

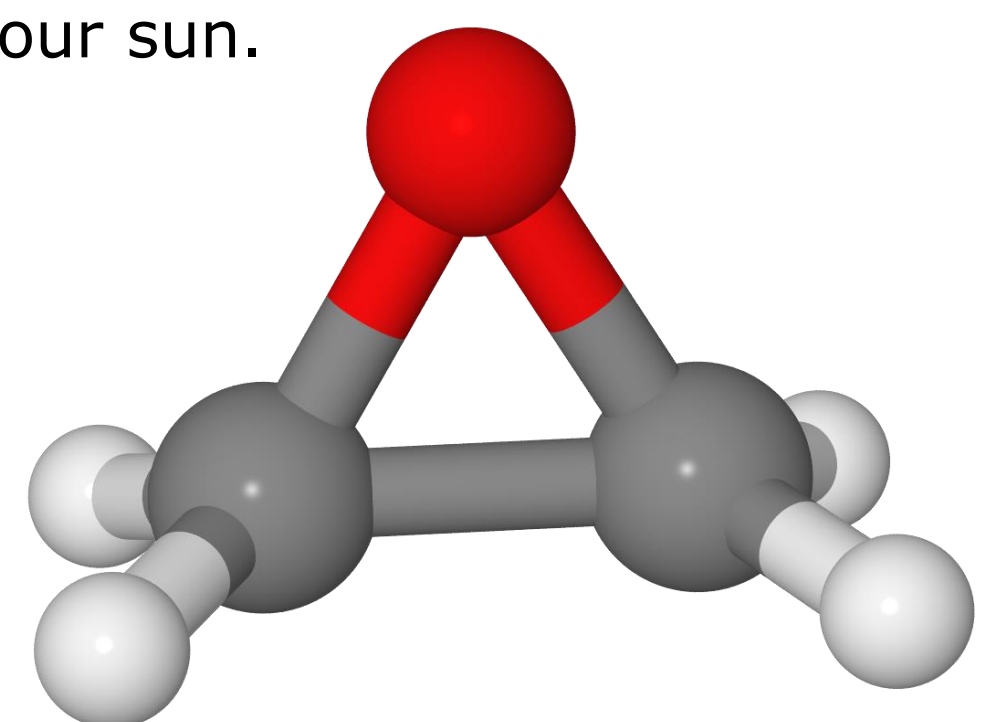
Mechanisms for Oxirane Formation in Interstellar Molecular Clouds

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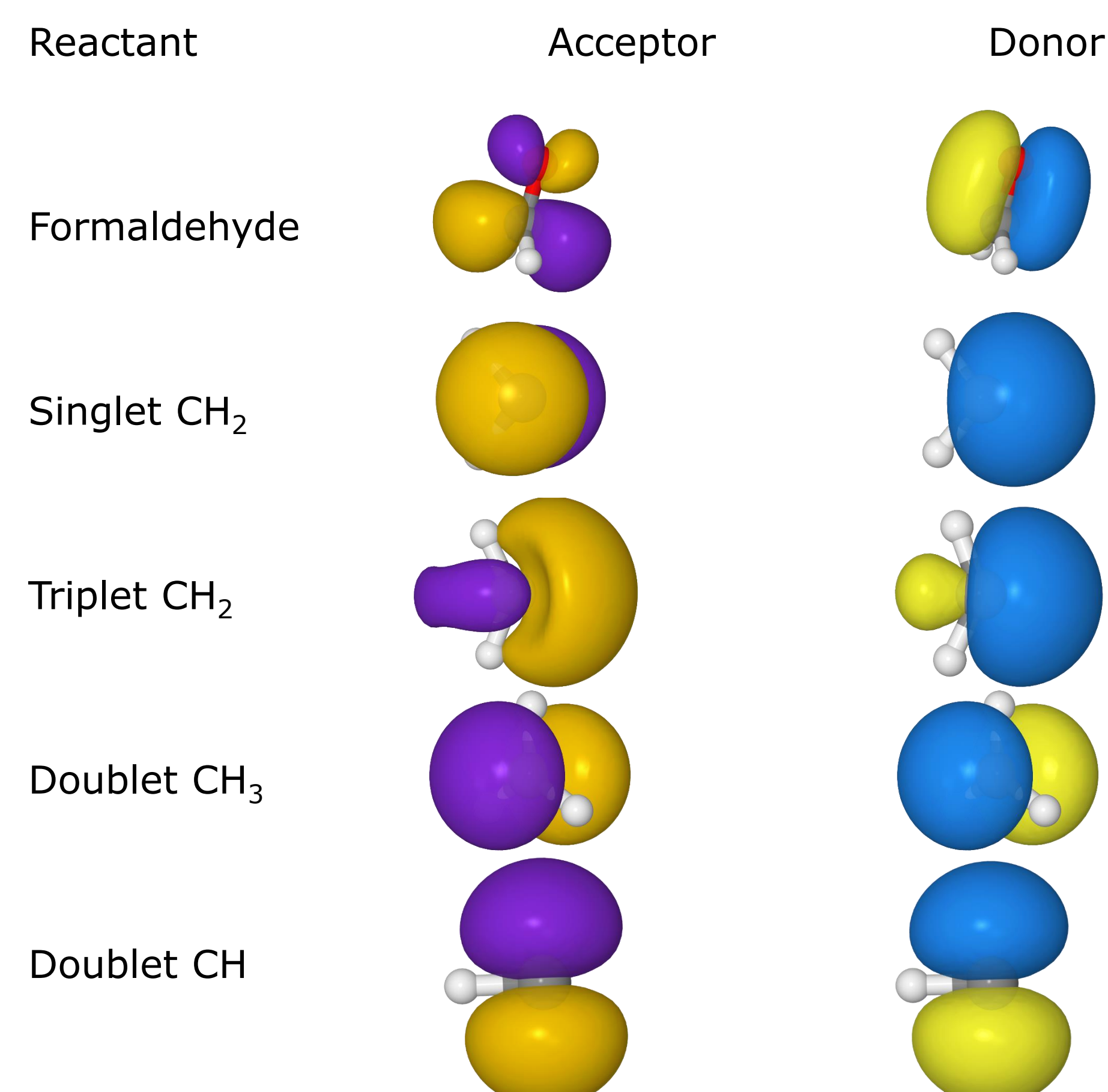
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Introduction

