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High yield epoxidation of fatty acid methyl esters with performic acid generated *in situ*

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ABSTRACT

The impact of the relevant process variables on the reaction of soybean oil fatty acid methyl esters with performic acid (PFA) generated *in situ* using concentrated hydrogen peroxide (up to 60 wt%), to produce an epoxidized product in high yield, is studied in detail. The degree of mixing, temperature, concentration and molar ratios of reactants and/or use of a diluent were considered.

Temperature increases are significantly detrimental for achieving high oxirane numbers, as the selectivity to ring-opening reactions increases. Higher concentrations of either formic acid or H_2O_2 are also harmful (particularly, the carboxylic acid) but much less than temperature.

A proposed alternative process, employing moderate temperature (up to 40 °C) and concentrated H_2O_2, compares favourably with the conventional one; higher conversion combined with high epoxide productivity *and* selectivity are attainable.

Using economically sound reactants molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are well dispersed, the epoxidation process can be adequately described using an (equilibrated) two-phase reaction model. The model accounts for both the reversible peracid formation (in the aqueous phase) and the epoxidation reaction proper, together with the attacks on the epoxide ring by formic acid and performic acid (in the organic phase).

1. Introduction

In recent years, a worldwide interest in renewable resources from the biomass has spurred the manufacture of biodiesel as a more benign fuel, capable of lower environmental impact. Pure or 'neat' biodiesel possesses negligibly low sulphur content, shows an excellent lubricity which extends the lifespan of the engines, is non-toxic and fully biodegradable. It is customarily produced by transesterification of the vegetable oil triglycerides of large-scale crops (e.g., soybean, palm, canola, etc.) with an aliphatic alcohol, usually methanol, employing sodium methoxide (or hydroxide) as homogeneous catalyst. The resulting product is referred to as fatty acid methyl ester (FAME) in the industrial and trade communities.

Thus, FAMEs have become widely available commodities which, in view of the stringent requirements of the automobile industry, are produced with great purity. This, in turn, has reopened new avenues to oleochemicals synthesis. One of these alternatives involves transforming the double bonds of the fatty acid molecules into oxirane (epoxide) groups. Epoxides have a high commercial importance and are widely utilized in plastics manufacture, lubricants, detergents and – more recently – as intermediates in chemical reactions [1–5].

Vegetable oils epoxidation can be economically accomplished by reacting the double bonds of FAMEs with a peracid (generally peracetic acid), generated for safety reasons *in situ* using hydrogen peroxide. The process usually requires employing an acidic catalyst and, even though traditionally mineral acid have been used due to their lower cost, their utilization prevents the achievement of high yields, because of the opening of the oxirane ring during the course of the main reaction [1,2,6–10].

A possible solution involves using a heterogeneous catalyst, such as ion exchange resins [10,11]. Likewise, amorphous Ti/SiO_2, rhenium or tungsten-based catalysts have been tried, with high yields and/or selectivity [12,13]. Presently, though, all these catalysts are extremely expensive and, so, unsuitable for large-scale commodity manufacturing. An alternative process would use performic acid (PFA) instead of peracetic acid (PAA), as no catalyst is needed to generate the former *in situ* [14–16] and, therefore, the parallel degradation reactions could be –in principle – minimized.

Some kinetic studies concerning the epoxidation of several vegetable oils, and of palm oil FAME as well, with PAA and PFA

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Nomenclature

IV	iodine value
$[j]^{L}$	concentration of compound *j* in the L phase (mol/l)
k	kinetic rate constant (l/(mol s)) or (l^2/(mol^2 s))
m_j	distribution constant of compound *j*
MW	molecular weight
n_j^{L}	total number of moles of compound *j* in the L phase (mol)
R	global observable conversion rate (mol/(l s))
S	selectivity
V	total reactor volume (m^3)
V_L	volume of the L phase (m^3)
X	conversion
%Ox	theoretical %Oxirane oxygen
Greek symbol	
ϕ	volume fraction
Subscripts and superscripts	
aq	aqueous phase
C=C	unsaturated group
Ep	epoxide group
FA	formic acid
i	FA or PFA
L	generic L phase
org	organic phase
PFA	performic acid
0	initial value

generated *in situ* under homogeneous catalytic conditions, have been carried out in the last years [2,4,5]. These models were pseudohomogeneous (*i.e.*, did not consider the presence of two immiscible phases) but nevertheless they established that the rate-determining step in the epoxidation is always the peracid generation. On the other hand, Rangarajan et al. were able to find the kinetic parameters of the reaction under about the same reaction conditions, but considering a two-phase liquid–liquid reacting system instead [1].

Further work, addressed to obtaining high oxirane values from feedstocks such as soybean or linseed FAMEs, in high throughput process units, needs to be done. In this study we have chosen soybean FAME to analyze in detail the epoxidation reaction network when performic acid is used as oxygen carrier and concentrated hydrogen peroxide (up to 60 wt% H_2O_2) is employed. The epoxidation reaction and the parallel, deleterious reactions linked to the oxirane ring opening, are depicted in Figs. 1 and 2, respectively. The influence of several process variables (viz., degree of mixing, temperature, mol ratio of FAME double bonds/hydrogen peroxide/formic acid and solvent addition) on the system was studied, seeking reaction conditions capable of achieving high epoxide yields. In particular, also, the relevant kinetic rate constants pertaining to this heterogeneous liquid–liquid reacting system were found.

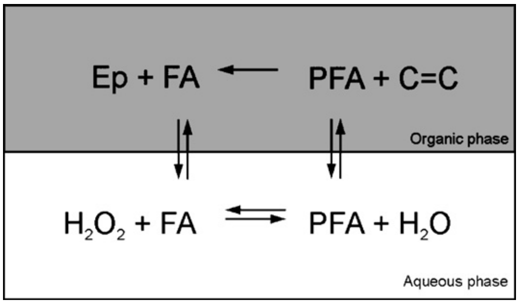

Fig. 1. Double bonds epoxidation reaction in the organic phase, with performic acid (PFA) generated in the aqueous (polar) phase from hydrogen peroxide. The organic acids, PFA and formic acid (FA) 'shuttle' between both liquid phases.

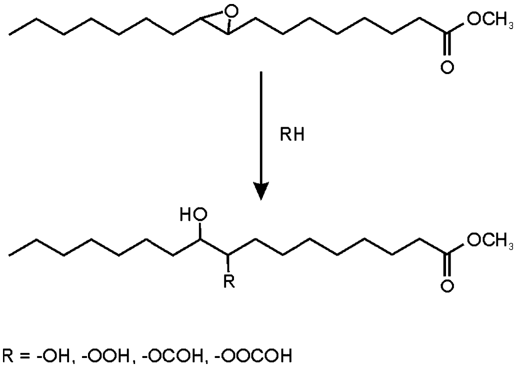

Fig. 2. Main degradation reactions of the oxirane ring.

