Abstract

Dibenzothiophene-S-oxide (DBTO) and its selenium analogue, dibenzo-selenophene-S-oxide (DBSeO), deoxygenate upon photolysis and form atomic oxygen, O(3P). This project focuses on the energetics of selenophene-Se-oxide (SeO). The vertical excitation energies were determined and potential energy surfaces were generated as a function of Se-O bond length at the CASSCF/G3Large*/CASSCF/6-31G(d) and MRMP2/G3Large*/CASSCF/6-31G(d) levels. The calculated energies and potential energy diagrams suggest that production of atomic oxygen is energetically feasible for SeO, which further supports the experimental observation that O(3P) is produced when DBTO and DBSeO are photolyzed.

Introduction

• Low quantum yield (ψ < 0.01)1
• Proposed intermediate: O(3P)
• Heavy atom substitution increases quantum efficiency2-4

• Proposed deoxygenation mechanism: charge separation along the stretching Se-O coordinate leads to ISC due to decreased singlet-triplet gap.

Relative Energies of Excited States at Equilibrium Geometry

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A' T1</td>
<td>52.4849</td>
</tr>
<tr>
<td>A' T2</td>
<td>83.6022</td>
</tr>
<tr>
<td>A' S1</td>
<td>92.4606</td>
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<tr>
<td>A' S2</td>
<td>106.200</td>
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<tr>
<td>A'' S2</td>
<td>46.9536</td>
</tr>
<tr>
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<td>55.1820</td>
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<tr>
<td>A'' S2</td>
<td>52.2577</td>
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</table>

Computational Methods

• GAMESS was used for all calculations and MacMolPlt 7.2.1 was used to view the molecules and orbitals generated.
• Generated orbitals for the different states of SeO using RHF and ROHF methods at 6-31G(d) with C2 symmetry.
• Used coordinates and orbitals from HF calculations as initial coordinates and orbitals for the active space of the CASSCF calculations.
• CASSCF active space: 18 electrons, 14 orbitals (lone pairs on oxygen and selenium, the Se-O σ and σ* orbitals, the C-Se σ and σ* orbitals, and the C-C π and π* orbitals).
• Obtained energy corrections using multi-reference second-order perturbation theory (MRMP2).
• For CASSCF and MRMP2 calculations, the basis set designated G3Large* (G3Large for Se and O and 6-31G(d) for C and H) was used.6

Results

• Mulliken charges indicate that none of the excited states show a maximum of charge separation beyond the equilibrium Se-O bond distance.
• Rules out hypothesis linking ISC to charge separation.

Conclusions

• Calculated Mulliken charges suggest that deoxygenation is not accompanied by developing charge.
• Resulting calculations and potential energy surfaces suggest that photochemistry occurs from the T2 state to produce O(3P).
• Proposed photochemistry from T1 state is consistent with low quantum yield of O(3P) production from DBTO and DBSeO.

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Acknowledgments

The photochemical deoxygenation of aromatic selenoxides: A computational approach.

Stephanie Y. Lee*, Stacey A. Stoffregen*, Pearl Dickerson*, and William Jenks*

*Department of Chemistry, Macalester College – St. Paul, MN; ‡Department of Chemistry, Iowa State University - Ames, IA

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