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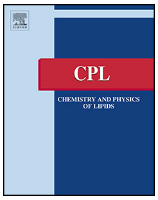

Chemical and thermochemical aspects of the ozonolysis of ethyl oleate: Decomposition enthalpy of ethyl oleate ozonide

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ABSTRACT

Neat ethyl oleate was ozonized in a bubble reactor and the progress of the ozonolysis was followed by infrared (FT-IR) spectroscopy and by the differential scanning calorimetry (DSC). The ozonolysis was conducted till a molar ratio $O_3/C{=}C \approx 1$ when the exothermal reaction spontaneously went to completion. A specific thermochemical calculation on ethyl oleate ozonation has been made to determine the theoretical heat of the ozonization reaction using the group increment approach. A linear relationship was found both in the integrated absorptivity of the ozonide infrared band at 1110 cm^{-1} and the ozonolysis time as well as the thermal decomposition enthalpy of the ozonides and peroxides formed as a result of the ozonation. The DSC decomposition temperature of ozonated ethyl oleate occurs with an exothermal peak at about 150–155 °C with a decomposition enthalpy of 243.0 kJ/mol at molar ratio $O_3/C{=}C \approx 1$. It is shown that the decomposition enthalpy of ozonized ethyl oleate is a constant value (≈243 kJ/mol) at any stage of the $O_3/C{=}C$ once an adequate normalization of the decomposition enthalpy for the amount of the adsorbed ozone is taken into consideration. The decomposition enthalpy of ozonized ethyl oleate was also calculated using a simplified thermochemical model, obtaining a result in reasonable agreement with the experimental value.

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1. Introduction

In recent years there was a growing attention to the ozonized vegetable oils because it was discovered that they have interesting germicidal properties and are being used as ingredients in pharmaceutical and cosmetic formulations (Lezcano et al., 2000; Fernández Torres et al., 2006; Díaz et al., 2006; Menéndez et al., 2008; Skalska et al., 2009; Hernández et al., 2009). Even wound healing effects were attributed to ozonated vegetable oils (Sakazaki et al., 2007). According to a review made by Kadesch in 1963, the disinfecting properties of ozonized vegetable oils are known since 1898. Germicidal and fungicidal properties of ozonized oils were assessed already in the thirties and forties of the previous century and consequently were proposed as ointments for the treatment of burns (Kadesch, 1963).

Although there is a great enthusiasm around ozonized vegetable oils, there is also some results which invite to be cautious in the application of such oils (Kataoka et al., 2009). In fact, the work of the latter authors refers to the application of crude ozonized oil which leads to the development of inflammatory responses, such as vasodilation, swelling and epidermal hyperplasia and contact hypersensitivity. However, it is common practice to use ozonized vegetable oils only as compounding ingredient in cosmetics and other topical applications with typical concentrations of about 10% of ozonized oil in the formulation (Cirlini et al., 2012). Furthermore, the toxicity of methyl linoleate ozonide was assessed in rats only by intravenous injection while no toxicity was observed by intraperitoneal injection (Hempenius et al., 1993) and topical applications.

The interest on ozonized vegetable oils and the ozonides of methyl esters of fatty acids goes also beyond the potential cosmetic and pharmaceutical application since it was found that these compounds are able to enhance the combustion performances of biodiesel and to change favourably the relative congealing point (Baber et al., 2005; El Rafie and Attia, 2008).

As a consequence of the potential applications of ozonized vegetable oils, a certain number of papers dealing with their synthesis and characterization of these oils appeared in literature (Ledea et al., 2001; Díaz et al., 2001, 2003; Díaz Gómez et al., 2004; Díaz et al., 2005a,b; Soriano et al., 2003, 2005; Martinez Tellez et al., 2006; Sadowska et al., 2008; Díaz et al., 2008; Sega, 2010; Díaz et al., 2012; de Almeida et al., 2012). The ozonization of the vegetable oils was studied with FT-IR, H NMR spectroscopy, and chromatography, by monitoring the acid number, the peroxide number, the iodine number, the viscosity and the refractive index of these oils as function of the ozonation time in order to throw more light on the chemical processes and chemical structures involved in the ozonation of vegetable oils as well as with the purpose of finding a suitable analytical instrument to monitor the degree of ozonation

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to the desired level, thus for quality control purposes. Despite the abundant studies available, none to the best of our knowledge has studied the ozonized vegetable oils from the thermochemical standpoint with the exception of the work of Soriano et al. (2005) who measured only the decomposition enthalpy of ozonized sunflower oil methyl ester.

The purpose of this paper is to show how the systematic application of thermal analysis of ozonized oils can be used to monitor the degree of ozonization reached by the oils and also throw more light on the complicated reactions involved. In this study we have selected ethyl oleate as a simple model molecule of fats and submitted it to ozonolysis monitoring the thermal decomposition enthalpy by DSC (differential scanning calorimetry) as function of the ozonation time as well as the evolution of the FT-IR spectrum. Furthermore, we have performed theoretical calculations on the heat of reaction produced in the ozonolysis of ethyl oleate and on the decomposition enthalpy of the resulting ozonides and compared the calculation results with the experimental data.

2. Experimental

2.1. Materials and equipment

Ethyl oleate (European Pharmacopoeia grade) was purchased from Fluka. All other reagents for iodometry (KI, acetic acid, acetic anhydride, sodium thiosulphate) were analytical grades from Aldrich.

