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Degradation of the oxirane ring of epoxidized vegetable oils in liquid–liquid heterogeneous reaction systems

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Abstract

The reaction regimes under which proceed some of the relevant and deletereous consecutive reactions that occur during the conventional epoxidation process of vegetable oils were analyzed in detail, considering – separately – each transport and intrinsic kinetic step. Epoxidized soybean oil (ESBO) was used as a model material.

In this process, peracetic acid is generated in situ by reacting acetic acid and H_2O_2 (aq) in a polar phase, so that the (acid catalyzed) reaction system is always heterogeneous. The distribution constants between the organic and the polar phases of soybean oil and ESBO were determined, as well as (in the case of the ring opening with acetic acid) the reaction rate constant in the homogeneous ESBO–glacial acetic acid reaction system.

The epoxide ring opening caused by hydrogen peroxide is always slow and, unlike the attack by the acetic acid, progresses only in the polar phase. When no catalyst is added, the attack by acetic acid is also moderate, and the ring-opening reaction proceeds slowly in both phases, albeit slightly above the kinetic regime in the aqueous phase. However, if a homogeneous catalyst (e.g., sulfuric acid) is added, the reaction makes way in the instantaneous (mass-transfer controlled) regime in said phase.

Keywords: Epoxidized vegetable oils; Oxirane ring; Degradation; Liquid–liquid reaction modeling

1. Introduction

Numerous reactions of industrial importance are carried out in heterogeneous, immiscible liquid–liquid reacting systems, in the presence of homogeneous catalysts. The careful analysis of the regime(s) under which these reactions are conducted (namely: kinetic versus diffusive control) allows to establish, on the one hand, well-founded criteria for reactor design and to determine, on the other hand, whether obtaining intrinsic kinetic data under process conditions is feasible.

An interesting example within this class of reacting systems appears in vegetable oil (VO) epoxidation reactions, which are generally performed using organic peracids (usually peracetic acid) formed in situ via the attack on a carboxylic acid with H_2O_2, in aqueous solution [1,2]. In the main reaction (Fig. 1), the peracid gives an oxygen atom to each of the double bonds of the unsaturated fatty acid chains of the VO, forming an oxirane ring in the organic phase, and the (thus 'regenerated') carboxylic acid re-starts the cycle, in the aqueous phase.

Besides the main reaction, several other, deleterious consecutive reactions occur (Fig. 2). They all imply process losses via oxirane ring opening and must be minimized. The hydrolysis of the triglycerides during VO epoxidation is not a concern, though [3].

Until recently, the only well-studied ring-opening reaction, in the case of epoxides obtained from VO and/or their fatty acid methyl esters (FAME), was the attack on the ring with the neat carboxylic acids themselves (formic and/or acetic acid), i.e., in the organic phase exclusively [2,4,5]. More recently, we studied each of the consecutive, irreversible degradation reactions on the oxirane ring of epoxidized soybean oil in the two-phase organic–polar liquid media (illustrated in Fig. 2), using sulfuric acid in aqueous solution as the homogenous catalyst [6,7].

This work presents a detailed analysis on the case of two of these liquid–liquid reacting systems (the only truly relevant in the VO epoxidation process [6,7]): the opening of the oxirane ring with hydrogen peroxide (H_2O_2) and with solvated acetic

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Nomenclature

a	interfacial area (m^2/m^3)
d^*	diameter number
d_{32}	Sauter mean diameter (m) $= (\sum n_i d_i^3)/(\sum n_i d_i^2)$
D_a	stirrer diameter (m)
D_j	diffusion coefficient of compound j in the aqueous phase (cm^2/s)
E	enhancement factor
E_∞	maximal enhancement factor for an instantaneous reaction
Ha	Hatta number
$[j]^L$	concentration of compound j in the L phase (mol/l)
J_j	molar flux density of j (mol/(m^2 s))
k_L	mass transfer coefficient in the L phase (m/s)
k_R	second order kinetic rate constant (l/(mol s))
m_j	distribution constant of compound j (dimensionless)
M_j	molecular mass of compound j (g/mol)
n_a	stirring rate (1/s)
n_i	number of drops with diameter d_i
n_j^L	total number of moles of compound j in the L phase (mol)
N_{sh}	Sherwood number
P	power dissipated by the stirrer (kg/(s^3 m^2))
R	overall observable conversion rate (mol/(l s))
T	absolute temperature (K)
V	total reactor volume (m^3)
V_j	molar volume of compound j (m^3/g).
V_L	volume of the L phase (m^3)
We	Weber number $= \rho_c n_a^2 D_a^3/\sigma$
x_i	molar fraction of solvent i

Greek symbols

ϕ	volume fraction
μ	viscosity (cP)
θ	solvent association factor
ρ	density (kg/m^3)
σ	surface tension (N/m)
ψ	power number

Subscripts and superscripts

AA	acetic acid
aq	aqueous phase
B	compound B
c	continuous phase
d	disperse phase
Ep	epoxide group
i,aq	aqueous interface
i,org	organic interface
j	compound j
L	generic L phase
M	solvent mixture
o	initial value
org	organic phase
PAA	peracetic acid
TGep	epoxidized triglyceride

acid (AA), taking into account each of the transport and intrinsic kinetic steps in both phases.

2. Experimental

2.1. Materials

Crude soybean oil, kindly provided by Oleaginosa Humboldt (Santa Fe, Argentina), was refined (i.e., degummed, neutralized, bleached and deodorized) in the laboratory and used as a model VO feedstock. Its fatty acid (FA) composition was determined by gas chromatography after derivatizing the triglycerides into fatty acid methyl esters, following the AOCS's recommended practice [8], and was the following (wt%): saturated FA: 6.8, oleic acid: 23.5, linoleic acid: 61.2; linolenic acid: 8.5. The iodine value was 137 [9]. Formic acid (acs, 99.8%), glacial acetic acid (acs, 99.8%), benzene (pa), hydrogen peroxide (50 wt%) and sulfuric acid (acs, 98%) were purchased from Fisher Scientific (Pittsburgh, PA).

2.2. Preparation of epoxidized soyben oil (ESBO) stock

The refined soybean oil was 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 [2]. 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

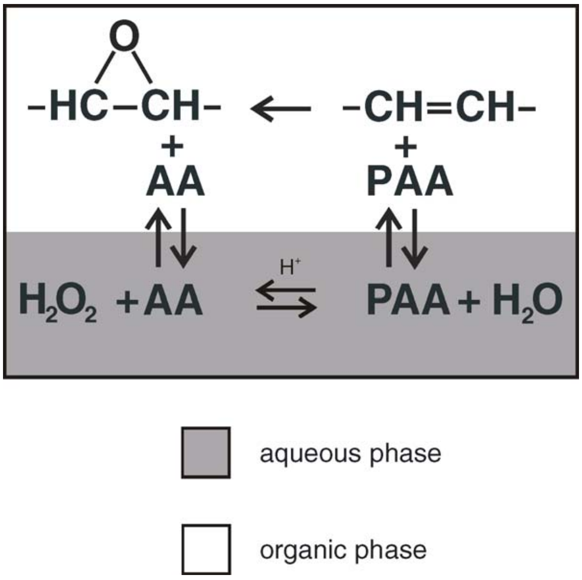

Fig. 1. Schematic diagram of the epoxidation reaction with peracetic acid (PAA) generated in situ from acetic acid (AA) and H_2O_2 (aq), by means of a homogeneous acidic catalyst.

