Investigation of 2,5-dimethylfuran oxidation reaction initiated by O(3P) atoms via synchrotron photoionization

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Introduction

Energy allows us to access convenient lifetimes. Owing to this provision of energy and the human population growth, the global demand for energy, which mostly relies on fossil fuels, is increasing rapidly.1 More than 80% of the world’s energy requirement has been fulfilled through fossil fuels, the limited thus depleting resource.1,2 To reduce the usage of fossil fuels and meet the requirement, renewable resources are being studied and biofuels have been recognized great amount.3 Among the candidates of biofuel, 2,5-dimethylfuran (2,5-DMF) attracts many researchers to investigate its properties. 2,5-DMF has a high volumetric density (31.5 ML/L) compare to gasoline (32.2 ML/L) with a high octane number (119).4 Higher octane numbers tend to reduce knocking in an engine and thus increase fuel efficiency and lessens damages to the engine.5 Due to its great potential as an alternative fuel, many studies regarding production and combustion of 2,5-DMF have been carried.

Our previous study proved methylene radical (CH and CD) reaction with 2,5-DMF and two main pathways, CH addition and isomerization assisted by a hydrogen atom, were reported.6 In this work, oxidation of 2,5-DMF initiated by O(3P) was studied at 550 and 700 K through synchrotron radiation coupled with multiphoton mass spectrometry mass spectrometry at the Lawrence Berkeley National Laboratory (LBNL). The measured photoionization (PI) spectra and kinetic traces were utilized to identify products. Reaction mechanisms of all the identified products are presented employing the potential energy surface (PES) scan method and electronic structure calculations.

Methods

The Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source (ALS) of LBNL was utilized to carry out this experiment.6 Reactant species were identified through recorded time- and energy-resolved mass spectrometry coupled with tunable synchrotron radiation for photoionization. The collected data consisted of the ion signal as a function of photon energy (eV), reaction time (ms), and mass-to-charge ratio (m/z), which formed a three-dimensional data block. Figure 1. Two-dimensional slices of the three-dimensional data were obtained for the data analysis by fixing one variable. The reagents show negative ion signal (depleting species) from kinetic time plots (ion signal vs kinetic time), whereas products have a positive signal. Figure 2 shows the time traces of the reaction (multiplied by -1) compared with a primary product and secondary products. The signal was integrated in the time range 0-40 ms to minimize the presence of secondary product signal at both temperatures.

Branching ratios of the products were calculated based on the following equation 1:

\[
\text{Branching ratio} = \frac{P_1}{P_1 + P_2 + P_3 + P_4} \text{ or } \frac{P_1}{P_1 + P_2}
\]

where MDF represents for mass discrimination factor, P1, P2, P3, and P4 are the measured signals in the PI spectra at a certain photon energy (11 eV in this study). The mass dependent response (P1 and P2) is approximately equal to the mass (m) of the identified species to the power of 0.67. The m and m+1 are the energy dependent photoionization cross-section, which were estimated using the semiempirical model at 11.8 eV presented by Bodebé et al. The propagation uncertainty calculations were performed based on the uncertainties of cross-section from literatures and ion signal uncertainties in this work. Molecular structures of the identified species were optimized through the CQS-PR3 composite method6 to obtain reliable zero-point vibration energy corrected total electronic energies (E0) that allow for calculation of various thermodynamic quantities, such as ionization potential energies and enthalpies of reaction. The B3LYP function level of theory with the basis set of 6-31G(d) was used to calculate the harmonic vibrations frequencies to obtain simulated photoionization spectra based on Frank-Condon and Frank-Condon-Herzberg calculations.7 The simulated and available literature photoelectron spectra are used to identify the detected products. The potential energy surface scan is utilized to investigate energy pathways, and Intrinsic Coordinate Reaction Method is used to verify the pathways.8

Results

Table 1. Branchings of the identified products that show fast forming rate at either both temperatures relative to 3-tert-pentene-2-one.

<table>
<thead>
<tr>
<th>Species</th>
<th>Branching ratios</th>
</tr>
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<tbody>
<tr>
<td>propyne</td>
<td>0.17 ± 0.07</td>
</tr>
<tr>
<td>ethylene</td>
<td>0.59 ± 0.14</td>
</tr>
<tr>
<td>3-tert-butenone</td>
<td>0.42 ± 0.14</td>
</tr>
<tr>
<td>(E)-2-butenal</td>
<td>0.72 ± 0.23</td>
</tr>
<tr>
<td>3-tert-butenone</td>
<td>1.00 ± 0.10</td>
</tr>
<tr>
<td>3-(E)-2-butenone</td>
<td>0.90 ± 0.13</td>
</tr>
<tr>
<td>(Z)-3-hexene-2,5-dione</td>
<td>1.26 ± 0.40</td>
</tr>
<tr>
<td>3-hydroxyhex-3-ene-2,5-dione</td>
<td>0.82 ± 0.25</td>
</tr>
<tr>
<td>2,3-dimethylfurans[3,2,0]one</td>
<td>1.15 ± 0.05</td>
</tr>
</tbody>
</table>

Figure 1. The three-dimensional dataset obtained at the ALS in Berkeley, CA.7

Figure 2. Time traces of reactant (inverted signal), i.e., multiplied by -1, primary, and secondary products at 700K.

Figure 3. Mass spectra at both temperatures (middle), and simulated photoionization spectra and photoelectron ionization spectra with appended literature/simulated photoionization curves. The primary products are propyne (m/z 40), ethylene (m/z 42), 3-butenone (m/z 70), 3-tert-pentene-2-one (m/z 84), (Z)-3-hexene-2,5-dione (m/z 112), and 2,5-dimethylfuran-3(2H)-one (m/z 121).

Figure 4. Reaction pathways of identified products formed from epoxide A at both temperatures. The relative energies of transition states compared to the adjacent intermediates are indicated in the parentheses. The left value corresponds to the energy barrier for the intermediate located on the left side whereas the right value is for the other intermediate. Identified molecules are highlighted with blue boxes.

Conclusions

In this investigation, oxidation of 2,5-dimethylfuran initiated by O(3P) was studied employing synchrotron radiation at the Lawrence Berkeley National Laboratory. A high temperature study was also performed to probe primary chemistry reaction pathways. Products branching ratios were calculated compared to 3-tert-pentene-2-one (set the 3-tert-pentene-2-one as 1.00) based on Equation 1. We observed two main reaction pathways, O(3P) addition and hydrogen abstraction. The O(3P) addition pathway, more favorable than hydrogen abstraction, forms two triplet diradicals (C and D), which undergo intersystem crossing into the singlet epoxide E. The hydrogen abstraction pathway generates only the double radical (A). In fact, the formation of the radical (B) is endothermic. An oxygen molecule then binds to A to generate products. From our previous study of the CI initiated oxidation of 2,5-dimethylfuran the mass expected product from this channel derives from the self-reaction of the peroxy radical and should be 3-methylfurfural, which is indeed observed. The experimental PI spectra of products in this work were identified by comparison with literature PI spectra and simulated PI spectra. The identified molecules at the both temperatures are propyne (m/z 40), ethylene (m/z 42), 3-butenone (m/z 70), 3-tert-pentene-2-one (m/z 84), (Z)-3-hexene-2,5-dione (m/z 112), and 2,5-dimethylfuran-3(2H)-one (m/z 121). 40K additional mass traces were demnted m/z 68, 82, 94 and 110, and identified as non-primary products based on their time traces.

Acknowledgments

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References