The DSC measuments were performed on a Mettler-Toledo DSC-1 Star System using conventional aluminium crucibles with punched caps as sample holder. Samples of 10 mg of ozonized oil were scanned at a rate of 10 °C/min under nitrogen flow.

The FT-IR spectra of ozonized ethyl oleate samples were analyzed on a Nicolet 6700 FT-IR from Thermo Scientific in reflectance mode using a ZnSe crystal as sample holder and the Omnic software to convert the reflectance spectra recorded to a conventional absorbance spectrum.

2.2. Ozonolysis of ethyl oleate

Ethyl oleate (130 mL, $d = 0.87$ g/mL, 113.1 g, 0.364 mol) was charged in a bubble reactor and treated with a stream of dried and ozonized air at a flow rate of 3.5 L/min. The amount of O_3 passed through the oil was of 0.0260 mol/h. The exit of the bubble reactor was connected with a train of gas washing bottles half-filled with 5% KI solution containing 1.5% acetic acid. The unreacted ozone escaping from the bubble reactor was trapped the KI solution and determined each hour by titration with $Na_2S_2O_3$ 0.1 M. The ozone reaction with ethyl oleate is nearly quantitative for hours and only when the molar ratio $O_3/C{=}C \approx 1$ is reached, the O_3 emerged unreacted from the bubble reactor (see Section 3). Sampling of the ozonized oil was made every hour taking out just a drop of the reaction mixture to perform both the DSC and FT-IR analysis. The study was repeated three times to confirm the repeatability of the results.

3. Results and discussion

3.1. FT-IR analysis of ozonized ethyl oleate

The FT-IR spectra of a series of ozonized ethyl oleate samples are shown in Fig. 1 in comparison to the reference spectrum of pristine ethyl oleate. The effect of the ozone addition to the double bond of ethyl oleate can be essentially observed at about 1110 cm^{-1}. Pristine ethyl oleate presents a medium-weak doublet in this region at about 1117 and 1097 cm^{-1} essentially attributable to the C—O stretching of the ester group (Bellamy, 1975). These two bands are gradually overlapped by the strong ozonide band at about 1110 cm^{-1} which is due to 1,2,4-trioxolane ring (Bellamy, 1975; Bailey, 1978; Razumovskii and Zaikov, 1984; Rakovsky and Zaikov, 1998; Soriano et al., 2003). The linear growth of the ozonide band at 1110 cm^{-1} as function of the ozonolysis time can be appreciated in Fig. 2. In this figure, the integrated intensity of the band, as measured with the Omnic software of the FTIR spectrometer was subtracted from the initial intensity of the bands at 1117 and 1097 cm^{-1} of pristine ethyl oleate and reported in the graph as function of the ozonolysis time. Fig. 2 suggests a linear

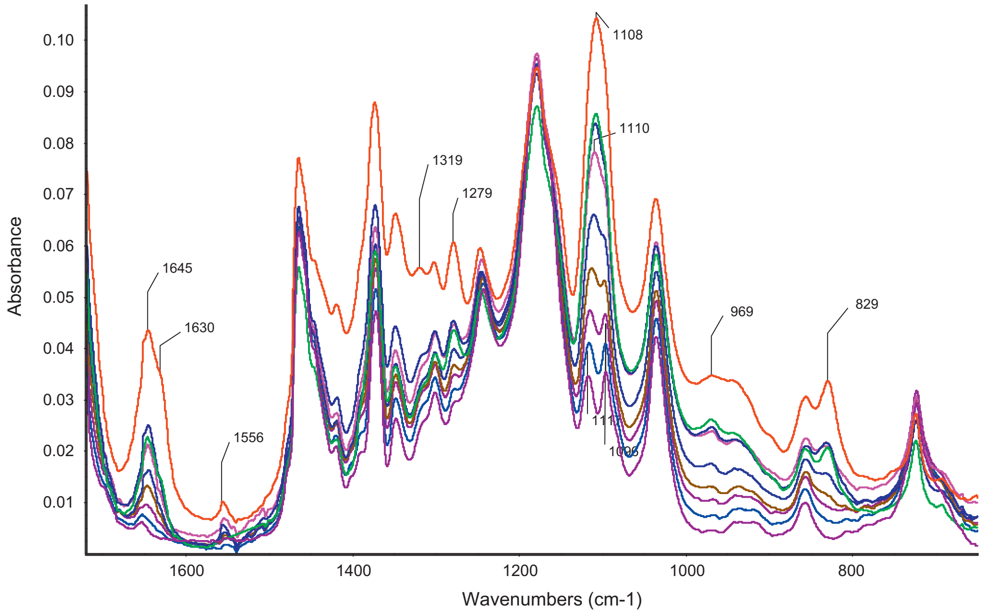

Fig. 1. FT-IR spectra of ethyl oleate. From bottom to top: reference, pristine ethyl oleate, spectra recorded after 1, 2, 3, 4, 6, 8, 10, 11 and 12.5 h ozonolysis respectively. Note the growth of the infrared band at about 1110 cm^{-1} as function of the ozonolysis time. Only in the later ozonolysis stage i.e. 12.5 h there is a generalized increase in the baseline between 1430 and 800 cm^{-1}.

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