, was an equilibrium mixture of acetic and peracetic acid together with water and hydrogen peroxide, where the molar ratio AA/PAA = 10.6 (the concentration of AA in this phase was 13.7 M). Consequently, to obtain comparable results with those corresponding to the attack by solvated acetic acid the volume ratio of the aqueous to the organic (ESO) phase was made equal to 88.27/15.

The detailed analysis of the runs where the stirring rate was purposely varied (runs 1 and 2 in Table 2) showed similar performances at both 1000 and 1500 rpm. Because perfect mixing was observed within aforementioned agitation range, the absence of appreciable external mass transfer resistances was confirmed. Nonetheless, 1500 rpm was chosen for the remaining runs, for practical reasons.

As pointed out above, the aqueous solution of preformed peracetic acid contains carboxylic acids (AA and PAA), water and hydrogen peroxide. Yet, for identical process conditions (*viz.*, pH, temperature and degree of mixing), the comparative impact of the latter reactants on the oxirane ring opening is minimal (Campanella and Baltanás, 2004). Hence, two competitive, simultaneous degradation reactions, each corresponding to the attack on the epoxide groups by acetic and peracetic acids, have to be considered to account for the observable reactivity:

$$v = v_{AA} + v_{PAA}, \qquad (4)$$

$$v = k_{AA} C_{AA}^{\alpha} C_{ep}^{\beta} + k_{PAA} C_{PAA}^{\gamma} C_{ep}^{\delta}. \qquad (5)$$

As both acids were used in molar excess with respect to the amount of epoxide groups, the reaction can be considered, again, as pseudo zero order with respect to both organic acids, that is:

$$v = (k_{AA} C_{AA}^{\alpha} + k_{PAA} C_{PAA}^{\gamma}) C_{ep}^{\beta} = k_{obs(AA+PAA)} C_{ep}^{\beta}. \qquad (6)$$

Figure 5 shows that the degradation reaction of the oxirane ring caused by the solvated mixture of acetic and peracetic acids is first order with respect to the molar concentration of epoxide groups.

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 of epoxidized, refined soybean oil by a stabilized (equilibrated) solution of peracetic acid.[a]

Run	T	Stirring	pH	Total duration	% Residual epoxide groups (Conversion)
	(°C)	(rpm)	(b)	(min)	(c)
1	60	1000	5	120	54.28 (41.73)
2	60	1500	5	120	53.96 (42.08)
3	50	1500	5	120	70.41 (24.42)
4	70	1500	5	120	41.44 (55.52)
5	60	1500	4	120	38.95 (58.19)
6	60	1500	3	120	0.30 (99.68)

(a) The volume ratio of the stabilized (PAA/AA/$H_2O+H_2O_2$ = 10.36/1.00/0.20 mol) solution to the organic (ESO) phase was 88.27/15, to have C_{AA}^o = 12 mol AA l^{-1} of *total* volume of the reacting system.

(b) By addition of H_2SO_4(aq.) as homogeneous catalyst.

(c) Initial mass percent of epoxide groups in the organic phase: 93.16.
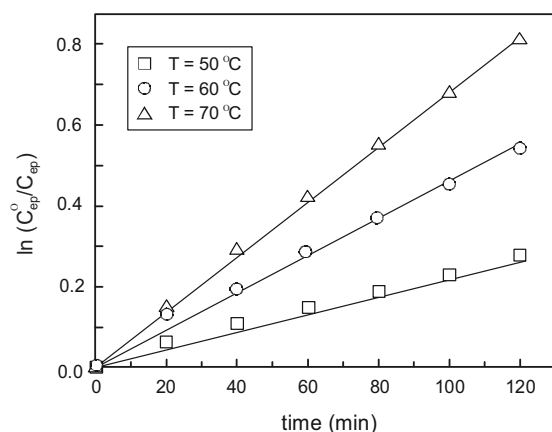
Figure 5: Effect of temperature in the oxirane ring opening of epoxidized soybean oil with a stabilized so-lution of peracetic acid (PAA/AA/$H_2O+H_2O_2$ = 10.36/1.00/0.20 mol). Process conditions: pH = 5; 1500 rpm; C_{AA}^o = 12 M.