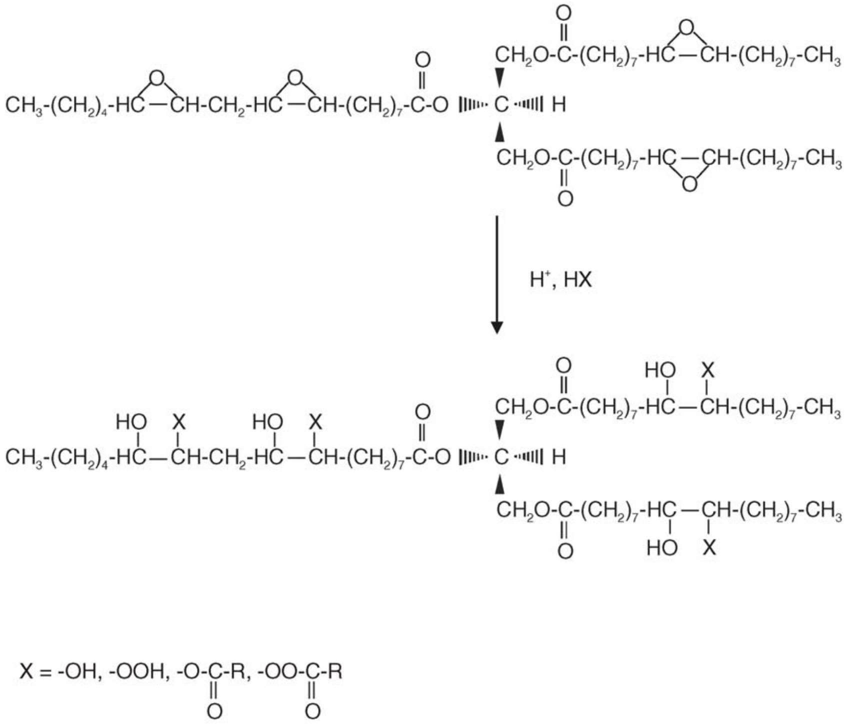

Fig. 2. Oxirane ring-opening reactions of epoxidized vegetable oils (epoxidized triacylglycerides) in the conventional acetic acid-hydrogen peroxide process.

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

2.3. Determination of distribution constants

The distribution constants, or – more appropriately – the equilibrium molar ratios of the refined soybean oil and the ESBO in pure water and in aqueous solutions of hydrogen peroxide, were determined at 60–80 °C, with and without H_2SO_4 added to the aqueous phase (pH 1).

For this purpose, 5 g of the soybean oil, or ESBO, were placed together with 20 g of water, or H_2O_2 (aq), in an erlenmeyer. The mixtures were equilibrated to the desired temperature in a thermostatized bath, under constant stirring, during 4 h. Then, the mixtures were left to stand for at least 60 min until complete separation of the phases was achieved. Afterwards, an aliquot of the aqueous phase was carefully taken, using a syringe and a 0.2 μm teflon pre-filter, to retain any droplet of organic phase still dispersed into the polar phase. The full set of experimental values is given in Table 1.

2.4. Opening of the oxirane ring using glacial acetic acid

The epoxidized oil was firstly used to assess the epoxide ring opening with glacial acetic acid (single phase process), so as to obtain experimental values of the reaction rate constant in the organic phase ($k_{R_{AA}}^{org}$). Fifteen milliliters of ESBO was placed into a 3-bore round-bottom flask, furnished with a reflux condenser and a mechanical stirrer (1500 rpm). The flask was heated to the desired working temperature in a thermostatized bath. Next, a suitable volume of glacial acetic acid, previously thermostatized at the same temperature, was added to the reactor. The reactor temperature was kept to within ±1 °C. Periodically, samples were taken and were thoroughly washed, to eliminate acidity, and dried using a rotary evaporator under reduced pressure, prior to their derivatization and chemical analysis. The

Table 1
Distribution constants (equilibrium molar ratios) of soybean oil (m_{oil}) and epoxidized soybean oil (m_{Ep}) between the organic and the aqueous phases[a]

T (°C)	$[H_2O_2]^{aq,o}$ (wt%)	pH[b]	m_{oil} ($\times10^6$)	m_{Ep} ($\times10^6$)
60	0	N.A.	1.19	1.58
	0	1	1.31	–
	30	N.A.	1.82	–
70	0	N.A.	1.43	2.09
	0	1	1.68	–
	15	N.A.	1.92	2.68
	15	1	1.97	–
	30	N.A.	2.09	2.76
	30	N.A.	2.68	–
	48	N.A.	3.21	–
80	0	N.A.	1.71	2.17
	0	1	1.98	–
	30	N.A.	3.38	–

[a] $m_i = [i]^{aq}/[i]^{org}$; i = soybean oil or epoxidized soybean oil (ESBO).
[b] By adding H_2SO_4 to the aqueous phase.

Table 2
Reaction conditions and conversion of epoxide groups in the acid-catalyzed degradation of epoxidized, refined soybean oil (ESBO) with glacial acetic acid (AA)

Run[a]	*T* (°C)	$[AA]^o$ (M)[b]	Initial epoxide/AA molar ratio	Total duration (min)	Final amount of epoxide groups (wt%)[c]	Final percent conversion[d]
1	60	12	0.080	150	4.79	26.0
2	70	12	0.080	180	3.57	51.5
3	80	12	0.080	180	1.68	74.0
4	70	14	0.034	180	1.95	69.8
5	70	8	0.240	180	4.34	32.9
6	70	4	0.720	180	5.79	10.4

[a] Stirring = 1500 rpm.

[b] Initial molarity of acetic acid (AA): $[AA]^o$ = mol AA/l of *total* volume of the reacting system.

[c] Final weight percent of epoxide groups in the organic phase ($\%Ep_{final}$).

[d] Percent conversion of epoxide groups, calculated as: $[(\%Ep_{initial} - \%Ep_{final})/\%Ep_{initial}] \times 100$, where $\%Ep_{initial}$ stands for the initial weight percent of epoxide groups in the organic phase (the $\%Ep_{initial}$ was 6.47).

experimental program covered a broad range of temperature and acetic acid concentration (Table 2).

2.5. Opening of the oxirane ring using H_2O_2 (aq) and solvated acetic acid

The stock of ESBO was used to follow the degradation of the epoxide groups with aqueous solutions of hydrogen peroxide and acetic acid under homogeneous acid catalysis in well-stirred media [6,7], using the same experimental set-up indicated above.

In the first case, the experimental program included several conditions of H_2O_2 concentration (15, 20, 30 and 40 wt%), 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 Table 3. In the second case, an appropriate volume of H_2SO_4–acidified acetic acid, diluted with doubly distilled, deionized water so as to get an initial concentration of AA in the reacting system, $[AA]^o$, equal to 12 M, was previously thermostatized at the same temperature and added to the reactor. That is (like in usual industrial conditions), a molar excess of the carboxylic acid with respect to the epoxide group was always used (e.g., a molar ratio AA/epoxide groups = 20 was used in runs 1–6, Table 4). The experimental program included several levels of pH (3–5) and temperature (50–80 °C).

Reaction procedures, sample handling and analyses were similar to the ones described in the previous section.

2.6. Analyses

Iodine, oxirane and hydroxyl values of the stock of epoxidized soybean oil were analyzed using AOCS recommended practices [9–11]. The determination of the distribution constants was done by measuring the amount of total organic carbon (TOC) in the aqueous phase, using a SHIMADZU model 5000 A TOC analyzer.

The oxirane ring-opening reaction was followed by gas chromatography (GC), using a Shimadzu GC-17ATF unit and a PE-5 (Perkin-Elmer, Norwalk, CT) capillary column: 30 m × 0.53 mm i.d. × 1.5 μm film. Analytical conditions were as follows: split/splitless injector, injector port at 250 °C, FID detector at 270 °C, H_2 carrier gas (90 psig, 20 ml/min) and isothermal oven at 200 °C. The response factors were obtained

Table 3
Reaction conditions and conversion of epoxide groups, in the acid-catalyzed degradation of the oxirane ring of epoxidized, refined soybean oil (ESBO) by H_2O_2 (aq)

Run	Volume ratio (v/v)[a]	*T* (°C)	Stirring (rpm)	pH[b]	$[H_2O_2]^{aq,o}$ (wt%)	Total duration (min)	Final percent conversion
1	25/15	70	1000	1	30	50	80.6
2	25/15	70	1300	1	30	50	98.2
3	25/15	70	1500	1	30	50	98.3
4	25/15	70	1600	1	30	50	98.3
5	35/15	70	1500	1	30	50	98.2
6	20/20	70	1500	1	30	50	98.2
7	25/15	70	1500	2	30	330	75.6
8	25/15	70	1500	3	30	600	78.7
9	25/15	70	1500	4	30	600	34.3
10	25/15	60	1500	1	30	50	40.9
11	25/15	80	1500	1	30	30	98.7
12	25/15	70	1500	1	48	15	98.4
13	25/15	70	1500	1	40	25	98.7
14	25/15	70	1500	1	20	50	52.3
15	25/15	70	1500	1	15	50	29.8

[a] Initial volume ratio of the H_2O_2 (aq) solution to the organic (ESBO) phase.

