

Thermal Stability of Oleic Acid and Ethyl Linoleate

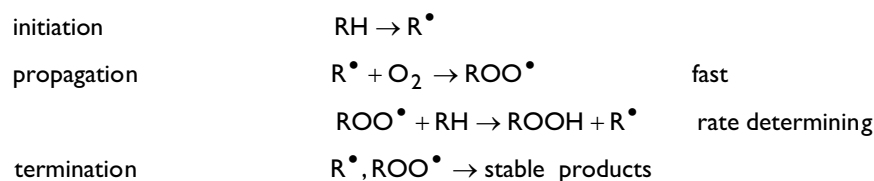
The first part of this work consisted of studying the thermal stability of oleic acid, which was initially a candidate as a starting material for the dehydrogenation of fatty acids using heterogeneous catalysis. The results induced us to search another starting material and to study its properties.

3.1.1 Introduction

Oil-derived products can be subjected to conditions that promote oxidation of their unsaturated components during storage and use. The materials arising during oxidation and subsequent degradation can seriously impair the quality and performance of such products [1, 2]. Thus, oxidative stability is an important issue to face before studying their catalytic reactivity.

The fatty acid alkyl chain is susceptible to oxidation both at double bonds and adjacent allylic carbons. Free-radical and photooxidation at allylic carbons are responsible for deterioration of unsaturated oils and fats [2-6]. Both autoxidation and photooxidation produce hydroperoxides in allylic bonds. During this process, the position and geometry of the double bond may change. The hydroperoxide mixtures produced by autoxidation and photooxidation are not identical, indicating that different mechanisms are involved [4-6].

The autoxidation reaction occurs in the presence of oxygen. Autoxidation is a free-radical chain reaction, which involves the series of reactions that initiate, propagate and terminate the chain [3].



The initiator is a free radical, most probably produced by decomposition of hydroperoxides already present or produced by photooxidation. This decomposition may be thermal, but it is more likely promoted by traces of variable redox state metal ions [1, 2]. The rate of autoxidation generally increases with

increasing unsaturation. Linoleate, as methyl or ethyl ester, reacts approximately 40 times faster than oleate, and for higher polyenes, the rate doubles for each additional bond [2]. The medium also influences the susceptibility to oxidation [7-8].

Consequently, inert conditions are required to work with fatty acids and derivatives due to their susceptibility to autoxidation in the presence of oxygen species.

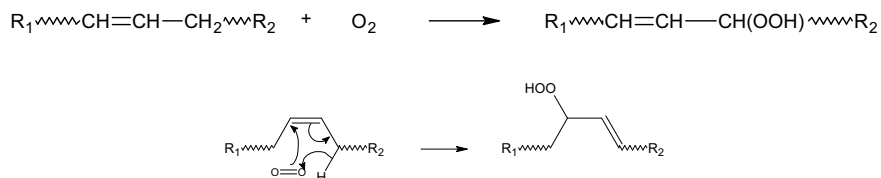


Figure 3.1.1 Ene reaction between singlet oxygen and an olefinic bond. The hydroperoxide may be attached to any of the initial double-bonded carbons.

The combination of light and oxygen promotes the oxidation of unsaturated fatty acids. Ultraviolet radiation decomposes existing hydroperoxides, peroxides, carbonyl and other oxygen-containing compounds, producing radicals that initiate autoxidation [2, 9]. Two types of mechanisms of photooxidation may occur. In type I, a hydrogen or electron is abstracted from the unsaturated oil, producing radicals that initiate chain propagation as in autoxidation. In type II photooxidation, molecular oxygen is converted to its excited singlet state. Singlet oxygen is highly electrophilic and reacts rapidly with olefins in an ene reaction producing hydroperoxides in one of the original olefinic carbons. The double bond is shifted acquiring a *trans* configuration (Fig. 3.1.1) [3]. Photooxidation is much faster than autoxidation [4]. There is less difference in the rate of photooxidation between monoenes and polyenes if compared with autoxidation [10].

The study of the stability of oleic acid consisted of monitoring its chemical changes by effect of temperature, light, metals (stainless steel), which may accelerate oxidation [1, 6, 11-13] and solvent addition [7, 14], which may favour its thermal stability. This stability was studied in terms of oleic acid decomposition. As a result of the study with oleic acid, a new starting material was proposed. The choice was ethyl linoleate. Its stability and advantageous properties are presented in the following section.

