A Kinetic Study of the Oxidation of Chemisorbed Hydrocarbons by the Non-Thermal Plasma
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1. Reactions of adsorb hydrocarbons with O(^{3}P).

For a general oxidation reaction described in equation 1, the kinetic rate law indicates that changes in the concentration of O(^{3}P) allow for adjustments in the rate of the reaction (equation 2). Thus, during Year 2 we have optimized the heterogeneous reaction protocol and determined that reactions must be carried out at 140 mtorr of O$_2$ base pressure. Under this condition, it is possible to conduct kinetic analysis and minimize the loss of surface-bound species.

$$C_nH_m(a) + yO(^3P)(g) \xrightarrow[Al_2O_3]{} C_nH_{m-y}(OH)_y(a) \tag{1}$$
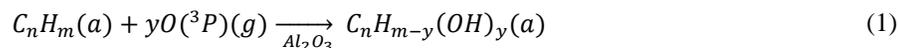
where *y* represents the extent of reaction on the substrate. The rate law of the formation of products (illustrated as a single first step oxidation in equation (1)) is proportional to the partial pressure of O(^{3}P):

$$\frac{d\ (C_nH_{2n}(OH)_y)}{dt} = k\theta_{C_nH_m}P_{O(^3P)}^y \tag{2}$$

Equation 2 suggests that the base pressure of oxygen is proportional to the rate of the reaction. Therefore, oxidation reactions carried out at an oxygen base pressure of 140 mTorr, were the partial pressure of O(^{3}P) ($P_{O(^3P)}$) reaches a minima (see Year 1 annual report). In addition, the reaction rate depends on the coverage of hydrocarbons in the alumina surface ($\theta_{C_nH_m}$), so all data is now normalized to the surface of alumina.

During Year 2, three different hydrocarbons have been processed by O(^{3}P) under the conditions described above: hexane, 1-hexene, and cyclohexane. The reaction method was developed and optimized to ensure surface coverage normalization of data. Figure 1 shows the vibrational spectroscopy sequence of the oxidation reaction of 1-hexene on alumina. At time t=0 the plasma discharge begins. The three regions highlighted in the Figures 1A, 1B, and 1C, represent different oxidation functional groups. The red region in Figure 1A shows a rapid growth of OH functional groups, while the dark blue region highlights the loss of C-H bonds. This suggests an oxidation step where O(^{3}P) abstracts a hydrogen to form an OH, leading to the formation of alcohols. Further reaction with O(^{3}P) forms carboxylic groups, as seen by the growth of peaks in Figure 1B. Also shown in Figure 1B is a decrease in absorbance due to the loss of the alkene double bond.
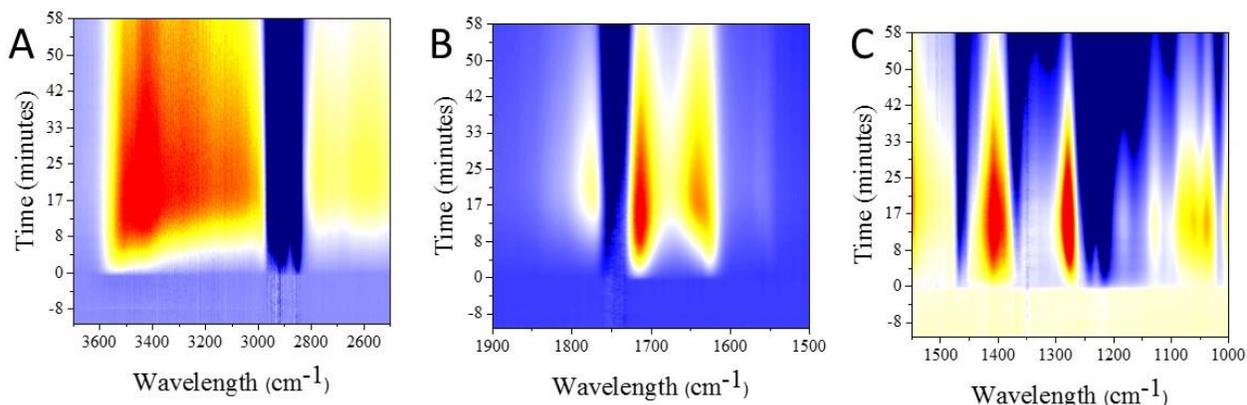

Figure 1. Vibrational spectroscopy contour of the oxidation reaction of 1-hexene with O(3P) at room temperature. For clarity, the intensity color map has been adjusted for three different section of the spectral sequence. Time t=0 (y-axis) indicates the plasma discharge. Red-yellow indicate a product has formed, dark blue indicates the loss of reactant 1-hexene.