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

Table 4
Reaction conditions and conversion of epoxide groups in the acid-catalyzed degradation of epoxidized, refined soybean oil (ESBO) with solvated acetic acid

Run	$[AA]^o$ (M)[a]	T (°C)	Stirring (rpm)	pH[b]	Volume ratio (v/v)[c]	Total duration (min)	Final percent conversion
1	12	70	1000	5	75/15	180	67.5
2	12	70	1500	5	75/15	180	67.4
3	12	60	1500	5	75/15	180	50.3
4	12	80	1500	5	75/15	180	85.0
5	12	70	1500	3.4	75/15	180	81.3
6	12	70	1500	3	75/15	120	94.8
7	14	70	1500	5	81/15	180	83.8
8	8	70	1500	5	55/15	180	54.2
9	4	70	1500	5	35/15	180	20.5

[a] Initial molarity of acetic acid (AA). $[AA]^o$ = mol AA/l of total volume of the reacting system.
[b] By addition of H_2SO_4 (aq) as homogeneous catalyst.
[c] Initial volume ratio of the AA (aq) solution to the organic (ESBO) phase.

using capillary GC grade, heptadecanoic acid methyl ester (99 wt%, Sigma–Aldrich, St. Louis, MO) as internal standard. Prior to injection, the dry samples were derivatized to FAME with sodium methoxide. This GC analysis is able to simultaneously discriminate among the fatty acid methyl esters of the saturated and unsaturated carbon chains, as well as their epoxides and glycols [12]. The results shown in Tables 2–4 are the means of three replicates; the coefficients of variation were always less than 6%. Standard deviations in the regression analyses are given for a 95% confidence interval.

3. Results and discussion

3.1. ESBO oxirane ring opening with H_2O_2 (aq)

As already indicated in Section 1, this heterogeneous liquid–liquid reacting system consists of two phases: aqueous and organic. Only the first one contains hydrogen peroxide, while the epoxide groups (Ep) of the ESBO, which is only slightly soluble in water (Table 1), are mostly in the organic phase. Therefore, in this – simpler – case, the ring-opening reaction proceeds just in the aqueous phase, which is also the continuous phase of the mixture.

The Ep travel from the organic droplets to the aqueous phase, across the interface, diffusing through two films (Fig. 3), and may react (irreversibly) with H_2O_2, both inside the aqueous-side film and in the bulk of the well-stirred hydrogen peroxide solution, to give a product (indicated as P in Fig. 3). The latter, in turn, is extracted back to the organic phase.

As it is well known, the overall expression of the reaction rate in a heterogenous liquid–liquid reacting systems must take into account both transport *and* chemical resistances. The relative value of said resistances can span a wide range, so that a wealth of possibilities does exist, among which the slow and instantaneous regimes represent opposite, asymptotic behaviors [13–17].

For the general case involving a single reaction, the Hatta number (Ha) is a valuable tool to appraise under which regime the reaction proceeds. The Hatta number for a reaction proceeding in the continuous (aqueous) phase, where the order of reaction of the compound that diffuses from the organic to the aqueous phase (Ep) is equal to n, and equal to m for the other reactant (in our case H_2O_2 (aq)), can be written as follows [13]:

$$\mathrm{Ha}=\frac{1}{k_\mathrm{c}}\left\{\frac{2}{n+1}k_\mathrm{R}D([\mathrm{Ep}]^{\mathrm{i,aq}})^{n-1}([\mathrm{H_2O_2}]^{\mathrm{aq}})^{m}\right\}^{0.5} \tag{1}$$

where k_R is the reaction rate constant, D the diffusion coefficient of the organic reactant in the aqueous phase (m^2/s), $[H_2O_2]^{aq}$ the bulk concentration of hydrogen peroxide in the aqueous phase (mol/l), $[Ep]^{i,aq}$ the concentration of Ep in the liquid–liquid interface (mol/l) and k_c is the mass transfer coefficient of Ep in the continuous phase (m/s).

The complete modeling of the reacting system calls for a suitable data base, able to supply adequate estimates of diffusion coefficients, interfacial area and mass transfer coefficients in the continuous and disperse phases. Accordingly, said parameters were calculated for the complete range of experimental condi-

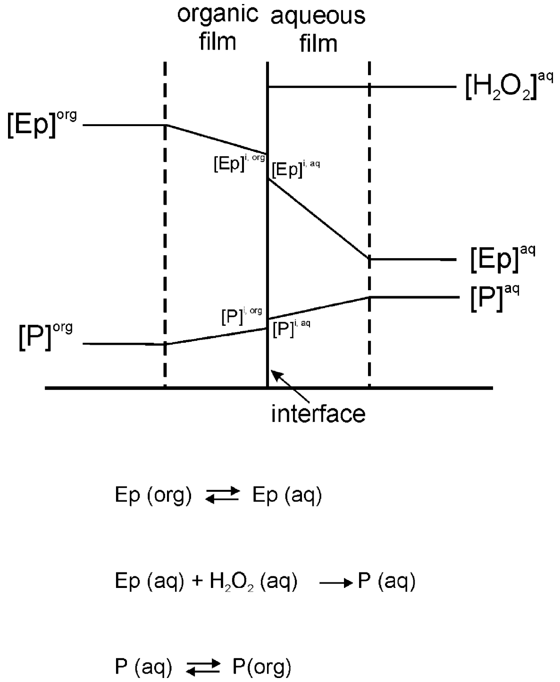

Fig. 3. Concentration profiles of reactants and products for the case of simultaneous mass transfer and slow chemical reaction only in the polar (aqueous) phase. The concentration of the attacking reactant (exemplified here by H_2O_2) is always much larger.

tions used in this work. The foundations for each calculation are given in Appendices A–C at the end of the paper.

Also, by considering the epoxide group (Ep) of the ESBO as the ‘reactant’ being irreversibly degraded by the single ring opening agent i, the expression $\mathrm{Ep} + \nu_i i \rightarrow \mathrm{P}$ suffices for a macrokinetic description of the process, where $\nu_i = 1$ for each oxirane ring opened with (hereby, i stands for either hydrogen peroxide or acetic acid).

In addition, as the density of ESBO is almost identical to that of the degradation products, and (by design) the polar reactants are always in large excess in the system, the total volume of the liquid–liquid system and the individual volumes of each phase can be taken as constant [6,7].

If the slow liquid–liquid reaction regime holds (which is verified below), the mass balances for the reactive compound (Ep) in the organic and the aqueous phases, taking into account that the impact of the hydrolysis of the oxirane ring is negligible under usual reaction conditions [6], can be written as follows:

Organic phase:

$$\frac{\mathrm{d}n_{\mathrm{Ep}}^{\mathrm{org}}}{\mathrm{d}t} = -J_{\mathrm{Ep}}^{\mathrm{org}} a V \tag{2}$$

where

$$J_{\mathrm{Ep}}^{\mathrm{org}} = k_{\mathrm{d}}([\mathrm{Ep}]^{\mathrm{org}} - [\mathrm{Ep}]^{\mathrm{i,org}}) \tag{3}$$

Aqueous phase:

$$\frac{\mathrm{d}n_{\mathrm{Ep}}^{\mathrm{aq}}}{\mathrm{d}t} = J_{\mathrm{Ep}}^{\mathrm{aq}} a V - R_{\mathrm{H_2O_2}}^{\mathrm{aq}} V \tag{4}$$

where

$$J_{\mathrm{Ep}}^{\mathrm{aq}} = k_{\mathrm{c}}([\mathrm{Ep}]^{\mathrm{i,aq}} - [\mathrm{Ep}]^{\mathrm{aq}}) \tag{5}$$

$$R_{\mathrm{H_2O_2}}^{\mathrm{aq}} = k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}} \phi_{\mathrm{aq}} ([\mathrm{H_2O_2}]^{\mathrm{aq}})^2 [\mathrm{Ep}]^{\mathrm{aq}} \tag{6}$$

In these equations $n_{\mathrm{Ep}}^{\mathrm{L}}$ indicates the number of moles of epoxide in the L phase (which is equal to $[\mathrm{Ep}]^{\mathrm{L}} V_{\mathrm{L}}$), $J_{\mathrm{Ep}}^{\mathrm{L}}$ the molar flux of Ep (mol/(m^2 s)), $[\mathrm{Ep}]^{\mathrm{i,L}}$ the concentration of Ep at the L side of the interface (mol/l), $[\mathrm{Ep}]^{\mathrm{L}}$ the concentration of Ep in the bulk of phase L (mol/l), a the interfacial area (m^2/m^3), k_{d} the mass transfer coefficient in the disperse phase (m/s), k_{c} the mass transfer coefficient in the continuous phase (m/s), $R_{\mathrm{H_2O_2}}^{\mathrm{aq}}$ the overall observable conversion rate, $k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}}$ the reaction rate constant (l^2/(mol^2 s)), V the total liquid volume in the reactor (m^3), V_{L} the volume of phase L and ϕ_{L} is the volumetric fraction of phase L.

