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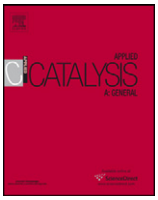

Fatty ketones from the rearrangement of epoxidized vegetable oils

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ABSTRACT

The rearrangement of epoxidized vegetable oils to produce fatty ketones, catalyzed by acidic resins, is disclosed. The non-microbial production of fatty ketones from epoxidized vegetable oils has not been previously reported. Some of the variables affecting the ketone formation such as acidic strength of the catalyst, temperature and solvent are studied in order to determine the conditions that favor the rearrangement. Epoxidized vegetable oils can be easily transformed to the respective ketones via a rearrangement reaction catalyzed by acidic resins. Other kind of acidic catalysts are active for this reaction if their Brönsted acid sites are accessible to protonate the epoxide. Formation of ketones, from the rearrangement of epoxidized methyl oleate, is favored in the presence of strongly acidic catalysts and enhanced by increasing temperature. Polar-protic solvents increase the ketone yield but decrease the ketone selectivity because they are added to the epoxide ring. The mechanism for the epoxide rearrangement is very likely to take place through a hydride migration to the carbocation generated in the acid-catalyzed epoxide ring opening.

1. Introduction

Epoxidation of vegetable oils is a commercially important reaction because the epoxides obtained from these renewable raw materials and from their alkyl esters, their transesterification products, have applications in such materials as plasticizers and polymer stabilizers [1,2]. Furthermore, these epoxides can be used as intermediates in the production of a variety of derivatives, because of the high reactivity of the strained epoxide ring. For example, monoalcohols, diols, alkoxyalcohols, hydroxyesters, N-hydroxyalkylamides, mercaptoalcohols, aminoalcohols, and hydroxynitriles could be produced via epoxide ring-opening reactions with suitable reactants [3]. Among these products, it was recently reported the addition of alcohols and organic acids to epoxidized vegetable oils to obtain derivatives that have shown good properties as biocompatible lubricants [4–7].

During our investigations dealing with the production of fatty epoxides and their transformation into other valuable products [4–9] we realized that ketones were produced as by-products, through an epoxide rearrangement reaction. Rearrangement of epoxides to ketones has been reported but for short-chain epoxides such as ethylene oxide and propylene oxide [10–13]. This reaction has been used to obtain important commercial products like phenylacetaldehydes, methyl isopropyl ketone and campholenic aldehyde from the respective epoxides and using heterogeneous catalysts such as acidic zeolites [14]. Yates [15] reported a method to oxidize olefins to the less substituted carbonyl compounds, involving two steps: hydroboration with borane dimethyl sulfide, followed by oxidation of the resulting alkylboranes with tetrapropylammonium perruthenate and N-methylmorpholine-N-oxide. Only short chain olefins were studied, with the unsaturation in terminal or cyclic position. The reaction was accomplished in ca. 4 h at room temperature. On the other hand, Deshmukh et al. [16] reported a method to convert olefins into the corresponding α-bromo ketones in the presence of 1.1 equivalents each of o-iodoxybenzoic acid and tetraethylammonium bromide. Similarly, Maksimchuk et al. [17] established that the mesoporous metal-organic framework MIL-101 (chromium terephthalate-based mesoscopic metal-organic framework) is an efficient heterogeneous catalyst for the selective allylic oxidation of alkenes with tert-butyl hydroperoxide. They found that the selectivity toward α,β-unsaturated ketones reached 86–93% and the temperature of the catalyst activation strongly affected the ketone yield. Wang and Jiang [18] developed a method for palladium-catalyzed dihydroxylation and oxidative cleavage of olefins (monosubstituted aromatic and aliphatic terminal alkenes, 1,2-disubstituted, and 1,1-disubstituted olefins) with oxygen to produce 1,2-diols, aldehydes, and ketones. Microbial production of ketones from fatty epoxides using *Rhodococcus rhodochrousand* and *Nocardia cholesterolicum* [19,20] has been reported. To the best of our knowledge, the

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non-microbial production of fatty ketones from epoxidized vegetable oils has not been previously disclosed. The disclosure of the rearrangement of epoxidized vegetable oils is a very important issue that will help to better understand previous and future experimental results on reactions dealing with these epoxides. For instance, there are many reports using epoxidized oils as reactants where the reactions were monitored by measuring the decrease in the epoxide content, via titration (oxirane value) or infrared spectroscopy. Most of these reports have assumed that the measured decrease in the epoxide content is due to the formation of the desired product and do not take into account the possible ketone formation.