The features growing in Figure 1C are associated to the formation of epoxy on the substrate. These vibrational frequencies have been elucidated using computational models described in the next section.

2. Computational model

The chemisorption of hydrocarbons on alumina was modeled and correlated to experimental data. Energy minimized structures and calculated vibrational frequencies were performed on a binuclear cluster including an Al$_2$O$_3$ active site. All energy minimizations and vibrational frequency calculations were performed on a binuclear cluster,

including an Al_2O_3 active site and the organic substrate. The calculations were performed using Becke's three parameter hybrid model with LYP correlation (B3LYP) using a basis set of 6-31+G(d). The calculations were performed and viewed using Gaussian 09 and GaussView software. These calculations suggest that the electron density of the hydrocarbons shifts towards the Al_2O_3 adsorption site, which increases the probability of reaction of free radicals with carbon atoms near the surface.

The energy minimization and vibrational frequency calculations were performed on a binuclear cluster including an Al_2O_3 active site. In addition, the energies of several heterogeneous reactions of cyclohexene and $O(^3P)$ were calculated. The experimental data indicates multiple oxidations of cyclohexane, leading to the ring being opened and ultimately the formation of carbon dioxide. We were able to match quantum chemical calculations of surface-bound species with experimental data. Figure 2 is a general reaction pathway for the oxidation reaction as model using Density Functional Theory (DFT). Oxidations of cyclohexane, begins with the initial formation of an alcohol via hydrogen subtraction. Further oxidation leads to carbonyl groups and a combination of alcohol and carbonyl group.
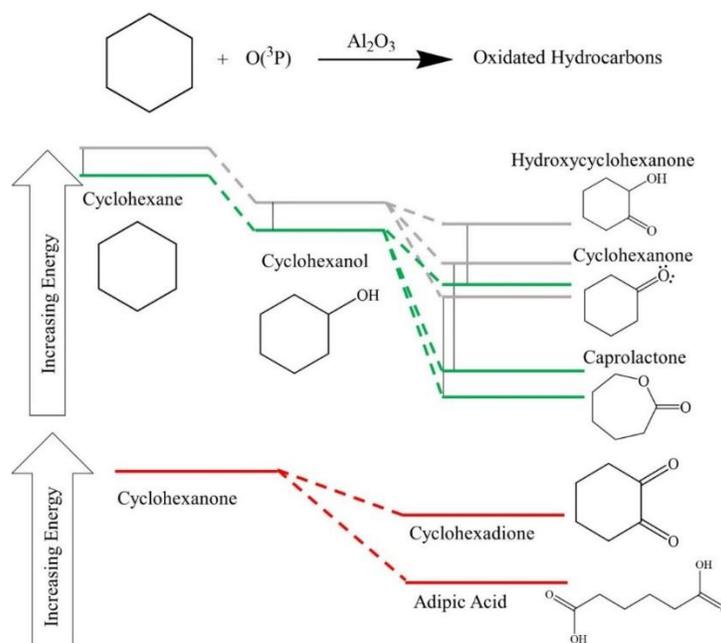

Figure 2: Computational model of cyclohexane oxidation by $O(^3P)$. Gray lines show the reaction occurring without the alumina surface. Green lines show the reaction occurring while adsorbed to the alumina surface. Average Surface Adsorption Energy was calculated at -55.6 kcal mol^{-1}. Similar calculations were conducted for 1-hexene and hexane.

3. Impact

This project has opened a new line of research in my scholarly work. The impact of Year 2, in particular, consisted of not only a novel spectroscopic experiment for heterogeneous processes but also new directions on computational chemistry. Support from PRF 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. Students supported during year 2 of this grant have been able to attend scientific conferences and gain experience on dissemination and presentations.

4. Year 3 goals

Year 3 will concentrate on kinetic model for the reaction between $O(^3P)$ and chemisorbed hydrocarbons. We will continue to examine the possibility of *ex situ* analysis via GC-MS by extracting any surface-bound products, desorbed products. We will continue with computational simulation of the adsorbed reactants and products and the simulation of the chemical reaction between adsorbed hydrocarbons and $O(^3P)$. Finally, we will write a manuscript based on this work with the initial intention to submit it to The Journal of Physical Chemistry A.