At the liquid–liquid interface (which is in equilibrium):

$$m_{\mathrm{Ep}} = \frac{[\mathrm{Ep}]^{\mathrm{i,aq}}}{[\mathrm{Ep}]^{\mathrm{i,org}}} \tag{7}$$

For Ep, the complete system comprises three equations – Eqs. (2), (4) and (7) – and four unknowns: $[\mathrm{Ep}]^{\mathrm{i,org}}$, $[\mathrm{Ep}]^{\mathrm{i,aq}}$, $[\mathrm{Ep}]^{\mathrm{aq}}$ and $k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}}$.

As $k_{\mathrm{d}}/(k_{\mathrm{c}} m_{\mathrm{Ep}})$ is much larger than 1, it can be assumed that $[\mathrm{Ep}]^{\mathrm{org}} \approx [\mathrm{Ep}]^{\mathrm{i,org}}$ [13,16,17]. If the following inequality holds: $k_{\mathrm{c}} a \gg \phi_{\mathrm{aq}} k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}} ([\mathrm{H_2O_2}]^{\mathrm{aq}})^2$ one can assume, also, that $[\mathrm{Ep}]^{\mathrm{aq}} \approx [\mathrm{Ep}]^{\mathrm{i,aq}}$ [13,16,17] and, so, the system gets reduced to the following equation:

$$\frac{\mathrm{d}[\mathrm{Ep}]^{\mathrm{org}}}{\mathrm{d}t} = -k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}} ([\mathrm{H_2O_2}]^{\mathrm{aq}})^2 [\mathrm{Ep}]^{\mathrm{org}} \tag{8}$$

Table 5 details the full set of reaction rate constants, which were calculated for the different working conditions; it also shows that the inequality $k_{\mathrm{c}} a \gg \phi_{\mathrm{aq}} k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}} ([\mathrm{H_2O_2}]^{\mathrm{aq}})^2$ always held. The calculated Hatta values were always under 0.3, which clearly shows that the system always operates under the slow (kinetic) regime and that the reaction proceeds in the bulk of the aqueous phase. Using the values of $k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}}$ for the different temperatures, the activation energy of the reaction was obtained: $E_{\mathrm{a}} = 20.17 \pm 1.14$ kcal/mol.

3.2. ESBO oxirane ring opening with solvated acetic acid

This system is entirely different from the preceding one because acetic acid is highly soluble in the organic phase and, thus, the epoxide groups of the ESBO can also react there with the carboxylic acid. The distribution constant of acetic acid ($m_{\mathrm{AA}} = [\mathrm{AA}]^{\mathrm{i,aq}}/[\mathrm{AA}]^{\mathrm{i,org}}$) does not change significantly with the extent of reaction [18]. Therefore, should the reactions in both phases were slow (this hypothesis will be tested below),

Table 5
Validation of the slow liquid–liquid reaction regime for epoxide ring opening of ESBO with hydrogen peroxide solutions[a]

T (°C)	pH[b]	$[\mathrm{H_2O_2}]^{\mathrm{aq,o}}$ (wt%)	$k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}}$ (×10^3 l^2/(mol^2 min))	$k_{\mathrm{d}}/(k_{\mathrm{c}} m_{\mathrm{Ep}})$	$\phi^{\mathrm{aq}} k_{R_{\mathrm{H_2O_2}}}^{\mathrm{aq}} ([\mathrm{H_2O_2}]^{\mathrm{aq}})^2 k_{\mathrm{c}} a$ (×10^4)	Ha (×10^2)
60	1	30	0.14	497	108	1.62
70	1	30	0.36	497	46	1.01
80	1	30	0.77	497	14	0.59
70	1	40	1.53	391	400	3.23
70	1	30	1.20	403	240	2.51
70	1	20	0.41	508	21	0.72
70	1	15	0.25	511	7.3	0.42
70	2	30	3.2	497	389	3.10
70	3	30	1.63	497	910	2.21
70	4	30	0.71	497	83.1	1.40

[a] Organic to polar (oil/aqueous) phases volumetric ratio = 15/25 (v/v); stirring rate = 1500 rpm.

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

the mass balances for Ep in the organic and aqueous phases would be written, respectively, as:

$$\frac{\mathrm{d}n^{\mathrm{org}}_{\mathrm{Ep}}}{\mathrm{d}t} = -J^{\mathrm{org}}_{\mathrm{Ep}}aV - R^{\mathrm{org}}_{\mathrm{AA}}V \qquad (9)$$

and

$$\frac{\mathrm{d}n^{\mathrm{aq}}_{\mathrm{Ep}}}{\mathrm{d}t} = J^{\mathrm{aq}}_{\mathrm{Ep}}aV - R^{\mathrm{aq}}_{\mathrm{AA}}V \qquad (10)$$

where, in each phase:

$$R^{\mathrm{L}}_{\mathrm{AA}} = k^{\mathrm{L}}_{R_{\mathrm{AA}}}\phi_{\mathrm{L}}([\mathrm{AA}]^{\mathrm{L}})^2[\mathrm{Ep}]^{\mathrm{L}} \qquad (11)$$

The set of five equations (Eqs. (7), (9), (10) and (11)—one for each phase) and five unknowns: $[\mathrm{Ep}]^{\mathrm{i,org}}$, $[\mathrm{Ep}]^{\mathrm{i,aq}}$, $[\mathrm{Ep}]^{\mathrm{aq}}$ $k^{\mathrm{org}}_{R_{\mathrm{AA}}}$ and $k^{\mathrm{aq}}_{R_{\mathrm{AA}}}$ fully describe the reacting system, but it is certainly preferable to uncouple both subsystems and obtain $k^{\mathrm{org}}_{R_{\mathrm{AA}}}$ separately.

3.2.1. Determination of the reaction rate constant in the organic phase

Glacial acetic acid was used to study the ring-opening reaction in the organic phase, within the same range of temperature (60–80 °C) and acetic acid concentration (4, 8, 12 and 14 M) as in the complete, heterogeneous system. In the organic phase, the degradation of the epoxide group follows the general expression:

$$R^{\mathrm{org}}_{\mathrm{AA}} = k^{\mathrm{org}}_{\mathrm{AA}}([\mathrm{AA}]^{\mathrm{org}})^{\alpha}([\mathrm{Ep}]^{\mathrm{org}})^{\beta} \qquad (12)$$

As acetic acid is in large excess in the system the reaction can be considered as zero-order with respect to the carboxylic acid, so that in the well-stirred, isothemal batch reactor the mass balance of the epoxide groups becomes:

$$\frac{\mathrm{d}[\mathrm{Ep}]^{\mathrm{org}}}{\mathrm{d}t} = -k^{\mathrm{org}}_{\mathrm{obs}_{\mathrm{AA}}}([\mathrm{Ep}]^{\mathrm{org}})^{\beta} \qquad (13)$$

where

$$k^{\mathrm{org}}_{\mathrm{obs}_{\mathrm{AA}}} = k^{\mathrm{org}}_{R_{\mathrm{AA}}}([\mathrm{AA}]^{\mathrm{org,o}})^{\alpha} \qquad (14)$$

By linearizing Eq. (14), the reaction was found to be second order with respect to acetic acid (Fig. 4b), in agreement with literature data [2,4,5]. The order of reaction with respect to the epoxide group was one (Fig. 4a). The calculated value of the activation energy was 16.52 ± 1.09 kcal/mol, which verifies Zaher et al.'s [4] reported data.