2. Experimental

2.1. Materials

Edible, refined soybean oil (Sojola brand, Aceitera General Deheza S.A., Arg.) was used for the production of the FAME stock. Formic acid (99.81%), methanol, benzene and sodium hydroxide were acs grade and purchased from Fisher Scientific (Pittsburg, PA). Hydrogen peroxide (60 wt%) was supplied by Atanor S.A., a local vendor. Water was doubly distilled (DD) and deionized.

2.2. Preparation of soybean FAME stocks

Batches of the refined soybean oil were interesterified with methanol in a 1000 ml glass reactor furnished with a reflux condenser, at 70 °C. The oil (700 ml) was first heated to the reaction temperature and, next, 270 ml of methanol and 8.28 g of NaOH were added, under moderate stirring. The mixture was so kept for 1 h, after which the agitation was stopped to allow for phase separation (30 min). The heavier, glycerol-rich fraction was discarded and, then, the soybean FAME was washed with 100 ml H_3PO_4 0.015N at 60 °C. After another three washes with distilled water (100 ml each) at same temperature, the soybean FAME was dried in a rotary evaporator at 10 mmHg and 60 °C, for 3 h.

2.3. Epoxidation of soybean FAME with performic acid generated *in situ*

The reaction was studied in an isothermal, mechanically stirred cylindrical glass reactor (600 ml) provided with a four-blade teflon turbine placed next to the vessel bottom and three teflon baffles on the sides. An internal 316 stainless steel coil allowed refrigerating the reaction mixture and a heating mantle was attached to the temperature controller. A reflux condenser completed the set-up.

About 0.3–0.5 moles of formic acid per mole of double bonds of the FAME were placed into the reactor and heated to the reaction temperature, under agitation. Afterwards, 1.1, 2 or 5 mol of H_2O_2 (~60 or ~30 wt%) were added, drop by drop (1 h in total) and the reaction mixture was held, at constant temperature and under stirring, for several hours (Table 1). Periodically, samples were taken from the reactor; the aqueous phase was eliminated and the organic

Table 1

Reaction conditions and final iodine values (IV_{final}), unsaturation conversion, percent oxirane oxygen ($\%Ox_{final}$), yield ($\%Y_{final}$) and selectivity (S_{final}) in the epoxidation of soybean FAME with performic acid generated *in situ* from formic acid and hydrogen peroxide

Run	Molar ratios C═C/H_2O_2/FA	T (°C)	Stirring (rpm)	$[H_2O_2]^{aq,0}$ (wt%)	Total duration (min)	IV_{final}	X_{final}[a]	$\%Ox_{final}$	$\%Y_{final}$[b]	S_{final}[c]
Ep-1	1/1.1/0.5	57	1400	59	690	4.7	96.3	3.87	51.8	0.54
Ep-2	1/1.1/0.5	57	350	59	690	7.5	94.2	4.19	56.1	0.59
Ep-3	1/1.1/0.5	40	350	59	690	15.5	87.8	5.71	76.4	0.87
Ep-4	1/1.1/0.5	60	350	35	690	57.2	55.3	3.58	47.9	0.87
Ep-5	1/2.0/0.5	40	350	59	690	4.22	96.7	6.24	83.5	0.86
Ep-6	1/1.1/0.3	40	350	59	690	24.5	80.8	5.55	74.3	0.92
Ep-7	1/5.0/0.3	40	350	59	690	11.1	91.3	5.99	80.2	0.88
Ep-8[d]	1/0.9/0.5	40	350	59	690	44.2	65.5	4.11	55.0	0.84
Ep-9[d]	1/1.1/0.5	40	350	59	690	32.1	74.9	4.74	63.4	0.85
Ep-10[d]	1/1.1/0.3	40	350	59	690	51.1	60.1	3.77	50.5	0.84
Ep-11	1/2.0/0.3	40	350	59	690	19.0	85.1	5.75	77.0	0.90
Ep-12	1/5.0/0.3	40	1000	59	540	5.46	95.7	5.99	80.3	0.84

[a] Percent conversion of double bonds calculated as $X = [(IV^0 - IV)/IV^0] \times 100$. The initial iodine value (IV^0) was 129.6.

[b] Percent oxirane oxygen yield = $[(\%Ox)/(\%Ox_t)] \times 100$, where $\%Ox_t$ represents the theoretical %Oxirane for IV^0: $\%Ox_t = \{(IV^0/MW_{I_2})/[100 + (IV^0/MW_{I_2})MW_O]\}MW_O \times 100 = 7.4$.

[c] Oxirane oxygen selectivity = $[(\%Ox)/(\%Ox_t)] \times [IV^0/(IV^0 - IV)]$.

[d] Organic solvent (heptane) added; molar ratio C═C/heptane = 1/2. See text for details.

phase was then thoroughly washed to eliminate acidity and dried, using a rotary evaporator, prior to their derivatization and chemical analysis.

After reaction completion the remaining mixture was washed with a solution of sodium bicarbonate (5 wt%), next with water until complete elimination of acidity in the organic phase and, last, with NaCl (5 wt%). The final product was then dried in a rotary evaporator.

2.4. Oxirane ring-opening studies

For these studies the soybean FAME was epoxidized in depth at low temperature (20–40 °C) with PFA generated *in situ*, using benzene as diluent of the organic phase (C═C/benzene molar ratio = 1/5) to minimize ring opening [2]. To this end, the chosen molar ratio of FAME double bonds/hydrogen peroxide/formic acid was 1/20/2. The soybean FAME, benzene and formic acid were jointly placed into the reactor and then dilute H_2O_2 (30 wt%) was added dropwise, at 20 °C. The reactor temperature was then slowly raised to 40 °C, to complete the reaction (>20 h). The mixture was next washed with distilled water until complete elimination of PFA and FA from the organic phase was achieved, and then with NaCl (5 wt%). Finally, water and benzene were separated from the epoxidized FAME (epFAME) in the rotary evaporator.

The stock of epFAME was used to study the degradation of the oxirane ring by formic acid dissolved in the organic phase and by FA/water and FA/aqueous hydrogen peroxide in the two-phase aqueous/organic mixtures, at 40 °C (Table 2). The epFAME was placed in a three-bore round-bottom flask, furnished with a reflux condenser and a mechanical stirrer. The flask, containing the epFAME, was heated to the desired working temperature in a thermostatized bath. Next, suitable volumes of the reactants, each of them previously thermostatized to the reaction temperature, were added to the reactor. Periodically, 5 ml samples were extracted, placed into a separatory funnel, and washed until complete elimination of acidity was achieved, in same manner as in the epoxidation process. The samples were then dried under reduced pressure in the rotary evaporator.

2.5. Distribution constants of formic acid

The distribution constant, or – more appropriately – the equilibrium molar ratio of formic acid in the aqueous (polar) and organic (soybean FAME) phases, was determined at 40 °C.

Thus, different amounts of FA, water and FAME were placed into a round-bottom flask, equipped with a reflux condenser and a mechanical stirrer (see Table 3). The set-up was immersed in a thermostatized bath; the mixtures were then stirred (1000 rpm) for 3 h and later left to stand (still at 40 °C) for another 3 h, after which the sample was centrifuged at 10,000 rpm for 10 min. A portion of the aqueous phase was then carefully separated using a syringe and a 0.2-μm teflon filter, to retain any traces of the disperse organic phase.

