Computational Study of the Combustion and Atmospheric Decomposition of 3-Ketohept-1-oxy Radicals

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Background

Biofuels have been introduced as an alternative energy source to reduce greenhouse gas emissions from fossil fuels. However, the combustion of biofuels releases volatile organic compounds that undergo oxidation reactions in the atmosphere, producing ozone through a series of sub-reactions, which can be individually modeled and analyzed. In the presence of NOx, volatile organic compounds produce smog and tropospheric ozone, which are harmful to ecosystems and the environment. The purpose of this study was to determine the kinetic and thermodynamic parameters of the unimolecular decomposition of 3-ketohept-1-oxy radicals, which are themselves intermediates of biofuel combustion. Based on the parameters, the favorability of each reaction pathway can be defined, which determines the extent of formation of products, and subsequently chain branching and first generation end products.

Methods

- All geometries and frequencies were calculated using the Gaussian09 suite of programs.
- Conformational analysis performed using B3LYP/6-31+G(d,p).
- Geometry and Frequency: B3LYP/6-311++G(3d,3pd).
- Energies calculated using CBS-QB3, G3, and G4 composite methods with relative accuracies of 4.5, 4.5, and 4.0 kJ mol⁻¹, respectively.
- Rates were determined using ChemRate. Hindered rotors: Pitzer and Gwinn 1D hindered rotors from relaxed scans at B3LYP/6-31+G(d,p). Enthalpy of formation from two sets of isodesmic reactions.

Reactions

1,2 Bond Scission, 1,2 H-migration, 1,3 H-migration, 1,5 H-migration, 1,6 H-migration, 1,7 H-migration, 1,8 H-migration

Results

Figure 1. Potential energy diagrams for the 1,2-bond-scion reaction and H-migration reactions of the 3-ketohept-1-oxy radicals.

Thermodynamic

- The 1,3 and 1,5 H-migration reactions were thermodynamically favored which is due to resonance stabilization of the products.
- Abstracting an H from C₁ was thermodynamically favorable due to the stabilizing inductive effect of the O group.
- However, the 1,2 H-migration reaction was found to be 14-17 kJ mol⁻¹ lower than that reported by Davis due to dihedral effects.
- The presence of a ketone in the ring structure reduces the steric cost of forming the transition state.
- It was noted that the barrier for the 1,6 H-migration reaction was the lowest, which could explain its kinetic favorability.
- The 1,2 bond scission reaction for the 3-ketohept-1-oxy is more thermodynamically favorable due to resonance stabilization of the products.

Kinetic

- At 1000 K, the bond scission reaction is the dominant reaction pathway by about 10x.
- The 1,6 H-migration reaction becomes dominant at 450 K.
- At atmospheric temperature (300 K), the 1,6 H-migration reaction is 10x faster than the bond scission, 1,5 and 1,7 H-migration reactions.

Table 1. Kinetic and thermodynamic parameters for the unimolecular reactions of the 3-ketohept-1-oxy radical. All energies are in kJ mol⁻¹ at 298 K. Rate parameters are fit to a three parameter Arrhenius Equation: 

$$k(T) = A \exp \left( \frac{-\Delta H_{\text{act}}}{RT} \right)$$

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Rate Type</th>
<th>$\Delta H_{\text{act}}$ (kJ/mol)</th>
<th>$\Delta H_{\text{act}}$ at 298 (kJ/mol)</th>
<th>$\Delta H_{\text{act}}$ at 1000 (kJ/mol)</th>
<th>$\Delta H_{\text{act}}$ at 3000 (kJ/mol)</th>
<th>log(A)</th>
<th>A</th>
<th>Ea</th>
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</thead>
<tbody>
<tr>
<td>1,2 Bond Scission</td>
<td>22.2</td>
<td>-48.8</td>
<td>25.9</td>
<td>49.8</td>
<td>61.9</td>
<td>-32.7</td>
<td>12.02</td>
<td>0.5</td>
</tr>
<tr>
<td>1,2 H-migration</td>
<td>22.5</td>
<td>-48.3</td>
<td>25.9</td>
<td>49.8</td>
<td>61.9</td>
<td>-32.7</td>
<td>12.45</td>
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<tr>
<td>1,3 H-migration</td>
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<td>-48.8</td>
<td>25.9</td>
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<td>61.9</td>
<td>-32.7</td>
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<td>0.5</td>
</tr>
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<td>1,5 H-migration</td>
<td>22.5</td>
<td>-48.3</td>
<td>25.9</td>
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<tr>
<td>1,6 H-migration</td>
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<td>-48.3</td>
<td>25.9</td>
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<td>61.9</td>
<td>-32.7</td>
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</tr>
<tr>
<td>1,7 H-migration</td>
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<td>-48.3</td>
<td>25.9</td>
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<tr>
<td>1,8 H-migration</td>
<td>22.5</td>
<td>-48.3</td>
<td>25.9</td>
<td>49.8</td>
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<td>-32.7</td>
<td>12.45</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Conclusions

- The ketone group allows for resonance stabilization of the products of the 1,3 H-migration and 1,5 H-migration reactions.
- Additionally, the ketone allows for reduced steric costs in the formation of the transition state, affecting the thermodynamic and kinetic favorability.
- The 1,6 H-migration reaction is the most dominant kinetic pathway at atmospheric conditions with the lowest energy barrier of all the 3-ketohept-1-oxy reactions.

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References