3.2.2. Determination of the reaction rate constant in the aqueous phase (no catalyst added)

To determine the reaction rate constant in the aqueous phase ($k^{\mathrm{aq}}_{R_{\mathrm{AA}}}$) using solvated acetic acid, a test of hypotheses was made considering three possible cases: slow regime, fast regime and instantaneous reaction.

Prior to this, the values of the reaction rate constant in the organic phase ($k^{\mathrm{org}}_{R_{\mathrm{AA}}}$) were used to verify whether the regime under which the ring-opening reaction in the organic phase proceeds is indeed slow. Table 6 shows that for the full range of process conditions the Hatta numbers are less than 0.3, which implies that the attack with acetic phase in that phase is always sluggish.

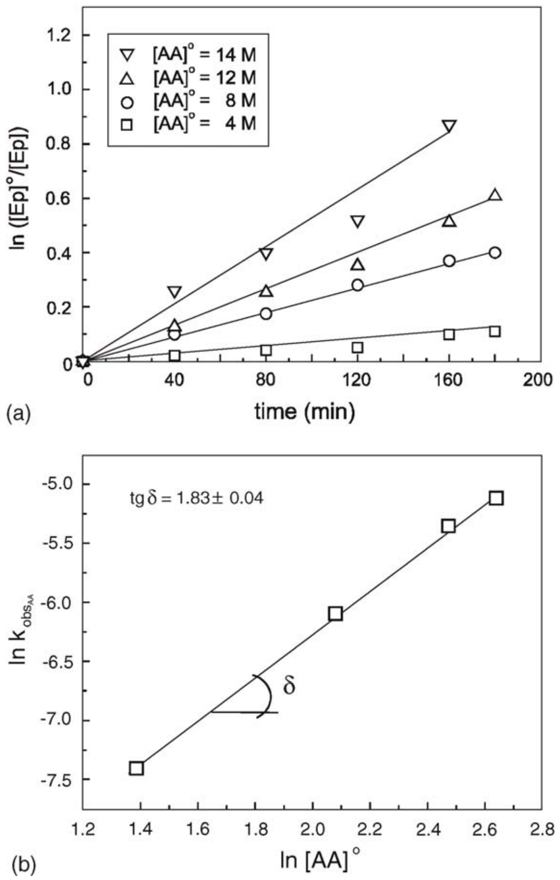

Fig. 4. (a) Effect of the concentration of (glacial) acetic acid (initial molarity of AA; mol AA/l of *total* volume of the reacting system) on the oxirane ring-opening reaction of epoxidized soybean oil (ESBO) in the organic (oil) phase (1500 rpm; 70 °C) and (b) determination of the reaction order with respect to AA (via tg δ). No catalyst was added.

Now, considering *slow regime in both phases* as a first hypothesis to test, the system of equations describing the attack on the oxirane ring by acetic acid is, simply, the following:

$$\frac{\mathrm{d}n^{\mathrm{org}}_{\mathrm{Ep}}}{\mathrm{d}t} = -k^{\mathrm{org}}_{R_{\mathrm{AA}}}\phi_{\mathrm{org}}([\mathrm{AA}]^{\mathrm{org}})^2[\mathrm{Ep}]^{\mathrm{org}}V \qquad (15)$$

$$\frac{\mathrm{d}n^{\mathrm{aq}}_{\mathrm{Ep}}}{\mathrm{d}t} = -k^{\mathrm{aq}}_{R_{\mathrm{AA}}}\phi_{\mathrm{aq}}([\mathrm{AA}]^{\mathrm{aq}})^2[\mathrm{Ep}]^{\mathrm{aq}}V \qquad (16)$$

Then, considering the total reaction rate of the epoxide groups ($R = R^{\mathrm{org}} + R^{\mathrm{aq}} = \mathrm{d}n^{\mathrm{org}}_{\mathrm{Ep}}/\mathrm{d}t + \mathrm{d}n^{\mathrm{aq}}_{\mathrm{Ep}}/\mathrm{d}t$) and introducing the distribution constants (m_{Ep} and m_{AA}), one gets:

$$\frac{\mathrm{d}[\mathrm{Ep}]^{\mathrm{org}}}{\mathrm{d}t} = -k_{R_{\mathrm{obs}}}[\mathrm{Ep}]^{\mathrm{org}} \qquad (17)$$

where

$$k_{R_{\mathrm{obs}}} = \left\{\frac{k^{\mathrm{org}}_{R_{\mathrm{AA}}}\phi_{\mathrm{org}}}{(m_{\mathrm{AA}})^2} + k^{\mathrm{aq}}_{R_{\mathrm{AA}}}\phi_{\mathrm{aq}}m_{\mathrm{Ep}}\right\}\frac{V([\mathrm{AA}]^{\mathrm{aq,o}})^2}{V_{\mathrm{org}} + V_{\mathrm{aq}}m_{\mathrm{Ep}}} \qquad (18)$$

Table 6 contains selected values of the calculated reaction rate constants, assuming the complete liquid–liquid system in

Table 6
Reaction rate constants for the oxirane ring opening with solvated acetic acid in the organic (oil) and aqueous phases, considering slow reaction regime in both phases[a]

T (°C)	pH	$[\mathrm{AA}]^{\mathrm{t,o}}$ (M)[b]	$[\mathrm{AA}]^{\mathrm{aq,o}}$ (M)[b]	$k_{R_{\mathrm{AA}}}^{\mathrm{org}}$ ($\times 10^5$ $\mathrm{l^2/(mol^2\ min)}$)	$\mathrm{Ha}^{\mathrm{org}}$ ($\times 10^4$)[c]	$k_{R_{\mathrm{AA}}}^{\mathrm{aq}}$ ($\mathrm{l^2/(mol^2\ min^1)}$)	$\mathrm{Ha}^{\mathrm{aq}}$ [d]
60	5	15	13.1	1.36	2.12	0.211	0.57
70	5	15	13.1	2.81	2.81	0.382	0.69
80	5	15	13.1	5.21	4.60	0.682	0.84
70	5	17	14.9	2.81	3.54	0.398	0.81
70	5	9	9.89	2.81	2.20	0.385	0.57
70	5	5	4.38	2.81	1.64	0.389	0.31

Validation via the Hatta number.

[a] Organic to polar (oil/aqueous) phases volumetric ratio = 15/25 (v/v); stirring rate = 1500 rpm.

[b] Initial molarity of acetic acid (AA) in the aqueous phase; $[\mathrm{AA}]^{\mathrm{aq,o}}$ = mol AA/l of aqueous phase, calculated using the following equation: $[\mathrm{AA}]^{\mathrm{t,o}} = [\mathrm{AA}]^{\mathrm{aq,o}} + [\mathrm{AA}]^{\mathrm{org,o}} = [\mathrm{AA}]^{\mathrm{aq,o}}(1 + m_{\mathrm{AA}})/m_{\mathrm{AA}}$.

[c] $\mathrm{Ha}^{\mathrm{org}} = (k_{\mathrm{d}})^{-1}\{(2/3)k_{R_{\mathrm{AA}}}^{\mathrm{org}} D_{\mathrm{AA}}(m_{\mathrm{AA}}^{-1}[\mathrm{AA}]^{\mathrm{aq,o}})[\mathrm{Ep}]^{\mathrm{org,o}}\}^{0.5}$.

[d] $\mathrm{Ha}^{\mathrm{aq}} = (k_{\mathrm{c}})^{-1}[Dk_{R_{\mathrm{AA}}}^{\mathrm{aq}}([\mathrm{AA}]^{\mathrm{aq,o}})^2]^{0.5}$.

slow regime, in both phases, together with the respective Hatta numbers. It can readily be appreciated that, even in the absence of any acidic catalyst, the Hatta number in the aqueous phase somewhat exceeds (albeit slightly) the upper boundary under which a slow reaction regime is granted ($\mathrm{Ha} < 0.3$).