2.6. Analyses and data processing

The stock of soybean FAME was analyzed to check its water content, by Karl Fisher (Schott TitroLine alpha) and the final concentration of glycerol, mono-, di- and triglycerides by GLC [17], using a Shimadzu GC-17ATF unit and an Agilent column: DB-5HT 15 m, 0.32 mm, and 0.10 μm. Iodine and acid values, as well as fatty acid composition of the FAME were evaluated using AOCS recom-

Table 2

Reaction conditions and percent oxirane oxygen conversion in the study of the degradation of epoxidized soybean FAME (epFAME)

Run	Attacking reactants	Molar ratios	T (°C)	Stirring (rpm)	Total duration (min)	$\%Ox_{final}$	Final oxirane conversion[a]
Deg-1	Formic acid (FA)	epFAME/FA = 1/0.3	40	350	180	5.34	7.11
Deg-2	FA	epFAME/FA = 1/0.5	40	350	180	5.23	7.83
Deg-3	FA, H_2O	epFAME/H_2O/FA = 1/1.1/0.3	40	350	180	5.27	7.78
Deg-4	FA, H_2O	epFAME/H_2O/FA = 1/1.1/0.5	40	350	180	5.17	8.97
Deg-5	FA, H_2O_2[b]	epFAME/H_2O_2/FA = 1/1.1/0.3	40	350	180	4.96	12.4
Deg-6	FA, H_2O_2[b]	epFAME/H_2O_2/FA = 1/2.0/0.3	40	350	180	4.78	17.4
Deg-7	FA, H_2O_2[b]	epFAME/H_2O_2/FA = 1/5.0/0.3	40	350	180	4.60	20.5
Deg-8	FA, H_2O_2[b]	epFAME/H_2O_2/FA = 1/2.0/0.5	40	350	180	4.30	24.0
Deg-9	FA, H_2O_2[b]	epFAME/H_2O_2/FA = 1/2.0/1	40	350	180	3.19	43.7

[a] Oxirane oxygen conversion = $[(\%Ox^0 - \%Ox)/\%Ox^0] \times 100$. The initial percent oxirane oxygen ($\%Ox^0$) was 6.7.

[b] Aqueous H_2O_2 (59 wt%) was employed. Performic acid was preformed, following Yadav et al. [22] technique. See text for details.

Table 3
Distribution constant of formic acid (m_{FA}) between the organic (soybean FAME) and the aqueous (distilled water) phases, at 40 °C

Protocol	Weight (g)			Molar ratios C=C/H_2O/FA	$[FA]^{org}$ (wt%)	$[FA]^{aq}$ (wt%)	m_{FA}[a] ($[FA]^{org}/[FA]^{aq}$)	m_{FA}[b]
	FAME	H_2O	FA					
DC-1	41.22	41.46	4.52	1/10.9/0.5	0.0029	0.097	0.030	0.031
DC-2	50.15	29.02	6.00	1/6.3/0.5	0.0150	0.42	0.036	0.037
DC-3	56.93	19.49	6.99	1/3.7/0.5	0.0076	0.24	0.032	0.031
DC-4	33.59	49.28	2.50	1/15.9/0.3	0.0013	0.047	0.028	0.033
DC-5	57.97	18.79	13.92	1/3.5/1.0	0.015	0.41	0.037	0.038
DC-6	39.88	40.53	7.93	1/11.0/0.8	0.0049	0.16	0.031	0.029
DC-7	40.05	40.52	11.85	1/10.3/1.3	0.0070	0.22	0.032	0.031

[a] Experimental.
[b] Calculated employing UNIFAC ([24] and references therein).

Table 4
Characterization of the soybean FAME

$[H_2O]$[a]	160 ppm
Monoglycerides[b]	0.85 wt%
Diglycerides[b]	0.11 wt%
Triglycerides[b]	0.13 wt%
Acidity[c]	0.10 wt%
Iodine value[c]	129.59
C16:0 (palmitic)[c]	9.83 wt%
C18:0 (stearic)[c]	3.93 wt%
C18:1 (oleic)[c]	21.0 wt%
C18:2 (linoleic)[c]	57.7 wt%
C18:3 (linolenic)[c]	7.03 wt%
C20:0 (arachidic)[c]	0.32 wt%

[a] By Karl Fischer.
[b] By GLC analysis [17].
[c] Following AOCS' Official and Recommended Practices [18].

mended practices [18]. The characterization results are shown in Table 4.

The evolution of the epoxidation reaction was followed by measuring the iodine (IV) and percent oxirane oxygen (%Oxirane), also according to AOCS' official and recommended practices [18] using a PE-5 capillary column: 30 m, 0.53 mm, and 1.5 µm. Only the oxirane value was measured to follow the ring-opening reactions. Each of the reported values of IV or %Oxirane is the mean of three replicates; the coefficients of variation were always less than 9.5%.

The distribution constant of FA was calculated by volumetric titration, using NaOH in the aqueous phase and KOH in the organic phase [18]. The water content in FAME was determined by Karl Fisher.

The kinematic viscosity of the soybean FAME and its epoxide was measured at 40 ± 0.2 °C, following the ASTM D 445 norm, using a capillary viscosimeter (Cannon-Fenske, Germany) calibrated with the manufacturer's calibration fluids. Likewise, their viscosity (Pa s) was measured with a stress-controlled rheometer Rheostress 80 (Haake Instrument Inc., Paramus, USA). A cone and plate geometry (40 mm diameter, 0.04 rad, 1 mm gap, 1 Hz) was used for all the samples. The experimental results, together with those of some vegetable oils and their epoxides, are shown in Table 5.

3. Results and discussion

3.1. *Epoxidation of soybean FAME with performic acid generated in situ*

The impacts of the following reaction parameters were considered: the degree of mixing, reaction temperature, mol ratios of hydrogen peroxide and/or formic acid with respect to the double bonds of the FAME and the – eventual – addition of a solvent addition on the system were considered. We focused on those reaction conditions capable of accomplishing both, high unsaturation conversion and high epoxide yield. In this respect, initial test trials showed that any variation of the French and Minn's recipe [19], namely the slow addition of H_2O_2 to a mixture of the FAME and formic acid was counterproductive and, therefore, the reactants were always added following their suggested procedure. All the experimental conditions are detailed in Table 1. The time course of the iodine value (IV) and the percent oxirane oxygen (%Oxirane) corresponding to each run is shown in Fig. 3.

The analysis of the degree of mixing on the heterogeneous liquid–liquid system (runs Ep-1 and Ep-2, Table 1), where the stirring rates were 1400 and 350 rpm, respectively, for otherwise equal reaction parameters (57 °C and C=C/H_2O_2(59 wt%)/FA = 1/1.1/0.5 mol ratios), showed minor differences in the relevant performance criteria under these non-demanding operating conditions: After 690 min the selectivity to oxirane and epoxide yield were somewhat higher in the second case, while the double bond conversion showed a slight improvement under the more vigorous agitation. Nonetheless, the degradation of the oxirane ring was evident in both situations (Fig. 3).

