Influence of Substituents on Ring-opening Energetics

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Abstract

The effect of an electron donating or withdrawing group (EDG or EWG) on the gas-phase ring contraction mechanism of a cyclohexene-derived cation has been studied using density functional theory.

The barrier to rearrangement of the parent cyclohexene cation(1) was previously calculated to be 7.7 kcal/mol which is in excellent agreement to experiment (7.4 ± 1 kcal/mol).

We find in this work that addition of an EWG (CH₃) 2 raises the average barrier to contraction, relative to the parent, while an EDG (CF₃) lowers the average barrier.

Calculated barrier heights range from 4.3 – 23.3 kcal/mol for 2 and 0.6 – 14.0 kcal/mol for 3.

Parent cation contraction

We found that B3LYP/6-311++G(2d,2p) is capable of replicating the expensive, high-level QCISD(T) structures, energies and kinetics.

CF₃ substituent

Relative energies (kcal/mol)

[Diagram showing relative energies for various structures]

Key points

* Ring contraction barriers for 2 are significantly larger than those for 1 and 3.
  Why? For 2, most likely reactions start from a tertiary carbocation with final product formed via secondary intermediates. However, for 1 and 3, the reaction starts with a secondary cation and heads downhill in energy to a tertiary product.

* Ring contraction barrier for 3 lower than for 1.
  Why? The presence of delocalizing interactions from the CF₃ to cation-cation stabilize intermediates and transition states.

For example, in 3 there is a favorable interaction of 0.78 kcal/mol (from MB analysis) between F lone-pair and carbon charge center. Similar interactions are evident in many other CF₃ intermediates.

Scope

Several questions need to be answered:

* Does this hold true for other EWG and EDG groups?
* How, if at all, do these reactions differ in a liquid environment?