

1. Kinetics of adsorb alkene reactions with O(³P).

During Year 3 we have carried out reactions between adsorbed hydrocarbons 1-hexene and cyclohexene at 140 mTorr of O₂ base pressure. Our in situ infrared spectroscopy allowed the study of product formation and the different oxidizing mechanisms for each hydrocarbon species. For 1-hexene, the *in situ* analysis shows immediate hydroxyl, carbonyl and epoxide formation (Figure 1). The valleys in the spectra indicate reactant loss and the peaks indicate product formation. As time progresses through the reaction, carbon-hydrogen and carbon-carbon bonds within the 1-hexene are broken, indicating oxygen radicals attaching to the hydrocarbon structure, as well as the possibility of a fragmentation of the molecule. As time progresses through the reaction, the O(³P) radicals degrade and entirely break apart the 1-hexene.

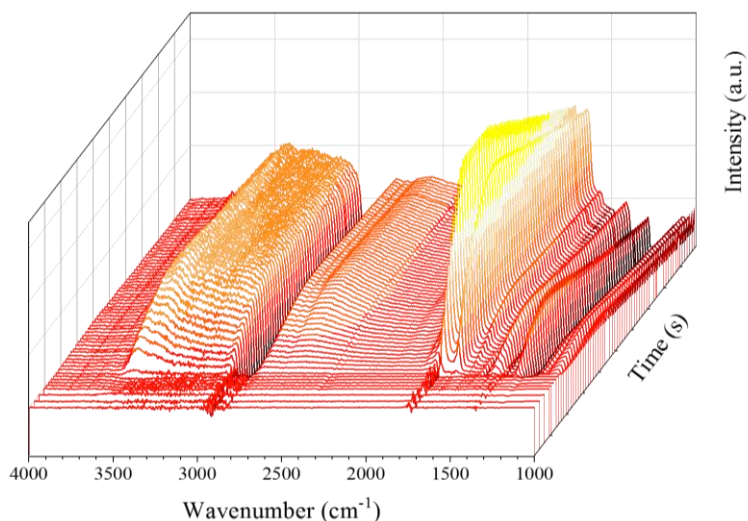


Figure 1. A time-progression of the surface reaction. Vibrational spectroscopy of the reaction 1-hexene and O(³P) (Oxygen pressure: 142 mTorr). Valleys correspond to reactant loss and peaks indicate product formation.

As mentioned in the annual report for Year 2 of this project, the oxidation reactions with the non-thermal plasma generated O(³P) radicals occur through pseudo first-order rate kinetics, with respect to the organic under constant oxygen pressure. During Year 3, we developed the mathematical model to describe the kinetics of the reaction, described below:

$$\frac{d[Organic]}{dt} = -k [O(^3P)][Organic] \quad (1)$$

Where [Organic] represent the hydrocarbon coverage on alumina. Under the assumption that the oxygen radical concentration will stay constant, $k' = k [O(^3P)]$:

$$\frac{d[Organic]}{dt} = -k' [Organic] \quad (2)$$

$$\int_0^t \frac{d[Organic]}{[Organic]} = - \int_0^t k' dt \quad (3)$$

$$\ln\left(\frac{[Organic]_t}{[Organic]_0}\right) = -k't \quad (4)$$

Since the reaction can be carried out to completion, a mass balance implies that [Organic]₀ is equal to [Organic]_∞, thus:

$$\frac{[Organic]_t}{[Organic]_\infty} = e^{-k't} \quad (5)$$

Where the concentration of adsorbed organics is equivalent to the integrated absorbance:

$$\frac{Abs_t}{Abs_\infty} = e^{-k't} \quad (6)$$

The oxygen pressure is kept constant throughout the reaction, which allows us to determine the rate constant (k') by examining the exponential curve for the absorbance changes in the organic throughout the reaction (Figure 2A).

The carbon-hydrogen peak (and all other spectral features) are surface normalized for every reaction by dividing the absorbance at a specific time and wavenumber by the individual surface area and average carbon-hydrogen peak absorbance (Figure 2). This method has allowed the direct comparison of the kinetics of several substrates, and derive a k' for the organic, specifically, 1-hexene and cyclohexene.