The degree of mechanical agitation, that is, the intensity of turbulence leads to higher interfacial areas between the two immiscible liquid phases and, under mass-transfer controlled regimes, to a faster epoxidation of the double bonds. Higher interfacial areas, in turn, can cause further opening of the oxirane ring, though. Therefore, in view of the previous results and of similar findings as regards this type of coalescing polar/organic mixtures [7–9], and to prevent poor yields as much as possible, the lower mixing regime (350 rpm) was chosen to proceed further (Fig. 3).

The impact of the reaction temperature was scrutinized at a lower level (40 °C), again for C=C/H_2O_2(59 wt%)/FA = 1/1.1/0.5 mol ratios (compare runs Ep-2 and Ep-3 in Table 1). Fig. 3 shows that although the reaction was slower at 40 °C, there was no oxirane decomposition with a high selectivity of ~87%. This temperature level was then selected to continue the study.

Table 5
Kinematic viscosity and viscosity of vegetable oils and their epoxides, soybean FAME and epoxidized soybean FAME, at 40 °C

Source	Kinematic viscosity (cSt)	Viscosity ($\times 10^3$ Pa s)
Sunflower oil	28	30
Epoxidized sunflower oil	123	400
High-oleic sunflower oil	41	32
Epoxidized high-oleic sunflower oil	100	110[a]
Soybean oil	25	32
Epoxidized soybean oil	184	330
Soybean FAME	–	4.7
Epoxidized soybean FAME	–	13

[a] At 45 °C.

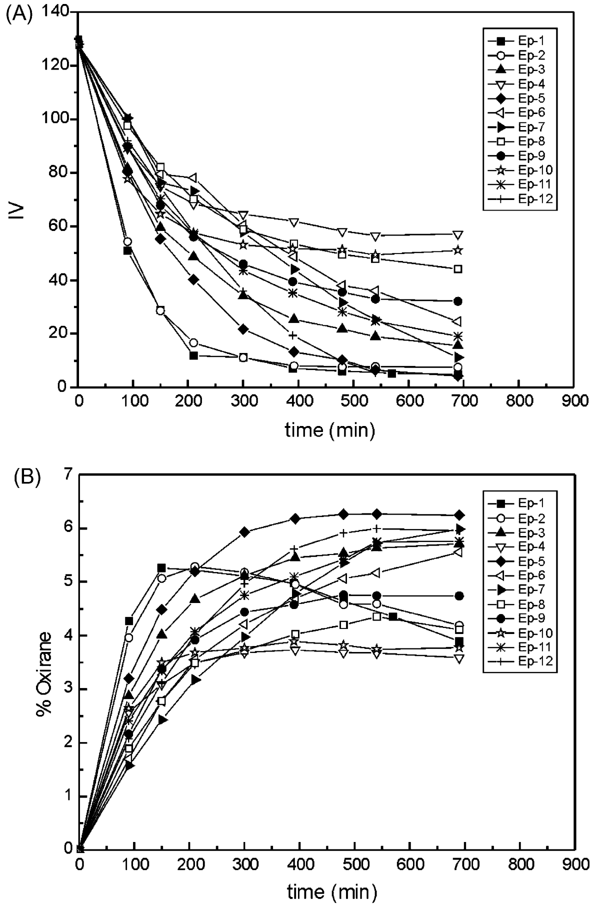

Fig. 3. Iodine value (IV) (A) and percent oxirane oxygen, or oxirane value (%Oxirane) (B), during the epoxidation of soybean FAME with PFA. The different reaction conditions are detailed in Table 1. Lines are meant as a guide to the eye.

The next step was devoted to analyzing the H_2O_2-to-double bonds molar ratio, by increasing the amount of hydrogen peroxide in the mixture. At the same time, the attack by PAA was moderated by lowering the molarity of formic acid to 0.3 mol per moles of double bonds (runs Ep-6, Ep-11 and Ep-7 in Table 1 and Fig. 3). The final yields after 13 h were 74.3%, 77.0% and 80.2% for $C{=}C/H_2O_2$(59 wt%) ratios equal to 1/1.1, 1/2 and 1/5, respectively. Concurrently, meanwhile, the decrease in oxirane selectivity by ring opening – even though the availability of active oxygen had been increased by almost fivefold – was just mild: 0.92 vs. 0.88.

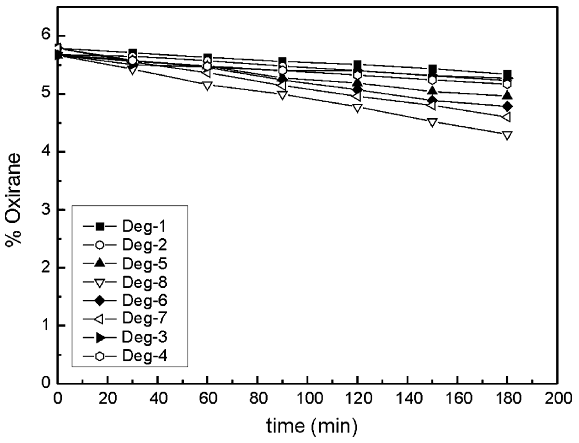

Fig. 4. %Oxirane vs. time during the degradation of epoxidized soybean FAME. The different reaction conditions are detailed in Table 2. Lines are meant as a guide to the eye.

Incidentally, upon using the rather unrealistic (in economic terms) high molarity of hydrogen peroxide, the impact of the degree of mixing in the reacting system was dramatic. This is illustrated in runs Ep-7 and Ep-12, for both of which the mol ratios were set to $C{=}C/H_2O_2$(59 wt%)/FA = 1/5/0.3 but using 1000 instead of 350 rpm in the second case. Then, after only 540 min of reaction time (instead of 690 min) the double bond conversion was significantly higher with about the same oxirane yield, although the final selectivity was somewhat lower already.

The epoxide yield is a strong function of the available amount of FA in the system. Formic acid is indeed crucial for producing enough PFA in the aqueous phase – which then passes to the organic phase to deliver an oxygen atom to the double bonds – but, also, is the main responsible for the opening of the oxirane rings. So, while keeping a moderately high concentration of hydrogen peroxide in the system as well, the concentration of FA was almost doubled (compare runs Ep-5 and Ep-11 in Table 1). Fig. 3 shows that, even though upon using 0.5 mol FA per mol of double bonds the epoxide yield is to some extent lower in run Ep-5, the final %Oxirane after 690 min of reaction is the highest of the set, and the final IV is less than 5 (these low IVs are needed in practical applications), whereas in run Ep-11 the iodine value is still almost 20. Last, it can be appreciated that when the $C{=}C/H_2O_2$(59 wt%)/FA molar ratio was changed from 1/2/0.3 (run Ep-11) to 1/2/0.5 (run Ep-5) the final selectivity did not decay substantially (0.90 and 0.86, respectively).

