Synchrotron Photoionization Study of the O(3P) + Alpha-Angelica Lactone (AAL) at 550 and 700K

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Introduction

Accessible energy is crucial for the sustainability of modern societies. During the last century, fossil fuels have been used as the main source of energy in the world; fossil fuel sources are diminishing while the global demand for energy is growing. Thus, investment in finding alternative fuels, which would be more efficient, sustainable, and environmentally friendly is increasing. In recent years biofuels have been receiving great attention because of their potential in decreasing carbon emissions and providing a long-term renewable solution to unsustainable fossil fuels.

Other advantages of biofuels to make them a more attractive alternative are their accessible source and their relative ease of processing. During the last century, fossil fuels have been used as the main source of energy.

Methods

The experiment was performed at Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source (ALS) of LBNL. Reaction species were identified by multiplexed time and energy-resolved mass spectrometry coupled with tunable synchrotron radiation for photoionization. A three-dimensional data block, consisted of the ion signal as a function of photon energy (eV), mass-to-charge ratio (m/z), and reaction time (ms), was collected. Two-dimensional slices of the three-dimensional data were obtained by fixing one variable (Figure 1). The reactants have negative signals from kinetic time traces (ion signal vs kinetic time) and products show positive signals. Figure 2 shows the kinetic time traces of primary products compared with the reactant which is multiplied by -1 at 550K. Then the signal was integrated in the 20-60 ms time range for minimizing the presence of nonprimary products at two temperatures.

In this research, the branching fraction of each primary product is calculated by the following equation:

\[ \text{Branching Fraction} = \frac{K_{n}}{K_{n} + K_{m} + K_{s}} \]

where \( K_n, K_m, \) and \( K_s \) are concentrations of the product and reactant, \( S_n \) and \( S_m \) represent signals from the PIS at 11 eV in this study. \( M_n \) and \( M_m \) are the mass of primary products and reactant to the power of 0.67, \( \phi_n \) and \( \phi_m \) represent the energy-dependent PI cross-sections.

The structures of identified molecules were optimized by the CBS-OB3 composite method to find zero-point vibrational energy (E0), which allows calculating the various thermodynamic quantities; for instance, enthalpy of reaction and adiabatic ionization energy (AIE). Then simulated PIS based on the Frank-Condon approximation were obtained using the B3/0P functional level of theory with the basis set of CBSQ7. The available literature or simulated PIS was used to identify the primary products (Figure 3).

Table 1. Primary products with mass-to-charge ratio and PI energy at 550K. The same products except for methyl ketene (m/z 56) and 5-methyl-2,4 furandione (m/z 114) are observed at 700 K.

<table>
<thead>
<tr>
<th>Primary Product</th>
<th>Mass-to-charge ratio (m/z)</th>
<th>PI energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketene</td>
<td>42</td>
<td>9.58</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>44</td>
<td>10.1</td>
</tr>
<tr>
<td>Methylaldehyde</td>
<td>44</td>
<td>10.1</td>
</tr>
<tr>
<td>Methyl ketene</td>
<td>56</td>
<td>9.64</td>
</tr>
<tr>
<td>Methyl vinylketone</td>
<td>70</td>
<td>9.64</td>
</tr>
<tr>
<td>Methyl glycol</td>
<td>72</td>
<td>9.59</td>
</tr>
<tr>
<td>Methyl glycolaldehyde</td>
<td>72</td>
<td>9.59</td>
</tr>
<tr>
<td>Dimethyl glycol</td>
<td>80</td>
<td>9.13</td>
</tr>
<tr>
<td>5-methyl-2,4 furandione</td>
<td>114</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Diagram of the three-dimensional dataset (the middle diagram) of photon energy, mass-to-charge ratio (m/z), and time (ms) obtained at the ALS in Berkeley, CA. PI curve (top left) and Time traces (top right).

Figure 2. Kinetic time traces of primary product (m/z 42) and the increased time traces of reactant at 550K. The kinetic time trace of the primary product matches well with the inverse curve of the reactant.

Figure 3. Experimental PIS plots with appended kinetic/evolved PIS curves of primary products at 550K. The primary products are ketene (m/z 42), acetaldehyde (m/z 44), methyl ketene (m/z 56), methyl vinylketone (m/z 70), methyl glycolaldehyde (m/z 72), dimethyl glycol (m/z 80), and 5-methyl-2,4 furandione (m/z 114). The product masses are multiplied by -1 at 550K.

Acknowledgments

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References

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Future Works

Ab initio calculations will be employed to study the potential energy surface to determine the reaction pathway leading to the formation of primary products. Also, branching fractions of primary products will be calculated.