

In situ ATR studies on the mechanism of limonene epoxidation over PW-Amberlite

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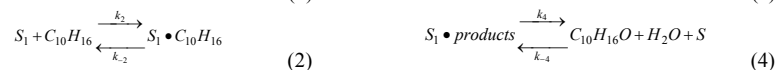
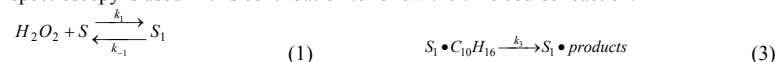
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Introduction

PW-Amberlite is a promising catalyst for limonene epoxidation with aqueous hydrogen peroxide and acetonitrile as solvent; limonene conversion and limonene epoxide selectivity higher than 80 % and 90 %, respectively, have been reported [1,2]. The mechanistic pathway proposed for limonene epoxidation on PW-Amberlite [3], includes the interaction of H₂O₂ with peroxophosphotungstate species to form polyperoxophosphotungstate active sites, where limonene is adsorbed and reaction takes place, Eqs. 1 - 4. The catalytic cycle is completed with reaction products desorption. *In situ* Attenuated Total Reflection (ATR) IR spectroscopy is used in this contribution to follow the time course reaction.



Materials and Methods

PW-Amberlite was synthesized as reported elsewhere [2]. FTIR spectra were collected with a Nicolet 740 spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. Each spectrum was recorded with 64 scans in the 4000 – 800 cm⁻¹ spectral range with a resolution of 4.0. A flow cell with a channel of 1.1 cm³ and a silicon gasket sealed ZnSe ATR element was used. A suspension (1.2 mg/mL) of PW-Amberlite in acetone was used for catalyst deposition onto the ZnSe ATR element [4]. The liquid samples contained in a 25 mL magnetically stirred glass flask heated with a thermal jacket at 38 °C were pumped through the cell at a flow rate of 36 cm³/min using a gear pump drive. The thermally isolated Teflon lines were as short as possible to avoid dramatic temperature gradients between the cell and the glass flask. The cell temperature was kept at 33 °C using a K thermocouple and a temperature controller. The background was collected allowing the solvent to flow through the cell; then, aqueous H₂O₂ was added to the glass flask and the spectra collected at 3 min intervals for two hours. Then, a new background was collected for avoiding signal overlapping and after that limonene was added to the mixture. Data acquisition continued for 8 h.

Results and Discussion

Limonene IR spectrum has a characteristic band signal in the 910-880 cm⁻¹ range that is attributed to the =CH and =CH₂ out of the plane bending vibration [4]. It was observed that its intensity decreased with time. The interaction between aqueous hydrogen peroxide, limonene and catalyst is evidenced in Fig. 1. The bands in the 1145 - 970 cm⁻¹ region are attributed to oxygen interaction with phosphorous, and to P-O-C symmetric and asymmetric stretching vibrations [5]. The bands between 960 - 800 cm⁻¹ have been assigned to oxygen

interactions with tungsten [5]. Given that IR signals of peroxophosphotungstate from catalyst samples and IR signals of solvent and water or aqueous hydrogen peroxide were subtracted as background, the observed signal should correspond to interactions of polyperoxophosphotungstate species with limonene. The weak multiple signals in the 880-840 cm⁻¹ region are due to the epoxy group vibration of limonene epoxide formation. As shown in Fig. 1 IR signals between 840-820 cm⁻¹ attributed to W=O and O-O interactions¹, might be related to reaction intermediates [5]. The possibility to assign these signals to other reaction products is not considered because only limonene and limonene epoxide were detected by GC analyses [1].

Significance

Spectroscopic evidences allow validation of the previously mechanistic pathway proposed. Thus, the kinetic expressions that have been derived [3] appear to be congruent with that mechanism.

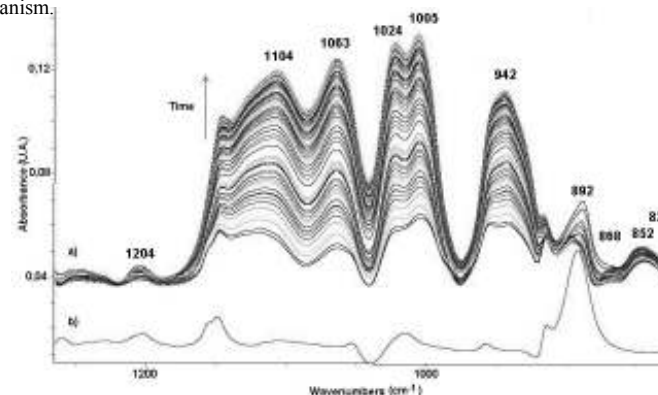


Figure 1. *In situ* IR ATR for limonene epoxidation on PW-Amberlite (33 °C). 1250 – 820 cm⁻¹ spectral region; a) spectra recorded at 15 min interval for reaction mixture; b) reaction mixture without oxidant (1 h).

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