It is affirmed in the literature that in the absence of an organic diluent it is not possible to achieve optimal oxirane values of epoxidized vegetable oils whenever formic acid is employed at or above 40 °C. Therefore, a non-polar organic solvent was used in the following runs, seeking to maximize the epoxide yield of the soybean FAME. Following US Pat. 3,360,351 [19], in which fatty acid methyl esters are epoxidized with peracetic acid generated *in situ* in presence of heptane, this aliphatic solvent was chosen as well, using a C=C/heptane = 1/2 molar ratio. Yet, comparing runs Ep-6 and Ep-10 (Table 1 and Fig. 3), where the reaction conditions are mild, and otherwise identical: 40 °C, 350 rpm and $C{=}C/H_2O_2$(59 wt%)/FA = 1/1.1/0.3 molar ratios, it is apparent that upon adding the organic solvent the double bond conversion merely improves during the first 3 h, but both the final conversion and epoxide yield after 690 min became severely affected. Owing to dilution effects, lower conversion levels were predictable in the second case but not *less* selectivity, though (0.92 resp. 0.84) because of the purported moderating impact of organic solvents on the deleterious ring-opening consecutive reactions. These low-performance features can also be appreciated in runs Ep-8 and Ep-9, in which the double bonds to FA ratio was raised to the ‘standard’ value of 0.5. It is quite likely that aliphatic solvents, rather than aromatic ones (*vide infra*) are less able to protect the epoxide ring from the attack of formic acid, but the subject deserves a more in-depth study.

Perhaps one of the most important findings of the present work is that it shows, as compared with the conventional peracid processes – which employ more dilute hydrogen peroxide (30–35 wt%), at 60 °C – that higher double bond conversion, together with excellent oxirane yield and selectivity can be achieved by using ~60 wt% H_2O_2 and a lower reaction temperature, as exemplified by runs Ep-3 and Ep-4 (Table 1 and Fig. 3), where the conventional $C{=}C/H_2O_2/FA{=}1/1.1/0.5$ mol ratios were employed.

Summing up, considering the complete set of conditions explored it is apparent that run Ep-5 gave the best oxirane yield and product quality (lowest IV), in less than 12 h of reaction time (Table 1). Therefore, it is suggested the employment of formic acid for the non-catalyzed epoxidation of FAME with

Table 6
Epoxidation of vegetable oils with performic acid generated *in situ* in the presence of benzene (molar ratio C=C/benzene = 1/5) as diluent[a]

Oil source	Initial iodine value (IV^0)	Total duration (h)	IV_{final}	X_{final}[b]	$\%Ox_{\text{final}}$	$\%Y_{\text{final}}$[c]	S_{final}[d]
Sunflower oil	120	22	1.78	98.5	6.3	89.4	0.91
High-oleic sunflower oil	83.7	20	0.72	99.1	4.9	98.6	0.99
Soybean oil[e]	132.5	22	1.31	99.0	6.9	89.4	0.90
Soybean FAME[f,g]	129.6	>20	4.22	96.7	6.24	83.5	0.86

[a] Reaction conditions: double bonds/H_2O_2(30 wt%)/FA molar ratios = 1/10/0.5; 20–40 °C; 350 rpm; benzene in 30% volume excess with respect to oil source.

[b] Percent conversion of double bonds calculated as $X = [(IV^0 - IV)/IV^0] \times 100$.

[c] Percent oxirane oxygen yield = $[(\%Ox)/(\%Ox_t)] \times 100$, where $\%Ox_t$ represents the theoretical %Oxirane for IV^0: $\%Ox_t = \{(IV^0/MW_{I_2})/[100 + (IV^0/MW_{I_2})MW_O]\}\, MW_O \times 100$. The theoretical %Oxirane values for each IV^0 were 7.03, 5.01 and 7.7 for sunflower oil, high-oleic sunflower oil and soybean oil, respectively.

[d] Oxirane oxygen selectivity = $[(\%Ox)/(\%Ox_t)] \times [IV^0/(IV^0 - IV)]$.

[e] Crude soybean oil refined (*i.e.,* degummed, neutralized, bleached and deodorized) in the laboratory was employed.

[f] Commercial, refined soybean oil (Sojola brand, Aceitera General Deheza S.A., Arg.).

[g] Run Ep-5 of Table 1. Reaction conditions: double bonds/H_2O_2(59 wt%)/FA molar ratios = 1/2.0/0.5; 40 °C; 350 rpm.

PFA generated *in situ* at 40 °C, with the following molar ratios: C=C/H_2O_2(59 wt%)/FA = 1/1.1/0.3 and moderate mixing.

The 'fully epoxidized' soybean FAME was compared with different epoxidized vegetable oils, soybean, sunflower and high-oleic sunflower oil. These fully epoxidized oils were prepared in similar way as the stock of FAME prepared for studying the degradation of the oxirane ring. That is, the oils were epoxidized in depth at low temperature using benzene (C=C/benzene molar ratio = 1/5) as a diluent so as to minimize ring opening. Benzene is a better diluent for epoxidation than heptane (compare Table 6 to runs Ep-8 to Ep-10, Table 1). At similar temperature extremely high oxirane yields and selectivities can be reached, albeit at the expense of large reaction times (they were about equal, *ca.* 20–22 h, for both the oils and the FAME) and hydrogen peroxide expenditure (as the C=C/H_2O_2 molar ratio was 1/10 in these benzene-moderated experiments).

The viscosity of the set of vegetable oils, soybean FAME and their epoxides was measured at 40 °C (Table 5). It can be promptly appreciated that the viscosity of the epoxidized oils is about an order of magnitude higher than that of the vegetable oils. Likewise, the viscosity of the epoxidized soybean FAME is more than 20-fold higher than that of the methyl ester. These dissimilarities are of course important from an industrial standpoint but, also, because viscosity changes usually bear a profound impact on reaction kinetics and/or reactor design [20,21], as well as on industrial applications themselves.

3.2. Ring-opening studies

Formic acid is soluble in vegetable oils and or their FAME. Therefore, it can degrade the oxirane ring in the organic phase, even a low temperature. Nevertheless, in the epoxidation process formic acid is mixed with an aqueous solution of H_2O_2, to generate highly reactive performic acid as the oxygen 'shuttler' to the organic phase. This means that *solvated* formic acid is always present in the reacting system.

The experimental data taken under similar working conditions (40 °C; 350 rpm) show that, when solvated formic acid is also available the degradation of the epoxide ring proceeds further. This can be is readily appreciated by comparing runs Deg-1 and Deg-2 with runs Deg-3 and Deg-4 (Table 2 and Fig. 4), in which the epFAME/FA molar ratio was 1/0.3 and 1/0.5, respectively. Solvated organic acids are partially dissociated in water (the solvating agent), and this contributes to amplify somewhat the – deleterious – observable reaction rate [9,23].

As for the concentration of formic acid itself, it is also apparent that the higher its molarity is the larger the degradation becomes (compare now the pairs of runs Deg-1 resp. Deg-2, and Deg-3 resp. Deg-4 in Table 2 and Fig. 4).