This paper is devoted to this reaction, i.e., the rearrangement of epoxidized vegetable oils to produce fatty ketones. Some of the variables affecting the ketone formation, such as acidic strength of the catalyst, temperature and solvent are studied in order to determine the conditions that favor the rearrangement.

2. Materials and methods

2.1. Materials

Oleic acid methyl ester was used as a substrate (Fuchs Petrolub AG, 97 wt% cis-9-octadecenoic acid methyl ester). Amberlyst 15 was purchased from Aldrich, SAC13 was kindly provided by DuPont. Amberlyst 15 is a copolymer of styrene and divinylbenzene (DVB). SAC13 is a composite material made of Nafion nanoparticles entrapped in a silica matrix. Nafion itself is a copolymer of tetrafluoroethene and perfluor-2-(fluorosulfonylethoxy)-propylvinyl ether. All the other reactants were from analytical grade and purchased from Aldrich.

The total amount of Brönsted acid sites in Amberlyst 15 and SAC13 was 4.72 and 0.22 meq H^+/g respectively, determined by ion exchange with NaCl solution 1.0 M (10 mL per gram of catalyst) and titrating the residual solution with NaOH 0.01 M. Surface area and porosity were measured with a Micromeritics Gemini V employing the BET method, prior to this measurement samples were degassed for 4 h at 100 °C and 10^{-2} Pa.

2.2. Characterization of reaction mixtures

Reaction mixtures were analyzed by gas chromatography on a Hewlet Packard HP 6890 using 60 m of the slightly polar column FS-SE54. Products were characterized by GC-Mass Spectrometry (GC Varian 3400 CX, MS Varian Saturn 3 at 70 eV and electron ionization), infrared spectroscopy (Nicolet Protégé 460, NaCl windows) and ^1H and ^{13}C NMR. ^1H (300 MHz) and ^{13}C NMR (75 MHz) were recorded in $CDCl_3$ as the solvent using a Mercury-300 BB spectrometer. For ^1H NMR spectra, a total of 16 scans were performed with a relaxation delay of 0.100 s and width of 8103.7 Hz. 320 scans were recorded for ^{13}C NMR spectra with a relaxation delay of 0.100 s and width of 19607.8 Hz.

2.3. Catalytic experiments

Oleic acid methyl ester was used as substrate. Epoxidized oleic acid methyl ester was produced following a known procedure [1]. Rearrangement reactions were carried out in round-bottom glass reactors immersed in a heated oil bath at 57 °C. The agitation was performed using a turbine impeller (2 cm radius, 500 rpm) to prevent attrition of the catalyst. Solvents and substrate were kept over a molecular sieve (UOP type 3A) to prevent water contamination that could lead to the hydrolysis of the epoxide. Catalysts were evacuated overnight at 120 °C under high vacuum and kept under argon atmosphere. Epoxide and solvent were mixed for 15 min at the desired temperature, then the catalyst (10% weight with respect to the epoxide) was added. To investigate the effect of stirring speed on the three-phase reaction system, reactions were carried out over a range of stirring speeds (100–1000 rpm). It was observed that the epoxides conversion increased with the stirring speed, but beyond 500 rpm there was no appreciable change in the rate of reaction. Therefore, all the subsequent experiments were carried out under a stirring speed of 500 rpm to ensure that there was no mass-transfer limitation in the liquid phases. Data plotted in the accompanying figures correspond to the means of triplicate experiments with a relative standard deviation <5% in all cases.

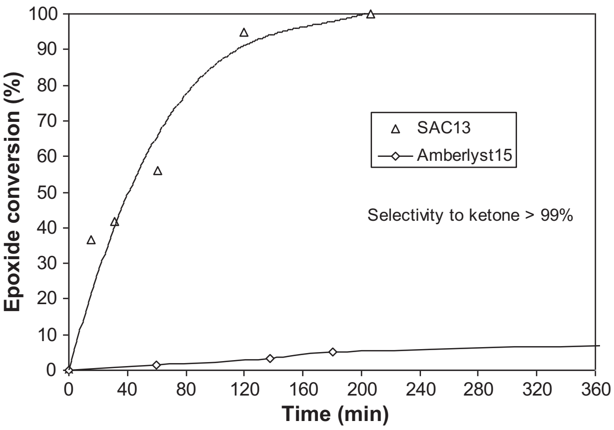


Fig. 1. Effect of the catalyst acid strength on the ketone formation rate from epoxidized methyl oleate. Epoxide/catalyst = 10 g/g, temperature = 70 °C.