With the second hypothesis: *slow regime in the organic phase and fast in the aqueous* one, and equating the Hatta number with the enhancement factor (E), one gets the following expression for the mass balance in aqueous phase:

$$\frac{\mathrm{d}n_{\mathrm{Ep}}^{\mathrm{aq}}}{\mathrm{d}t} = -a[k_{R_{\mathrm{AA}}}^{\mathrm{aq}} D]^{0.5}[\mathrm{AA}]^{\mathrm{aq}}[\mathrm{Ep}]^{\mathrm{i,aq}}V \tag{19}$$

As Eq. (15) maintains its validity for the organic phase, and considering again that $R = \mathrm{d}n_{\mathrm{Ep}}^{\mathrm{org}}/\mathrm{d}t + \mathrm{d}n_{\mathrm{Ep}}^{\mathrm{aq}}/\mathrm{d}t$, with the respective values of m_{Ep} (Eq. (7)) and m_{AA} (=$[\mathrm{AA}]^{\mathrm{i,aq}}/[\mathrm{AA}]^{\mathrm{i,org}}$), the system of equation reduces to Eq. (17) where, in this case:

$$k_{R_{\mathrm{obs}}} = \left\{\frac{k_{R_{\mathrm{AA}}}^{\mathrm{org}}\phi_{\mathrm{org}}[\mathrm{AA}]^{\mathrm{aq,o}}}{(m_{\mathrm{AA}})^2} + a[k_{R_{\mathrm{AA}}}^{\mathrm{aq}} D]^{0.5} m_{\mathrm{Ep}}\right\}\frac{V[\mathrm{AA}]^{\mathrm{aq,o}}}{V_{\mathrm{org}} + V_{\mathrm{aq}} m_{\mathrm{Ep}}} \tag{20}$$

With the values of $k_{R_{\mathrm{AA}}}^{\mathrm{aq}}$ given by Eq. (20), new values of the Hatta number in the aqueous phase were obtained. As shown in Table 7, these values were between 32 and 283, which indicates that the reaction between the solvated acetic acid and the epoxide groups is in the fast regime in the polar phase, even though no sulfuric acid was added to the reacting media.

For completion purposes, the third hypothesis (*slow regime in the organic phase and instantaneous in the aqueous phase*) will be analyzed as well. In the particular case of an instantaneous reaction that is first order with respect to the compound that diffuses from the organic phase, the Hatta number is equal to the maximum enhancement factor (E_∞), whichever the order of reaction of the other reactant is [13,17]. Therefore, the expressions used to describe the second scenario, fast regime in the aqueous phase and slow in the organic one, also hold here.

For an instantaneous reaction the E_∞ ($\cong \mathrm{Ha}^{\mathrm{aq}}$) would be of about 10^3–10^4, in which case the reaction zone would become reduced to a reaction plane located inside the aqueous phase film near the liquid–liquid interface. Clearly, this is not compatible with our calculated Hatta numbers.

Table 7
Reaction rate constants for the oxirane ring opening with solvated acetic acid in the organic (oil) and aqueous phases, considering slow reaction regime in the former and fast reaction regime in the latter phase[a]

T (°C)	pH	$[\mathrm{AA}]^{\mathrm{t,o}}$ (M)[b]	$[\mathrm{AA}]^{\mathrm{aq,o}}$ (M)[b]	$k_{R_{\mathrm{AA}}}^{\mathrm{org}}$ ($\times 10^5$ $\mathrm{l^2/(mol^2\ min)}$)	$\mathrm{Ha}^{\mathrm{org}}$ ($\times 10^4$)[c]	$k_{R_{\mathrm{AA}}}^{\mathrm{aq}}$ ($\mathrm{l^2/(mol^2\ min)}$)	$\mathrm{Ha}^{\mathrm{aq}}$ [d]
60	5	15	13.1	1.36	2.11	9.84×10^3	123
70	5	15	13.1	2.81	2.84	2.48×10^4	176
80	5	15	13.1	5.21	4.61	7.89×10^4	283
70	5	17	14.9	2.81	3.53	2.69×10^4	208
70	5	9	9.89	2.81	2.20	2.50×10^4	146
70	5	5	4.38	2.81	1.61	2.52×10^4	32
70	3.4[e]	15	13.1	2.81	2.84	1.19×10^{11}	2.73×10^6
70	3[e]	15	13.1	2.81	2.82	4.26×10^{12}	1.58×10^7

Validation via the Hatta number.

[a] Organic to polar (oil/aqueous) phases volumetric ratio = 15/25 (v/v); stirring rate = 1500 rpm.

[b] Initial molarity of acetic acid (AA) in the aqueous phase; $[\mathrm{AA}]^{\mathrm{aq,o}}$ = mol AA/l of aqueous phase, calculated using the following equation: $[\mathrm{AA}]^{\mathrm{t,o}} = [\mathrm{AA}]^{\mathrm{aq,o}} + [\mathrm{AA}]^{\mathrm{org,o}} = [\mathrm{AA}]^{\mathrm{aq,o}}(1 + m_{\mathrm{AA}})/m_{\mathrm{AA}}$.

[c] $\mathrm{Ha}^{\mathrm{org}} = (k_{\mathrm{d}})^{-1}\{(2/3)k_{R_{\mathrm{AA}}}^{\mathrm{org}} D_{\mathrm{AA}}(m_{\mathrm{AA}}^{-1}[\mathrm{AA}]^{\mathrm{aq,o}})[\mathrm{Ep}]^{\mathrm{org,o}}\}^{0.5}$.

[d] $\mathrm{Ha}^{\mathrm{aq}} = (k_{\mathrm{c}})^{-1}[Dk_{R_{\mathrm{AA}}}^{\mathrm{aq}}([\mathrm{AA}]^{\mathrm{aq,o}})^2]^{0.5}$.

[e] By adding H_2SO_4 (as homogeneous acid catalyst).

Summarizing, the experimental data indicate that the reaction regime in the aqueous phase when no catalyst is added is moderately over the upper limit usually established for slow reactions. In this regard, considering both phases in the slow regime, $k_{R_{\mathrm{obs}}}$ – as given by Eq. (18) – can be written as equal to:

$$k_{R_{\mathrm{obs}}} = (\varepsilon_{\mathrm{org}} + \varepsilon_{\mathrm{aq,slow}})([\mathrm{AA}]^{\mathrm{org,o}})^2 \tag{21}$$

As it can be appreciated in Fig. 5, where Eq. (21) was linearized, the fitting of the experimental data to Eq. (21) is highly satisfactory. So, for design purposes our reacting system can be assumed as practically in the slow regime altogether, if and when no catalyst is added.

With the values of $k_{R_{\mathrm{AA}}}^{\mathrm{aq}}$ for the different temperatures, the activation energy in the aqueous phase was also determined: $\mathrm{Ea}^{\mathrm{aq}} = 13.70 \pm 0.14$ kcal/mol.

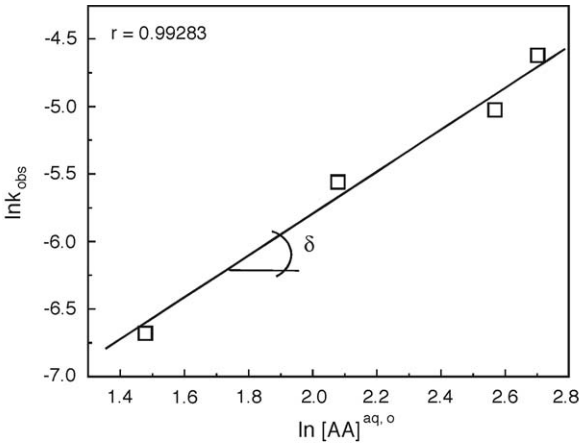

Fig. 5. $\ln k_{\mathrm{obs}}^{\mathrm{org}}$ vs. $\ln[\mathrm{AA}]^{\mathrm{aq,o}}$ in the oxirane ring opening of ESBO with solvated acetic acid (1500 rpm; 70 °C). No catalyst was added.