3.1.2 Experimental part

In a 250 mL three-necked flask provided with a cooler, 100 mL of oleic acid supplied by Aldrich was stirred, and subjected separately to light, metals (0.1g, stainless steel) and solvents (hexadecane and ethanol) at different temperatures. Hexadecane (99%) and ethanol (99%) were respectively, supplied by Sigma-Aldrich (Germany) and Panreac (Spain). First, ethanol was chosen as a solvent. The volume ratio of mL oleic acid/ mL ethanol was 1:10. The mixture was heated up to the

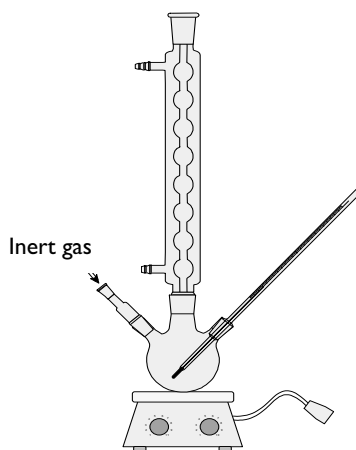


Figure 3.1.2 Apparatus for the study of the stability of fatty acids and derivatives.

wanted temperature. After 15 minutes, a sample was extracted from the mixture and analyzed by GC. The same experiment was repeated in the absence of solvent. The experiments using hexadecane as a solvent were performed under argon stream and in the absence of light. Several mixtures with ratios (mL oleic acid / mL hexadecane) from 4 to 0.11 were prepared. They were heated up at different temperatures (65 °C – 300° C). Samples were taken and analyzed by GC. In order to study the effect of light on oleic acid, the apparatus was covered by an opaque foil. Argon (C-50 purity) was used as inert gas. The whole apparatus (Fig. 3.1.2) was placed in a bath filled with a special high-temperature silicone oil. Ethyl linoleate (>97 %) was supplied by Fluka (Germany). Stability tests proceeded as with oleic acid.

3.1.3 Results and discussion

Presence of light

The exposure of oleic acid to light had a similar effect between 200 °C to 300 °C under inert conditions (Fig. 3.1.3). Ultraviolet light is responsible to decompose oxygen-containing substances which give place to radicals [2]. These radicals will

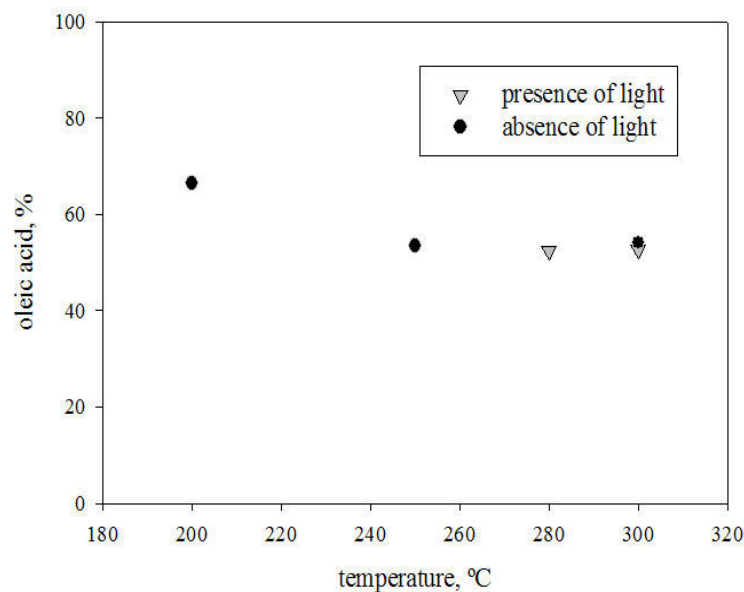


Figure 3.1.3 Effect of ultraviolet exposure in the stability study of oleic acid solved in ethanol (1:10).

promote autoxidation causing a decrease of % of oleic acid. However, temperature effect appeared to be more important than light effect, since the same % of oleic acid was obtained from 240 °C to 300 °C with and without light. In all cases the value of % of oleic acid was around 53 %, which indicated an important degradation.

Effect of stainless steel

The important levels of degradation detected in stainless steel presence indicated that stainless steel components, such as iron, chromium, nickel, etc. performed a

catalytic role in the oxidation reaction. Stainless steel accelerated the oxidation, so that only 23 % of oleic acid did not decompose. Stainless steel brought about the formation of peroxides, which are the species formed initially during oxidation [1, 15]. This instability of oleic acid in front of stainless steel presence forced the use of quartz reactors during our research work.