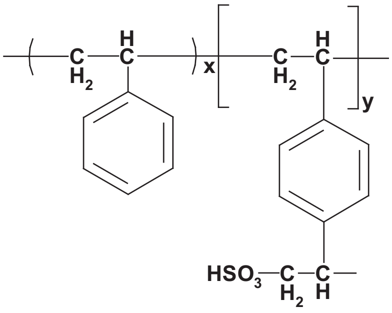
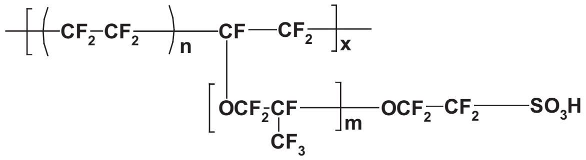
3. Results and discussion

Experiments on the rearrangement of epoxidized methyl oleate were carried out to analyze the effect of the catalyst's acid strength, reaction temperature and solvent on the epoxide conversion and ketone yield. Fig. 1 shows the results with the first variable, i.e. acidic strength of the catalyst.

The catalyst SAC13 (13% Nafion® entrapped in silica) is quite better than the catalyst Amberlyst15 for the ketone production. At 70 °C, ca. 3.5 h are required for complete epoxide conversion on SAC13 while Amberlyst15 needs ca. 30 h to completely convert the epoxide at 100 °C. SAC13 is a very strong acid, which explains its superior activity; Hammet acidity and NMR of mesityl oxide (Table 1) indicate that the acidity of this catalyst is equivalent to 85% sulfuric acid solution, while the acidity of Amberlyst 15 is equivalent to 45% sulfuric acid solution. This fact is a consequence of the fluor atom in the Nafion resin (component of SAC13), which owing its high electronegativity increases the dissociation of the acidic proton.

When different temperatures were studied, the results shown in Figs. 2 and 3 were obtained for the epoxide rearrangement on Amberlyst15 and SAC13, respectively. It is clear that the temperature plays a crucial role on the ketone formation rate, which is favored by increasing the temperature. If the ketone formation is to be minimized then mildly acidic catalysts, like Amberlyst15, and temperatures lower than 70 °C have to be used. When the catalyst is strongly acidic (SAC13) the ketone formation is appreciable even at temperatures as low as 50 °C. The reaction order was estimated from data of Figs. 2 and 3. By plotting $-\ln(1-\eta)$ vs. t, where η is the conversion and t the reaction time, it was found that the reaction exhibits the first order kinetics typical for intramolecular (rearrangement) reactions. This result is supported by the high values obtained for the correlation coefficients (R^2), which were higher than 0.96 in all cases (for both catalysts at 50, 70 and 100 °C). Rate constants (k) and correlation coefficients (R^2) are shown in Table 2.

Table 1
Physicochemical properties of the acidic resins.

	Amberlyst 15	SAC13
Structure		
Composition	Styrene + 20% divinylbenzene	Tetrafluoroethene + perfluoro-2-(fluorosulfonylethoxy) propylvinyl ether entrapped on silica
Acid strength [21]	Ho = −2.2 (Hammet acidity) NMR of mesityl oxide: $\Delta\delta$ = 32.4 ppm, equivalent to 45% H_2SO_4	Ho ≥ −12 (Hammet acidity) NMR of mesityl oxide: $\Delta\delta$ = 50–51 ppm, equivalent to 85% H_2SO_4
Acidity (meq H^+/g)	4.72	0.22
Surface area (m^2/g)	51	220
Pore size (nm)	40–80	10–25

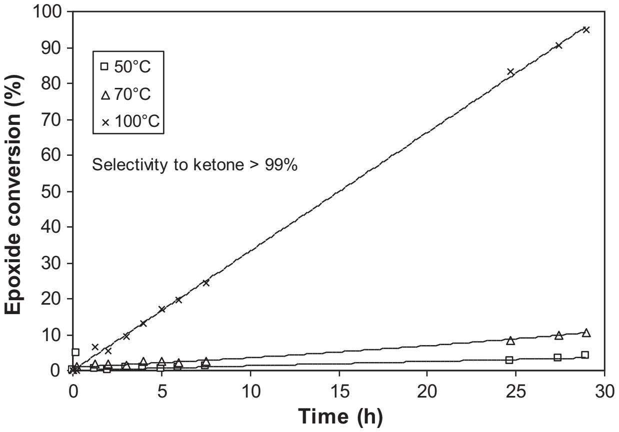


Fig. 2. Effect of temperature on the ketone formation rate from epoxidized methyl oleate. Epoxide/catalyst = 10 g/g, catalyst Amberlyst15.