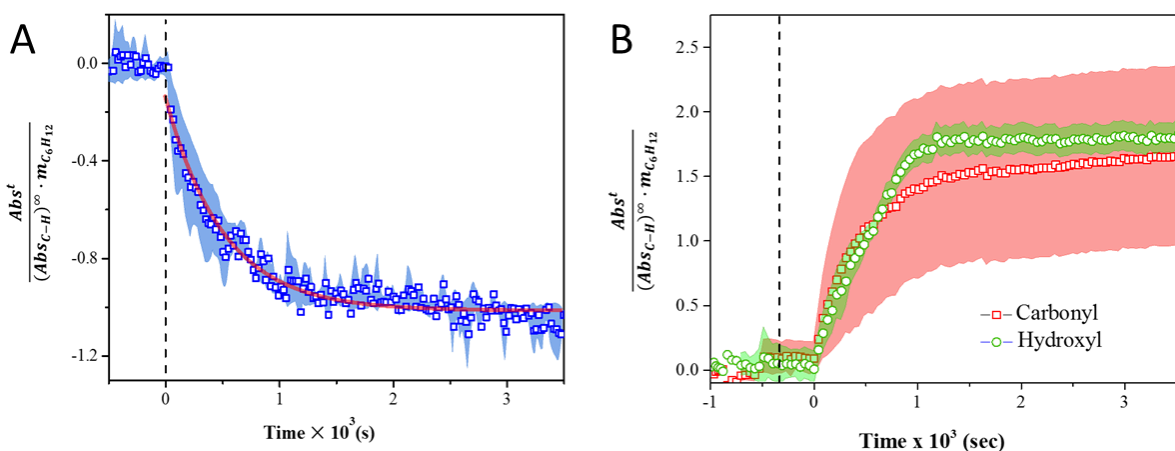


Figure 2. (A) Normalized measurements of the C-H stretch ($\sim 3000\text{-}2820\text{ cm}^{-1}$), of 1-hexene under reaction with non-thermal plasma generated $O(^3P)$ radicals ($\sim 145\text{ mTorr}$). (B) Normalized measurements of the hydroxyl ($\sim 3600\text{-}3000\text{ cm}^{-1}$) and carbonyl ($\sim 1740\text{-}1530\text{ cm}^{-1}$) wavenumber range of 1-hexene under reaction with non-thermal plasma generated $O(^3P)$ radicals ($\sim 145\text{ mTorr}$). Shaded region represent standard deviations over multiple experiments.

To derive the k' value, since the reaction is first-order with respect to the organic, an exponential curve can be fit to the slope of the carbon-hydrogen absorbance intensities throughout the reaction. As shown in Figure 2, the data points were fit to an exponential curve which yielded a k' value of $(1.96 \pm 0.08) \times 10^{-3}\text{ s}^{-1}$.

2. Ex situ analysis of surface bound products.

Upon non-thermal plasma oxidation with a cyclohexene-alumina surface, the reacted organic coating was extracted by partitioning it in a methanol bath. The extracted organic fraction was analyzed in a method developed using gas chromatography-mass spectrometry (GC-MS). Through the GC-MS analysis, the products of the Eley-Rideal reaction were identified. The main surface bound products are in good agreement with the *in situ* vibrational spectral analysis: epoxy-cyclohexane, hydroxycyclohexanone, 2,5-cyclohexadienone, 1-cyclohexen-1,2-diol, cyclohexanone, cyclohexenone, cyclohexene, 1,4-cyclohex-2-enedione, cyclohexadienone, and cyclohexenol.

In addition, GC-MS analysis also indicated that the reacted hydrocarbons also polymerized on the alumina surface, affecting oxidation patterns and product formation. GC-MS evidence of the adsorbed molecules on neighboring sites of the surface reacting indicated that Langmuir-Hinshelwood mechanisms were also occurring. Upon surface analysis, products like 1,1-bi(cyclohexan)-1-ene, and [1,1'-bi(cyclohexan)]-2'-ene-2,3-diol were found.

3. Impact

This project has opened a new line of research in my scholarly work. The impact of Year 3 has been mostly on the development of a method for kinetic analysis and the study of products via GC-MS. Support from PRF has allowed me to establish a network with another computational chemist, bringing the necessary scientific discussions between specialists that sometimes is not found at small primarily undergraduate institutions.

In addition, several students have received hands-on experience in spectroscopic techniques, surface science, and computational methods. Two students supported during Year 3 of this grant have been able to attend scientific conferences and gain experience on dissemination and presentations.