Preformed PFA was used in the set of runs Deg-5 to Deg-9, in which the two-phase liquid–liquid system also contained formic acid and hydrogen peroxide. The peracid was prepared following Yadav et al.'s technique [22] for making peracetic acid: Formic acid was made to react with H_2O_2 (60 wt%) for 24 h, after which equilibrated mixtures of FA, PFA, water and hydrogen peroxide were obtained. These mixtures were then contacted with the epFAME. The different molar ratios employed to perform this set of runs are indicated in Table 2 and, as expected, the degradation of the ring was larger the higher the concentration of either of the PFA precursors, formic acid and H_2O_2, was. However, the impact of the H_2O_2 molarity on ring opening was far less deleterious than that of FA, as shown by comparing runs Deg-5 to Deg-7 versus runs Deg-6, Deg-8 and Deg-9. Therefore the effects of FA were studied in more detail, as it is discussed below.

4. Kinetic modelling

4.1. Modelling of the epoxidation reaction (equilibrium two-phase model)

The reacting system features two immiscible phases, one of them polar (the aqueous phase) and the other one organic (Fig. 1). Hydrogen peroxide reacts in the aqueous phase with formic acid (FA) to give PFA, which in turn reacts inside the organic phase combining with the double bonds (C=C) of the unsaturated fatty acid chains to form the epoxide (Ep) ring together with FA. The latter then returns to the aqueous phase to reinitiate the 'oxygen-shuttling' cycle.

As already stated in Section 1, besides the epoxide ring formation several other consecutive, deleterious ring-opening reactions coexist in the system (Fig. 2). To achieve high oxirane value products all of them must be minimized. In recent years, studies aimed at the detailed and systematic evaluation of these reactions have been conducted [7–9]. They indicate that under most of the reaction conditions used in this work, where no homogeneous, aqueous soluble acidic catalyst is used, the only reagents capable of significant ring-opening activity (just in the organic phase) are the carboxylic and percarboxylic acids, FA and PFA. In other words, the following set of reactions suffices to model the reaction system:

$$H_2O_2\ (aq) + FA\ (aq) \underset{k_2}{\overset{k_1}{\leftrightarrows}} PFA\ (aq) + H_2O\ (aq)$$

$$PFA\ (aq) \leftrightarrows PFA\ (org)$$

$$FA\ (org) \leftrightarrows FA\ (aq)$$

$$\mathrm{C{=}C\ (org) + PFA\ (org)} \xrightarrow{k_3} \mathrm{Ep\ (org) + FA\ (org)}$$

$$\mathrm{Ep\ (org) + FA\ (org)} \xrightarrow{k_4} \mathrm{Deg_1}$$

$$\mathrm{Ep\ (org) + PFA\ (org)} \xrightarrow{k_5} \mathrm{Deg_2}$$

So, considering our set-up as a well-stirred, ideal isothermal batch reactor in the slow kinetics regime, where (a) the individual volumes of each liquid phase remain nearly constant and (b) the concentration gradients in both liquid phases are negligible, so the bulk concentrations are related by the partition equilibria of FA and PFA, the following *overall* mass balances for each component in the equilibrium two-phase model can be written:

Mass balances for H_2O and H_2O_2

$$\frac{dn^{aq}_{H_2O_2}}{dt} = \frac{V_{aq}d[H_2O_2]^{aq}}{dt} = (-R^{aq}_1 + R^{aq}_2)V_{aq} \tag{1}$$

$$\frac{d[H_2O_2]^{ad}}{dt} = (-R^{aq}_1 + R^{aq}_2) \tag{2}$$

$$\frac{dn^{aq}_{H_2O}}{dt} = -\frac{dn^{aq}_{H_2O_2}}{dt} \tag{3}$$

where

$$R^{aq}_1 = k^{aq}_1[FA]^{aq}[H_2O_2]^{aq} \tag{4}$$

$$R^{aq}_2 = k^{aq}_2[PFA]^{aq}[H_2O]^{aq} \tag{5}$$

Mass balance for formic acid

$$nFA = n^{aq}_{FA} + n^{org}_{FA} = [FA]^{aq}V_{aq} + [FA]^{org}V_{org} \tag{6}$$

Considering the volume fractions of the aqueous and organic phases, ϕ_{aq} and ϕ_{org} together with the partition equilibrium of FA,

$$m_{FA} = \frac{[FA]^{org}}{[FA]^{aq}} \tag{7}$$

Eq. (6) can be recast, upon derivation, as follows:

$$\frac{dn_{FA}}{dt} = \left(\frac{1-\phi_{org}(1-m_{FA})}{m_{FA}}\right)V\frac{d[FA]^{org}}{dt} \tag{8}$$

Besides:

$$\frac{dn_{FA}}{dt} = \frac{dn^{aq}_{FA}}{dt} + \frac{dn^{org}_{FA}}{dt} = (-R^{aq}_1 + R^{aq}_2)V_{aq} + R^{org}_4 V_{org} \tag{9}$$

Equating Eqs. (8) and (9) and rearranging:

$$\frac{d[FA]^{org}}{dt} = \left(\frac{1-\phi_{org}(1-m_{FA})}{m_{FA}}\right)^{-1}[(-R^{aq}_1 + R^{aq}_2)\phi_{aq} - R^{org}_4\phi_{org}] \tag{10}$$

where as it is fully explained in what follows:

$$R^{org}_4 = k^{org}_4([FA]^{org})^2([Ep]^{org}) \tag{11}$$

Mass balance for performic acid

Proceeding in similar fashion as above, the following expression results:

$$\frac{d[PFA]^{org}}{dt} = \left(\frac{1-\phi_{org}(1-m_{PFA})}{m_{PFA}}\right)^{-1}[(R^{aq}_1 - R^{aq}_2)\phi_{aq} - R^{org}_5\phi_{org}] \tag{12}$$

where

$$m_{PFA} = \frac{[PFA]^{org}}{[PFA]^{aq}} \tag{13}$$

and

$$R^{org}_5 = k^{org}_5([PFA]^{org})^2([Ep]^{org}) \tag{14}$$

Mass balance for FAME unsaturation (double bonds: C=C)

$$\frac{dn^{org}_{C=C}}{dt} = \frac{V_{org}d[C{=}C]^{org}}{dt} = -R^{org}_3 V_{org} \tag{15}$$

$$\frac{d[C{=}C]^{org}}{dt} = -R^{org}_3 \tag{16}$$

where

$$R^{org}_3 = k^{org}_3[PFA]^{org}[C{=}C]^{org} \tag{17}$$

Mass balance for the epoxide groups (Ep)

$$\frac{dn^{org}_{Ep}}{dt} = \frac{V_{org}d[Ep]^{org}}{dt} = (R^{org}_3 - R^{org}_4 - R^{org}_5)V_{org} \tag{18}$$

$$\frac{d[Ep]^{org}}{dt} = (R^{org}_3 - R^{org}_4 - R^{org}_5) \tag{19}$$

The distribution constants of formic acid for each reaction condition were experimentally determined (Table 3). The order of magnitude of these values is quite similar to those of acetic acid [1,24]. Table 3 also contains the m_{FA} values predicted using UNIFAC (UNIquac Functional-group Activity Coefficient) ([24] and references therein), which are very similar to the measured ones. Therefore, the distribution constant of performic acid was estimated employing UNIFAC.