Table 2
Kinetic parameters for ketone formation from epoxidized methyl oleate.

Catalyst (%)	Temp. (°C)	k (h^{-1})	R^2
Amb. 15	50	0.0012	0.961
Amb. 15	70	0.0035	0.983
Amb. 15	100	0.0937	0.967
SAC13	50	0.0034	0.960
SAC13	70	0.0229	0.978
SAC13	100	0.1586	0.996

Epoxide/catalyst = 10 g/g, solvent/epoxide = 2 g/g.

The influence of different solvents on the epoxide rearrangement reaction was determined. For these studies the solvents used were tert-butanol and neopentanol (polar-protic), nitrobenzene and sulfolane (polar-aprotic), toluene (slightly polar) and cyclo-hexane (apolar). Tert-butanol and neopentanol were chosen because they proved to be the less reactive alcohols in the epoxide ring-opening reaction. Results are shown in Figs. 4 and 5.

In the presence of the apolar and slightly polar solvents cyclohexane and toluene the formation rate of the ketone is decreased, probably as a consequence of the dilution. The polar-aprotic solvents sulfolane and nitrobenzene completely inhibit the ketone formation. The reaction rate showed to be enhanced by the presence of the polar-protic solvents tert-butanol and neopentanol, but in this case the main product obtained is the hydroxy-ether. After ca. 22 h of reaction, in presence of tert-butanol, the ketone yield began to decrease due to the formation of the trans-esterified product in a consecutive reaction.

Regarding the mechanism for the epoxide rearrangement, experiments showed that it did not take place via a pinacol-like

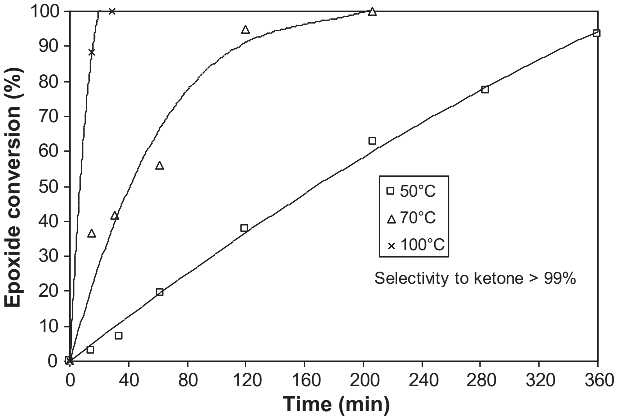


Fig. 3. Effect of temperature on the ketone formation rate from epoxidized methyl oleate. Epoxide/catalyst = 10 g/g, catalyst SAC13.

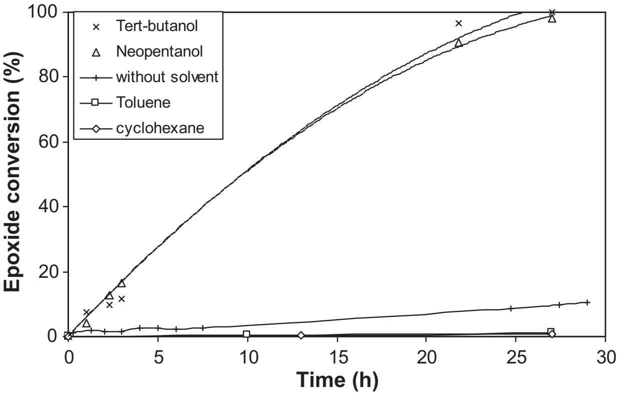


Fig. 4. Effect of solvents on the conversion of epoxidized methyl oleate. Epoxide/catalyst = 10 g/g, catalyst Amberlyst 15, solvent/epoxide = 2 g/g and temperature = 70 °C.