3.2.3. Determination of the reaction rate constant in the aqueous phase (acidic catalyst added)

To analyze this case in more detail, one must keep in mind that the acidic catalyst is present only in the aqueous phase and that, then, the rate of reaction in the organic phase does not change at lower pH. Moreover, as rightly pointed out by Szakács et al. [19], the reaction mechanism in each phase is different: In the organic phase the reaction involves the addition of acetic acid to the epoxide group via a hydrogen bond, whereas in the aqueous

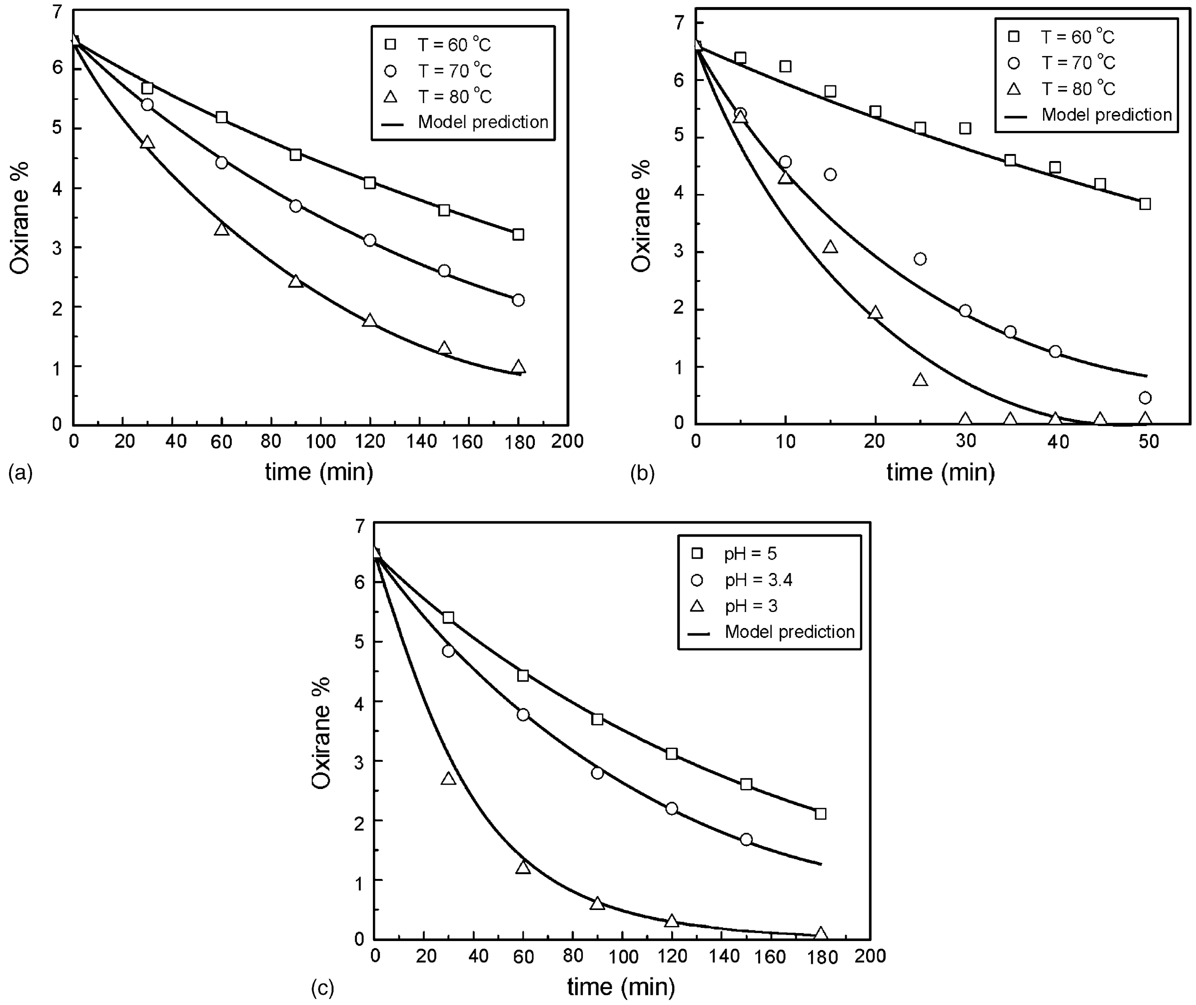

Fig. 6. Comparison between experimental data and model predictions in the oxirane ring opening of ESBO with (a) hydrogen peroxide ($[\mathrm{H_2O_2}]^{\mathrm{aq,o}} = 30$ wt%; pH 1), (b) solvated acetic acid ($[\mathrm{AA}]^{\mathrm{o}} = 12$ M; pH 5) and (c) solvated acetic acid ($[\mathrm{AA}]^{\mathrm{o}} = 12$ M; 70 °C) vs. pH. Volume ratio: 25/15; 1700 rpm. Full lines represent model predictions.

Table 8
Estimates of selected properties of some of the liquid–liquid reacting systems, at 70 °C (see Appendices A–C)

Liquid–liquid system	pH	D ($\times 10^5$ cm^2/s)[a]	d_{32} (mm)	a (m^2/m^3)[b]	k_c ($\times 10^5$ m/s)[c]	k_d ($\times 10^5$ m/s)[d]
ESBO–H_2O_2 30 wt%	–[e]	0.95	1.76[f]	1.28	6.50	0.35
	1[g]	1.25	1.67[h]	1.34	1.58	0.49
ESBO–solvated AA ($[AA]^{aq,o} = 15$ M)	–[e]	0.69	0.082[f]	12.6	4.15	5.94
	1[g]	0.71	0.077[h]	13.4	3.90	6.12

[a] Eq. (A.1).
[b] Eq. (B.1).
[c] Eqs. (C.3) and (C.4).
[d] Eq. (C.8).
[e] Without acidic catalyst addition.
[f] Eqs. (B.2) and (B.4).
[g] With catalyst addition (H_2SO_4; pH 1).
[h] Eqs. (B.2) and (B.3).

phase – where the protonic, dissociated acid is present – the mechanism is just similar to the hydrolysis of the oxirane ring [6].

Eq. (15) is, then, still valid for the reaction in the organic phase, while the aqueous phase is in the fast regime (where $E = \mathrm{Ha}$), so that:

$$\frac{\mathrm{d}n_{\mathrm{Ep}}^{\mathrm{aq}}}{\mathrm{d}t} = -a[(k_n^{\mathrm{aq}} + k_{R_{\mathrm{AA}}}^{\mathrm{aq}}[\mathrm{H}^+]^{\mathrm{aq}})D[\mathrm{AA}]^{\mathrm{aq}}]^{0.5}[\mathrm{Ep}]^{\mathrm{i,aq}}V \qquad (22)$$

As $k_{\mathrm{d_{Ep}}}/k_{\mathrm{c_{Ep}}}m_{\mathrm{Ep}}$ is much greater than 1, one can assume that $[\mathrm{Ep}]^{\mathrm{org}} \approx [\mathrm{Ep}]^{\mathrm{i,org}}$. Recalling that R ($=\mathrm{d}n_{\mathrm{Ep}}^{\mathrm{org}}/\mathrm{d}t + \mathrm{d}n_{\mathrm{Ep}}^{\mathrm{aq}}/\mathrm{d}t$) is the total rate of reaction of the epoxide groups in the system, using again the distribution constants (m_{Ep} and m_{AA}) and considering, besides, that $k_n^{\mathrm{aq}} \to 0$ [7], the complete mass balance can be cast into Eq. (17) where, for this case:

$$k_{R_{\mathrm{obs}}} = \left\{ \frac{k_{R_{\mathrm{AA}}}^{\mathrm{org}}\phi_{\mathrm{org}}([\mathrm{AA}]^{\mathrm{aq,o}})^2}{(m_{\mathrm{AA}})^2} + a[k_{R_{\mathrm{AA}}}^{\mathrm{aq}}D[\mathrm{H}^+]^{\mathrm{aq,o}}[\mathrm{AA}]^{\mathrm{aq,o}}]^{0.5} \right\} \frac{V}{V_{\mathrm{org}} + V_{\mathrm{aq}}m_{\mathrm{Ep}}} \qquad (23)$$

Table 7 displays the calculated values of the reaction rate constants, together with the corresponding Hatta numbers, for pHs equal to 3.4 and 3 (last two entries). These Hatta numbers are much higher than 10^4, which implies that in the presence of the homogenous, acid catalyst and even at moderate pH values, the reaction regime in the aqueous phase is instantaneous and takes place in a ‘reaction plane’ (actually, a spherical ‘reaction surface’) inside the aqueous liquid film which surrounds each organic droplet. Therefore, the degradation of the epoxide groups in the aqueous phase is severely mass-transfer controlled in this case.

Finally, Fig. 6 compares the experimental results and model predictions (employing Euler’s numeric method) in the oxirane ring opening of epoxidized soybean oil with H_2O_2 (aq) and solvated acetic acid, for the different temperatures and pHs used in this work. The proposed models adequately describe the concentration profile as a function of time in both cases.