The kinetic rate constant of the epoxidation reaction, k^{org}_3, was calculated employing Eqs. (1)–(19), using averages of the experimental values of m_{FA} (0.035) and the predicted values of m_{PFA} (0.095). The kinetic rate constants for the formation of PFA in the aqueous phase are well known, given the similar molecular structure of acetic and formic acids [1]. At 40 °C these values are the following: $k^{aq}_1 = 5.5 \times 10^{-4}$ l/(mol min) and $k^{aq}_2 = 7.5 \times 10^{-4}$ l/(mol min). The remaining kinetic rate constants corresponding to the attack of FA and PFA on the epoxide ring in the organic phase, k^{org}_4 and k^{org}_5, were calculated as described below.

4.2. Modelling of the degradation reaction caused by FA and PFA

Fully epoxidized soybean FAME (epFAME) was used to study the degradation of the oxirane ring by formic and performic acids at the chosen reaction temperature (40 °C). To this end, the ring opening by pure FA (i.e., only in the organic phase) as well by an aqueous solution of the carboxylic acid were studied, together with designed runs where both FA and PFA were present (Table 2).

The general constitutive equations expressing the attack by neat carboxylic or percarboxylic acids on the epoxide ring in the organic phase can be written as

$$R^{org}_i = k^{org}_i([I]^{org})^{\alpha i}([Ep]^{org})^{\beta i} \tag{20}$$

where i = FA or PFA, whereas, for aqueous-solvated acids, k^{org}_i is equal to $k_{in} + k_{iR}$ [H$^+$] and, in turn, [H$^+$] = f_i ([FA]^{org,0}). In general, though, $k_{in} \ll k_{iR}$ [H$^+$] [21].

In previous work, and in agreement with other research groups [1,6], we reported that each of the oxirane ring-opening reactions is first order with respect to the molar concentration of the epoxide groups in the organic phase [7–9]. We found, also, that the attack by acetic and peracetic acids was second order with respect to their concentration. Thence, considering the close structural similarity

Table 7
Kinetic rate constants corresponding to the degradation (opening) of the epoxide ring of soybean FAME in the organic phase caused by FA and PFA, at 40 °C

Run	Molar ratios	k_4^{org} ($\times 10^5$ $\mathrm{l^2/(mol^2\,min)}$)	k_5^{org} ($\times 10^3$ $\mathrm{l^2/(mol^2\,min)}$)
Deg-1	epFAME/FA = 1/0.3	6.0 ± 0.13	–
Deg-2	epFAME/FA = 1/0.5	5.6 ± 0.26	–
Deg-3	epFAME/H_2O/FA = 1/1.1/0.3	6.5 ± 0.10	–
Deg-4	epFAME/H_2O/FA = 1/1.1/0.5	6.0 ± 0.096	–
Deg-5	epFAME/H_2O_2/FA = 1/1.1/0.3	6.5 ± 0.10	2.2 ± 0.36
Deg-6	epFAME/H_2O_2/FA = 1/2.0/0.3	6.5 ± 0.10	4.4 ± 0.77
Deg-7	epFAME/H_2O_2/FA = 1/5.0/0.3	6.5 ± 0.10	5.6 ± 0.48
Deg-8	epFAME/H_2O_2/FA = 1/2.0/0.5	6.0 ± 0.096	5.1 ± 0.20
Deg-9	epFAME/H_2O_2/FA = 1/2.0/1	6.0 ± 0.096	N.A.[a]

[a] Ring-opening reaction under the fast kinetic regime [10].

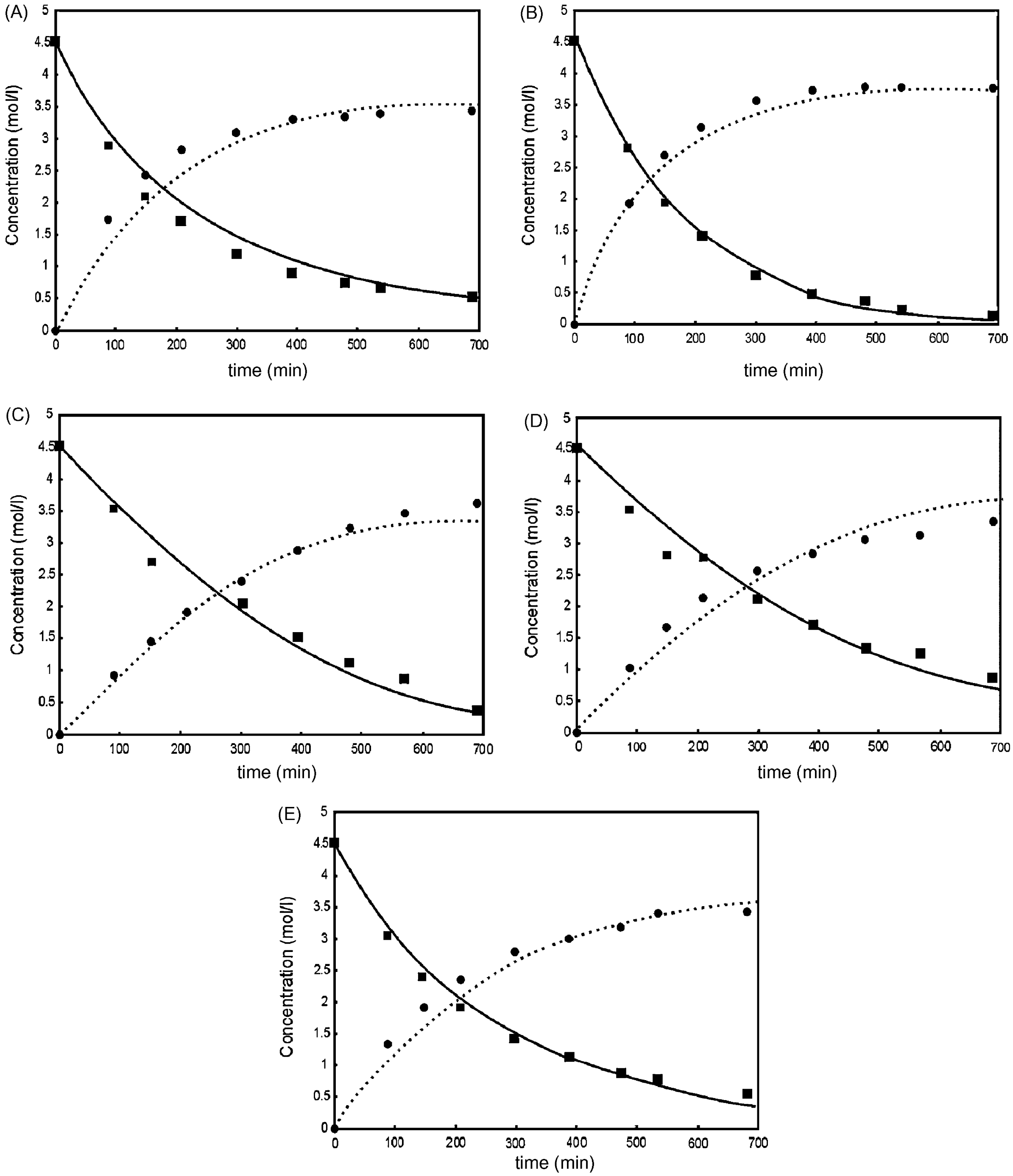

Fig. 5. Experimental vs. model (simulated) molar concentration of double bonds (mol C=C/l) and epoxide groups (mol Ep/l) vs. time, during the epoxidation. Markers are experimental data, curves are model predictions. Plots in (A), (B), (C), (D) and (E) correspond to runs Ep-3, Ep-5, Ep-6, Ep-7 and Ep-11 listed in Table 1, respectively.