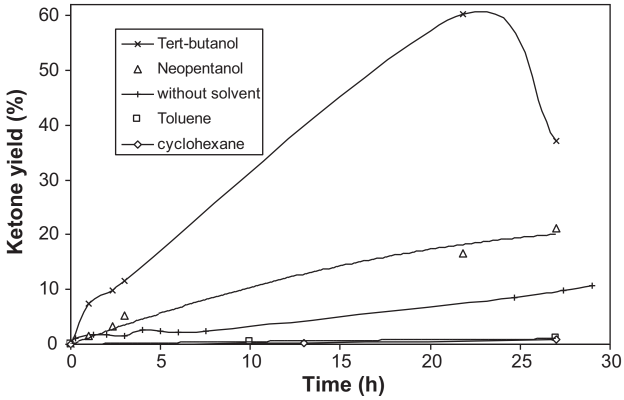


Fig. 5. Effect of solvents on the ketone formation from epoxidized methyl oleate. Epoxide/catalyst = 10 g/g, catalyst Amberlyst 15, solvent/epoxide = 2 g/g and temperature = 70 °C.

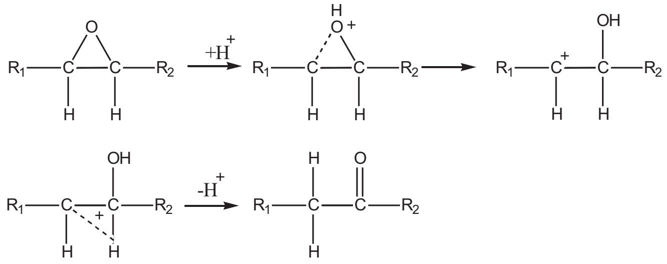


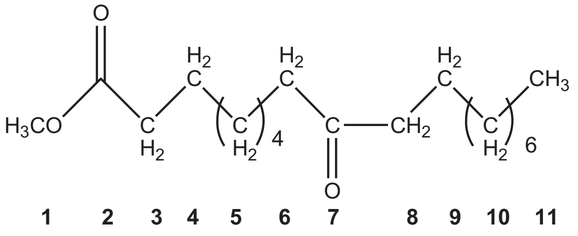
Fig. 6. Scheme for the epoxide rearrangement mechanism.

rearrangement because the reactions starting with the glycol (produced after hydrolysis of the epoxidized methyl oleate) did not show formation of ketone at all. Additionally, no glycol was detected during the experiments of epoxide rearrangement. Instead, a pathway involving two distinct steps is proposed. The first step is the acid catalyzed rupture of the oxirane ring to produce a carbocation and the second step is a hydride migration as shown in Fig. 6. Such as mechanism has been already proposed for the rearrangement of propene oxide and supported by high level ab initio calculations [12,13].

Ultimately, other acidic catalysts like clays (montmorillonite K10 and KSF/O) and mesoporous zeolite H–Y were also active for this reaction (results not shown). Results indicate that the necessary condition is the Brönsted acid sites to be accessible to protonate the epoxide, which is the first step in the rearrangement.

3.1. Product characterization

^{1}H NMR and ^{13}C NMR spectra, presented below, show the formation of the ketone moiety and the disappearance of the ethylenic and epoxide moieties. Besides, the formation of the ketones was observed in the GC–MS analysis by comparison with the mass spectra available in the data bank of the equipment.



Octadecanoic acid, 9-oxo, methyl ester

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.59 (s, 1), 2.33–2.8 (t, 6.8), 2.25–2.2 (t, 3), 1.54–1.48 (m, 4), 1.19 (m, 5, 9.10), 0.83–0.78 (t, 11). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 214 (7), 174.6 (2), 51.8 (1), 43.2 (6.8), 34.44 (3), 32.25–32.2 (9), 30.07–29.32 (5.10), 25.28 (4), 14.48 (11).

The IR spectrum (not shown) shows the usual vegetable-oil transmittance bands (oleic acid methyl ester), but the band at 3040–3010 cm^{-1}, characteristic of ethylenic groups, is absent which indicates the complete conversion of the unsaturations. The IR spectrum also shows a band at 1710 cm^{-1} characteristic of carbonyl groups. Bands at 3600–3200 cm^{-1}, characteristic of —OH groups in hydrogen bonding are not present indicating that the epoxide was not opened by proton-donor molecules (like water).

4. Conclusions

Epoxidized vegetable oils can be easily transformed to the respective ketones via a rearrangement reaction catalyzed by acidic resins. Other kind of acidic catalysts are active for this reaction if their Brönsted acid sites are accessible to protonate the epoxide. Formation of ketone, from the rearrangement of epoxidized methyl oleate, is favored by the presence of strongly acidic catalysts like SAC13 and enhanced by increasing temperature. Polar-protic solvents increase the ketone yield but decrease the ketone selectivity because they are added to the epoxide ring. The mechanism for the epoxide rearrangement is very likely to take place through a hydride migration to the carbocation generated in the acid-catalyzed epoxide ring opening.

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