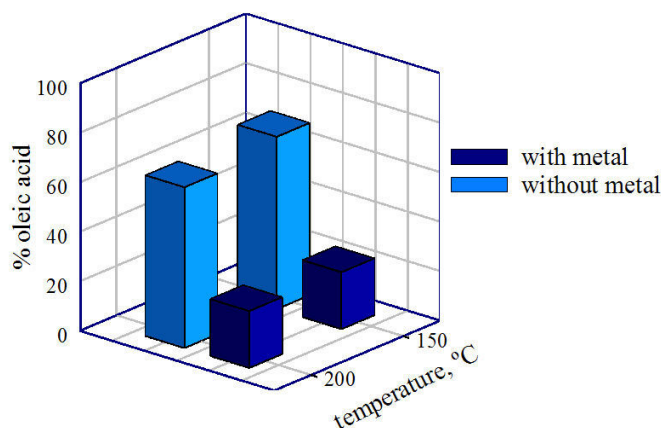


Figure 3.1.4 The effect of metal presence and absence.

Addition of a solvent

As far as a liquid-phase catalytic reaction is concerned, the use of a solvent makes easier the mass transfer of the reactants towards the active sites of the catalyst. The introduction of a solvent may also hinder the oxidation of fatty acids [14, 16]. The % of remaining oleic acid after 15 min. versus temperature with and without ethanol is presented in Fig. 3.1.5. The results in both cases at 150° C and 200° C do not significantly differ showing a % of oleic acid around 70 %. Nevertheless, the difference increases at 250° C. At this temperature, the % of remaining oleic acid considerably decreases in the absence of ethanol. Despite the use of ethanol, inert conditions and absence of ultraviolet light, oleic acid still exhibited considerable degradation. At this point, another solvent was considered to be used. The main reason was the low boiling point of ethanol, which made difficult the sampling due to constant reflux. Moreover, the constant gaseous state of the solvent in the mixture flask due to high temperatures (150 °C-300 °C) did

not help to achieve a solvation effect, which is supposed to partly avoid the oxidation of oleic acid.

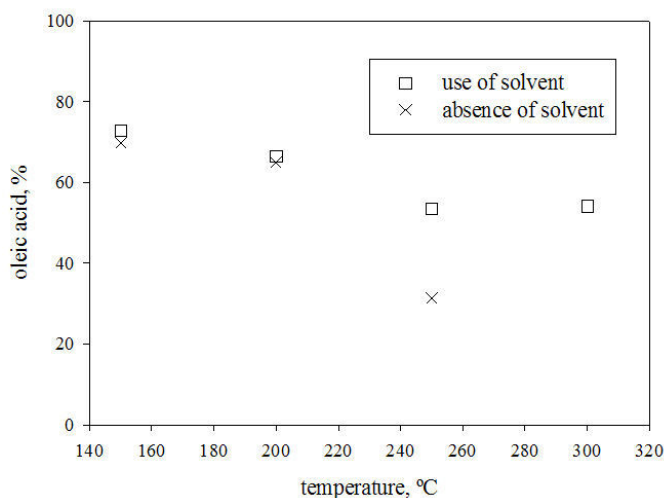


Figure 3.1.5 Effect of ethanol in the thermal study of oleic acid.

Hexadecane was chosen as an alternate solvent because of its similar boiling point and vapour pressure to those of oleic acid, which should facilitate the simultaneous evaporation of both fluids, so that the solvation effect of hexadecane still remains in the vapour phase. Oleic acid appeared to be more stable than with ethanol as a solvent. Oleic acid hardly oxidized, when the mixture ratios were lower than 0.36 (Fig. 3.1.6). At ratios between 0.11 and 0.36, the percentage of oleic acid reached values near 100%. However, a strong oxidation of the fatty acid was induced at ratios of 2.5 and 4 and % of oleic acid decreased achieving values from 40 % to 55 %. At low ratios, the hexadecane as a solvent even avoids the oxidation due to temperature. When the amount of hexadecane in the mixture is

higher than that of oleic acid, a good solvation effect may be achieved, in such a way that oleic acid molecules remained well isolated. Unlike the case of ethanol, the solvation effect takes place in liquid and gaseous phases. This fact may explain the high resistance of the mixture oleic acid/hexadecane to the oxidation at high temperatures. Thus, hexadecane avoids the thermal degradation of oleic acid probably because of a solvation effect. Although this solvation effect arises as a disadvantage in catalytic reactions, as it may difficult the adsorption step, it might be

interesting in other cases, such as in the storage processes of biodiesel, where oxidative stability is required [12, 13].