Table 8
Reaction rate constant (individual runs) corresponding to the epoxidation of soybean FAME with performic acid generated *in situ*, from formic acid and H_2O_2(aq.), at 40 °C

Run	Molar ratios C=C/H_2O_2/FA	k_3^{org} ($\times 10^2$ l/(mol min))
Ep-3	1/1.1/0.5	4.7 ± 0.21
Ep-5	1/2/0.5	4.2 ± 0.18
Ep-6	1/1.1/0.3	3.8 ± 0.11
Ep-7	1/5/0.3	3.1 ± 0.34
Ep-11	1/2/0.3	3.6 ± 0.23

between acetic and formic acids, and assuming that the same (second) reaction order applies in the case of FA and PFA, Eq. (20) can be rewritten as

$$R_i^{org} = k_i^{org}([I]^{org})^2([\mathrm{Ep}]^{org}) \tag{21}$$

Indeed, these equations were already introduced above, within the set of Eqs. (1)–(19), without explicit justification. The reaction rate constant k_4^{org} was found for each of the individual experimental runs Deg-1 to Deg-4 indicated in Table 2. This rate constant was then employed to obtain k_5^{org} for runs Deg-5 to Deg-9. The reaction rate constants were obtained by using Euler's numerical method in the MATLAB package, employing the Nelder–Mead algorithm [25], by minimizing the differences (least squares method) between the experimental vs. predicted values of concentrations.

4.3. Kinetic modelling results

Table 7 gives the obtained values of k_4^{org} and k_5^{org} for each of the individual degradation runs. Both of them are fairly constant, thus validating the equilibrium two-phase model used here. Also, it can be promptly appreciated that the attack on the epoxide ring by either 'neat' or solvated FA is just about equal. Lastly, it is worth noticing that the k_4^{org} kinetic rate constant has the same order of magnitude than that of solvated acetic acid [10] and that the attack on the oxirane groups by the peracid (PFA) is much more intense than the one of the corresponding carboxylic acid (FA): $k_5^{org}/k_4^{org} \approx$ 80-fold, in similar fashion as in the case of peracetic vs. acetic acids, respectively.

The kinetic rate constant for the epoxidation of the double bonds by PFA in the organic phase (k_3^{org}) was calculated by solving the set of simultaneous ODEs using Euler's numerical method in MATLAB, as above, for each of the experimental runs Ep-3, Ep-5 to Ep-7 and Ep-11 indicated in Table 1 ($T = 40$ °C). The corresponding calculated values are listed in Table 8. Fig. 5 plots the experimental concentration values of double bonds and epoxide groups vs. time on these runs, together with the simulated ones, using an average value of $k_3^{org} = 3.88 \times 10^{-2}\,\mathrm{l\,mol^{-1}\,min^{-1}}$. Both fits are fair.

These k_3 values are similar to those found by La Scala and Wool [3], who used preformed performic acid at 20 °C to epoxidized different fatty acid methyl esters. However, they did not include the degradation of the oxirane ring in their reaction model.

While trying to maximize oxirane selectivity and yield, several refined vegetable oils were epoxidized with formic acid at 40 °C using a large excess of H_2O_2 (30 wt%) and adding benzene (molar ratio C=C/benzene = 1/5) as a diluent (or 'ring-integrity preserver'). Table 6 shows that in every case these goals were achieved. So, to further exploit the equilibrium two-phase model presented hereby, the kinetic rate constant (k_3^{org}) associated with the epoxidation of sunflower oil was calculated using the set of ODEs, but excluding any of the ring-opening reactions. Fig. 6 compares the excellent fit between the experimental and simulated concentration vs. time data of $[\mathrm{C{=}C}]^{org}$ and $[\mathrm{Ep}]^{org}$. As before, k_1^{aq} and k_2^{aq} were calculated using Rangarajan et al.'s data [1]. At this temperature, the calculated value of k_3^{org} was $0.0016 \pm 0.00024\,\mathrm{l\,mol^{-1}\,min^{-1}}$; which is of an order of magnitude lower than the previously calculated and entirely compatible with the diluting-moderating action of the added solvent.

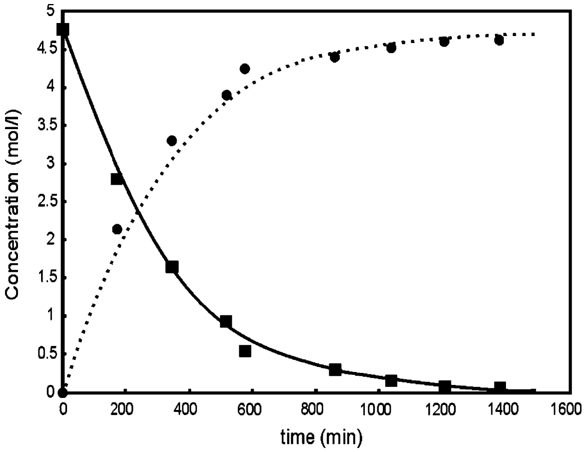

Fig. 6. Epoxidation of refined sunflower oil with PFA generated *in situ* using benzene as diluent. Markers are experimental data, curves are model predictions. Process conditions are given in Table 6.

5. Conclusions

In the epoxidation of soybean fatty acid methyl esters with PFA generated in situ from FA using highly concentrated hydrogen peroxide (up to 60 wt%) and moderate temperature (preferably 40 °C), the impact of temperature increases is significantly detrimental for achieving high yields and/or high oxirane-number. Higher concentrations of either formic acid or hydrogen peroxide are also harmful (particularly, the carboxylic acid) but much less than temperature.

Nevertheless, this process alternative compares favourably to the conventional one, which is conducted at 60 °C using 30 wt% H_2O_2; higher double bond conversion combined with high epoxide productivity and excellent selectivity are attainable.

Using economically sound FA-to-double bonds and H_2O_2-to-double bonds molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are always well dispersed, the epoxidation process can be adequately described using an (equilibrated) two-phase reaction model accounting for just the reversible peracid formation (in the aqueous phase) and the epoxidation reaction proper, together with the attacks on the epoxide ring by FA and PFA (in the organic phase).

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