4. Conclusions

The opening (degradation) of the oxirane ring of ESBO caused by hydrogen peroxide in the heterogeneous liquid–liquid reacting system: ESBO–H_2O_2 (aq), can be adequately modeled as a pseudo-homogeneous reaction, because such reaction is always slow (i.e., the calculated Hatta number calculated for the full range of typical industrial conditions is under 0.3).

Under typical reaction conditions, the attack on the ring by solvated acetic acid progresses in both phases, but is slow in the organic phase. If no catalyst is added, the attack is also slow in the aqueous phase, so that the degradation of the ESBO proceeds uniformly in the bulk of both phases. However, whenever a (homogeneous) acidic catalyst is employed the reaction progresses under the instantaneous regime in the polar phase and the overall process is entirely controlled by mass transfer.

The conventional – acid catalyzed – peracetic process requires a good degree of agitation, to maximize the contact between both phases and thus allow the peracetic acid to react inside the organic droplets. Yet, an excessive degree of mixing also brings about, inescapably, deletereous conditions that diminish the achievement of high yields (i.e., high oxirane numbers).

Acknowledgments

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Appendix A. Estimation of diffusion coefficients

The diffusion coefficients in the multicomponent liquid mixtures were estimated using the simple, semi-empirical model of Perkins and Geankoplis based on a modified version of the Wilke and Chang equation [20]:

$$D_{\mathrm{AM}} = \frac{F\mathrm{T}}{\mu_{\mathrm{M}}} \qquad (\mathrm{A.1})$$

$$F = \frac{4.67 \times 10^{-6}(\theta_{\mathrm{M}}M_{\mathrm{M}})^{0.5}}{V_{\mathrm{A}}^{0.6}} \qquad (\mathrm{A.2})$$

$$\theta_{\mathrm{M}} M_{\mathrm{M}} = \sum x_i \theta_i M_i \tag{A.3}$$

where D_{AM} is the diffusion coefficient of solute A in the solvents mixture (cm^2/s), μ_{M} the viscosity of the mixture (cP), θ_{M} the association factor of the mixture, M_{M} the mean molecular mass of the mixture (g/mol), V_{A} the molar volume of solute A at its normal boiling point (m^3/mol), T the absolute temperature (K), x_i the molar fraction of solvent i, θ_i the association factor of solvent i and M_i is the molecular mass of solvent i (g/mol).

Selected values of some of the estimated values of the diffusion coefficients (calculated at 70 °C, as a way of example) are shown in Table 8.

Appendix B. Estimation of interfacial area

The interfacial area was calculated using the following expression [17,21,22]:

$$a = \frac{6\phi_d}{d_{32}} \tag{B.1}$$

where d_{32} is the Sauter mean diameter (m), with value equal to $(\sum n_i d_i^3)/(\sum n_i d_i^2)$, and n_i represents the number of drops with diameter d_i.

The equation used to estimate d_{32} was the following [17]:

$$\frac{d_{32}}{D_{\mathrm{a}}} = \frac{A f(\phi_{\mathrm{d}})}{We^{0.6}} \tag{B.2}$$

where D_{a} is the stirrer diameter (m), We the Weber number $(\rho_{\mathrm{c}} n_{\mathrm{a}}^2 D_{\mathrm{a}}^3/\sigma)$, n_{a} the stirring velocity (1/s), ρ_{c} the continuous phase density (kg/m^3), σ the surface tension (N/m) and A is a parameter whose value ranges between 0.04 and 0.4. The function $f(\phi_{\mathrm{d}})$ can be represented in two ways, both of which account for re-dispersion and coalescence effects. A linear function, for instance, gives:

$$f(\phi_{\mathrm{d}}) = 1 + B\phi_{\mathrm{d}} \tag{B.3}$$

where B is a constant between 2 and 9 for redispersions in which $\phi_{\mathrm{d}} < 0.2$ [17,22]. As indicated by Delichatsios and Probstein [23], when $\phi_{\mathrm{d}} > 0.3$ Eq. (B.3) is no longer valid, and therefore another function must be used. These authors have recommended, instead, the following:

$$f(\phi_{\mathrm{d}}) = \left(\frac{\ln(c_2 + c_3\phi_{\mathrm{d}})}{\ln c_2}\right)^{-3/5} \tag{B.4}$$

where c_2 (=0.011) and c_3 are constants. The latter constant is proportional to the ratio between the coalescence and dispersion coefficients, whose value must be empirically determined, and differs from one system to another (such value is always close to 1.0).

Even though our experimental device had a two-blade stirrer ($D_{\mathrm{a}} = 10$ cm), our calculations of d_{32} were made using the former authors' data (where a 4 cm turbine was used instead), because for this small-reactor scale no significant differences in performance exist among stirrers [6,7]. According to this, then, the power number in our particular case is equal to 5. Eq. (B.2) was used to estimate the Sauter mean diameter. The linear function given by Eq. (B.3) was used for the ESBO–solvated acetic acid system, and Eq. (B.4) for the rest (ESBO–hydrogen peroxide and ESBO–water). Using these d_{32} values the interfacial areas were determined, in turn, through Eq. (B.1). Table 8 shows selected values of the Sauter mean diameters and interfacial areas at 70 °C, as a way of example.

Appendix C. Estimation of mass transfer coefficients in the liquid–liquid systems

Numerous correlations are available in the literature to estimate mass transfer coefficients of the continuous (k_{c}) and the disperse (k_{d}) liquid phases. The overall mass transfer coefficients, based either on the continuous or the disperse phases, respectively, can be written as [13,17]:

$$\frac{1}{k_{\text{overall c}}} = \frac{m}{k_{\mathrm{d}}} + \frac{1}{k_{\mathrm{c}}} \tag{C.1}$$

$$\frac{1}{k_{\text{overall d}}} = \frac{m}{k_{\mathrm{d}}} + \frac{1}{m k_{\mathrm{c}}} \tag{C.2}$$

The order of magnitude of the individual coefficients in both phases in well-mixed liquid–liquid dispersions (k_{c} and k_{d}) for the case of mass transfer without chemical reaction is in the 10^{-4} and 10^{-5} m/s range.

C.1. Mass transfer coefficients in the continuous phase

The correlation of Calderbank and Moo-Young [17,24] was used in this work:

$$k_{\mathrm{c}} = 0.13\left(\frac{P\mu_{\mathrm{c}}}{V_{\mathrm{c}}\rho_{\mathrm{c}}^2}\right)^{0.25}\left(\frac{\mu_{\mathrm{c}}}{\rho_{\mathrm{c}} D_{\mathrm{a}}}\right)^{-0.67} \tag{C.3}$$

$$P = \psi \rho_{\mathrm{m}} n_{\mathrm{a}}^3 D_{\mathrm{a}}^5 \tag{C.4}$$

where P is the power dissipated by the agitator (kg/(s^3 m^2)), μ_{c} the viscosity of the continuous phase ((N s)/m) and ψ is the power number.

The values of dissipated power (Eq. (C.4)) and the mass transfer coefficients in the continuous phase (Eq. (C.3)) for the different liquid–liquid systems were calculated using $\psi = 5$ for each temperature. Selected values of these parameters are shown in Table 8.

C.2. Mass transfer coefficients in the disperse phase

The value of the mass transfer coefficient in the disperse phase depends on the drop behavior; mostly upon whether the drop can be considered as a rigid particle or not [17]. To be able to evaluate the latter, the diameter number (d^*) must be calculated [22]:

$$d^* = d_{32}\left(\frac{\mu_{\mathrm{c}}^2}{\rho_{\mathrm{c}} g\,\Delta\rho}\right)^{-1/3} \tag{C.5}$$

where d^* must be less than 10 for the drops to be considered as rigid spheres.

For a rigid sphere, Treybal [25] gives the following relationships:

$$N_{\mathrm{Sh}} = \frac{2\pi^2}{3} \tag{C.6}$$

$$N_{\mathrm{Sh}} = \frac{k_{\mathrm{d}} d_{32}}{D_{\mathrm{a}}} \tag{C.7}$$

Considering both, Eqs. (C.6) and (C.7):

$$k_{\mathrm{d}} = \frac{2\pi^2 D_{\mathrm{a}}}{3 d_{32}} \tag{C.8}$$

As the calculated values of d^* were less than 10, the organic phase drops can be taken as rigid spheres. Thus, k_{d} values were calculated using Eq. (C.8) (see Table 8).

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