In the previous section we reported that a second order of reaction with respect to (solvated) acetid acid in the oxirane ring opening reaction was found. Assuming the same order of reaction for the peracetic acid attack to the ring (given the similar molecular structure of both organic acids), $k_{obs(AA+PAA)}$ can be written as follows:

$$k_{obs(AA+PAA)} = k_{AA} C_{AA}^2 + k_{PAA} C_{PAA}^2. \qquad (7)$$

From Fig. 5, values of $k_{obs(AA+PAA)}$ for each temperature can be extracted which, together with the corresponding values of k_{AA} (obtained using Eq. 2) allowed us to calculate k_{PAA} employing Eq. 7. These calculated values were equal to 1.10×10^{-4}, 3.46×10^{-4} and 4.31×10^{-4} l^2 mol^{-2} min^{-1} at 50, 60 and 70 °C, respectively. Thus, an estimate of the *relative* reactivity ratio between solvated peracetic and acetic acid for the ring-opening reaction is immediate. At 70 °C for example, k_{PAA}/k_{AA} = 17.9, which certainly indicates that the specific degradation capability of the peracid is far greater than that of acetic acid. Yet, compared to formic acid (AF), a carboxylic acid that also exhibits second order of reaction in the epoxide ring opening of vegetable oils, the latter is far more reactive: Taking the experimental data of Zaher and El-Shami (1990), the calculated values of k_{AF}/k_{PAA} = 252 at 70 °C. The activation energy for the opening of the oxirane ring with peracetic acid is slightly lower than for acetic acid, 10.6 ± 0.38 kcal mol^{-1}.

The degradation of the ESO with the peracid is also highly dependent on pH (runs 4-6, Table 2). The analysis of these data showed that k_{PAA}, as was already found for solvated acetic acid attack, also grows linearly with proton concentration (*i.e.,* the reaction system reveals a typical homogeneous catalysis behavior).

There are good reasons to assume that peracetic acid is always in very low amount in the reacting system. This is due to the enormous difference that exists between the reaction rates for peracetic acid production/formation and that of epoxidation (Chou and Chang, 1986; Rangarajan *et al.*, 1995). While the first one is slow, the second one is very rapid, and the peracid formed would consume immediately. Therefore, it seems valid to assume that at no time peracid acid is accumulated in the organic phase and that its concentration is very low at any time. On the other hand, under process conditions acetic acid is constantly regenerated in the reacting system (Eq. 2, Fig. 1), so that its concentration is kept about equal with time. Hence, one can conclude safely that the most important degradation reaction of the epoxide ring -in practical conditions- is the opening with acetic acid.

IV. CONCLUSIONS

The reaction of epoxide ring opening of ESO with solvated acetic acid, using H_2SO_4 as homogeneous catalyst, is first order with respect to the epoxide

concentration and second order with respect to the carboxylic acid [$k_{AA}(70ºC) = 4.27 \pm 0.12 \times 10^{-5}$ l^2 mol^{-2} min^{-1}; $Ea_{AA} = 12.9 \pm 0.64$ kcal mol^{-1}]. The degradation increases notoriusly the lower the pH of the reacting media is, such increase being directly proportional to the concentration of protons, as is usually found in homogeneous catalysis.

Similarly to the attack on the ring with solvated acetic acid, the degradation reaction with peracetic acid is first order with respect to the epoxide [$k_{PAA}(70ºC) = 4.31 \times 10^{-4}$ l^2 mol^{-2} min^{-1}; $Ea_{PAA} = 10.6 \pm 0.38$ kcal mol^{-1}] and it also increases linearly with proton concentration. At 70 ºC the ratio of these kinetics rate constants, k_{PAA}/k_{AA}, indicated that the *specific* attack by the peracid is almost 10 fold more intense. However, as acetic acid is constantly being regenerated in this process, its concentration is always far larger than that of peracetic acid and, thus, the degradation of the oxirane ring is mostly caused by the carboxylic acid.

NOTATION

C   concentration, per *total* volume of the reacting system (mol l^{-1}).
Ea   activation energy (kcal mol^{-1}).
k   reaction rate constant (l^2 mol^{-2} min^{-1}).
k_{obs} observable reaction rate constant (min^{-1}).
v   pseudohomogeneous reaction rate (mol l^{-1} min^{-1}).

Greek letters
α order of reaction with respect to acetic acid, AA.
β order of reaction with respect to epoxidized oil.
γ order of reaction with respect to peracetic acid, PAA.
δ order of reaction with respect to epoxidized oil

Subscripts and superscripts
AA   solvated acetic acid.
AA'   glacial acetic acid.
ep   epoxidized soybean oil.
H^+ proton.
n   neutral (noncatalyzed) conditions.
o   initial value.
PAA   peracetic acid.

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