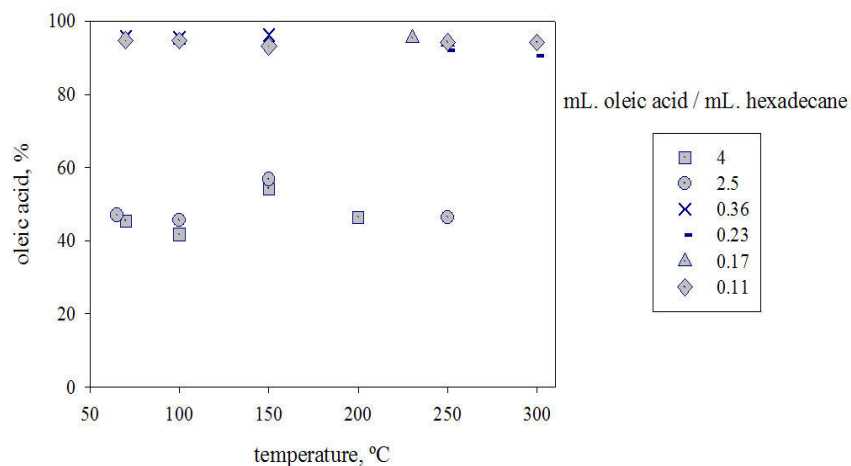


Figure 3.1.6 Effect of volume ratio (mL oleic acid/mL hexadecane) in the stability of oleic acid vs. temperature.

Concerning the physical properties of oleic acid, concretely its relatively high boiling point, it represented a major difficulty to work with it. The ease of carboxylic acids to form hydrogen bonds (Fig. 3.1.7) induces the formation of dimers, which increase the boiling point up to 360 °C [17] This feature prevented us once more from using oleic acid as a starting material.

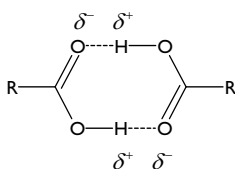


Figure 3.1.7 Dimer formation of carboxylic acids.

Ethyl linoleate in vapour and liquid phase

Due to the negative results in the catalytic activity of oleic acid, their thermoxidative properties and its high boiling point, an alternate option was searched. The new

choice had to show mainly two features: one concerning the thermal and chemical stability, and another one concerning favourable thermodynamics.

In organic synthesis, the ester group can be inserted into a molecule by chemical modification of a functional group, such as alcohol or carboxylic functionality in order to obtain chemoselectivity in a subsequent chemical reaction [18, 19] This protective effect of the ester was used in this case to favour the reactivity in the hydrocarbon unsaturated chain avoiding the reactivity of the carboxyl group. Besides, this protective group configures an added stability to the compound. Consequently, ethyl linoleate presented an important advantage, since the decomposition caused by temperature was negligible under inert conditions in both liquid and gas phase in quartz reactors. A clean GC chromatogram and no darkness indicating degradation of the compound were detected when heating ethyl linoleate at 200 °C. The fact of using ethyl linoleate added likewise a benefit from the point of view of reaction thermodynamics, which is more favourable than in the case of oleic acid (see *Introduction*). For all these reasons, ethyl linoleate was chosen as the starting material to study its catalytic dehydrogenation in vapour and liquid phases.

3.1.4 Conclusions

Photooxidation was not presumably the main factor responsible for the oxidation of oleic acid, since similar results were obtained with and without light exposure. Oleic acid presented a low thermal stability basically due to autoxidation at high temperature, even under inert conditions, possibly because of endogenous peroxides. Stainless steel metallic components played a catalytic role accelerating the decomposition of oleic acid in their presence.

The use of a suitable solvent, such as hexadecane, avoids the decomposition of oleic acid at temperatures up to 300 °C. However, it may show some other complexities concerning the reactivity towards dehydrogenation. From the point of view of fatty acid stability, ethanol was a poorer stabilizer than hexadecane in the temperature range between 150 °C and 300 °C.

The use of a fatty acid ester instead of an oleic acid as a dehydrogenating starting material rewards us with milder experimental conditions, better reaction thermodynamics, lower boiling point and a decrease/removal of thermal degradation.

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