Interstellar molecular clouds (IMCs) provide an environment conducive to formation of complex organic compounds. Of particular interest are heterocyclic molecules, which can be precursors to some biomolecules. Our heterocycle of interest, oxirane, was recently confirmed in the Taurus Molecular Cloud (TMC-1), a star-forming region like that believed to have formed our sun.



TMC-1, and other molecular clouds like it, provides a favorable molecule factory because of its low temperatures and, for an interstellar cloud, high density. With a temperature around 10 K, a hydrogen molecule (H_2) undergoes around 6 collisions in a year. The low temperatures allow for less stable molecules to exist in these clouds that would not exist for extended periods on Earth. These molecules are key to the open-shell and excited-state reactions considered here, including the reactions of formaldehyde, CH_2O , with doublet CH, singlet and triplet CH_2 , and doublet CH_3 .



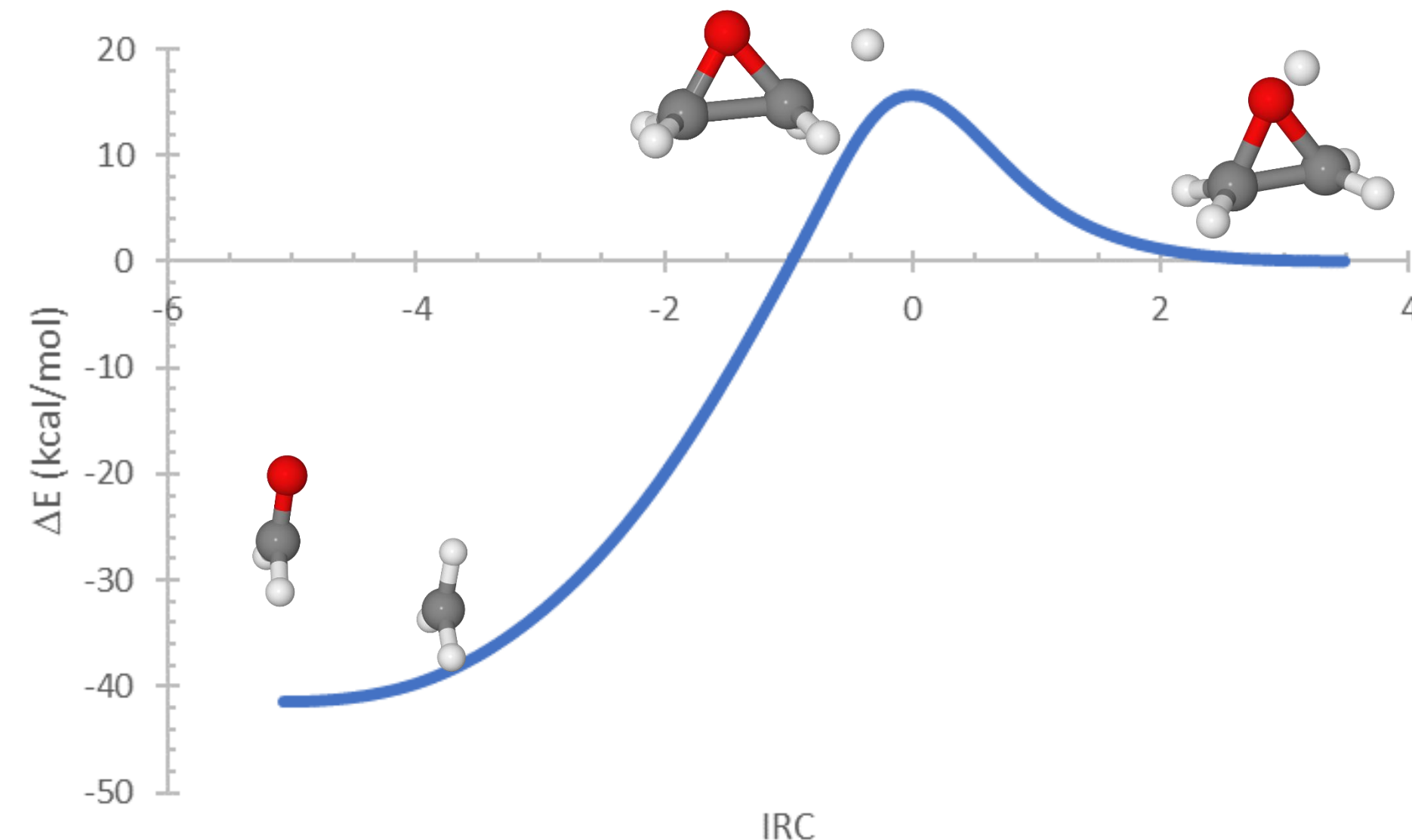
In this work we use computational chemistry methods to examine several possible reaction pathways for oxirane formation in TMC-1. Density functional theory (DFT) and intrinsic reaction coordinate (IRC) calculations at the B3LYP level with the cc-pVDZ basis sets were used to calculate ground state energies.

Calculations were performed using the Gaussian-16 program, orbital images were created using Jmol, and qualitative analysis of the calculated states was obtained using natural bond orbital (NBO) analysis.

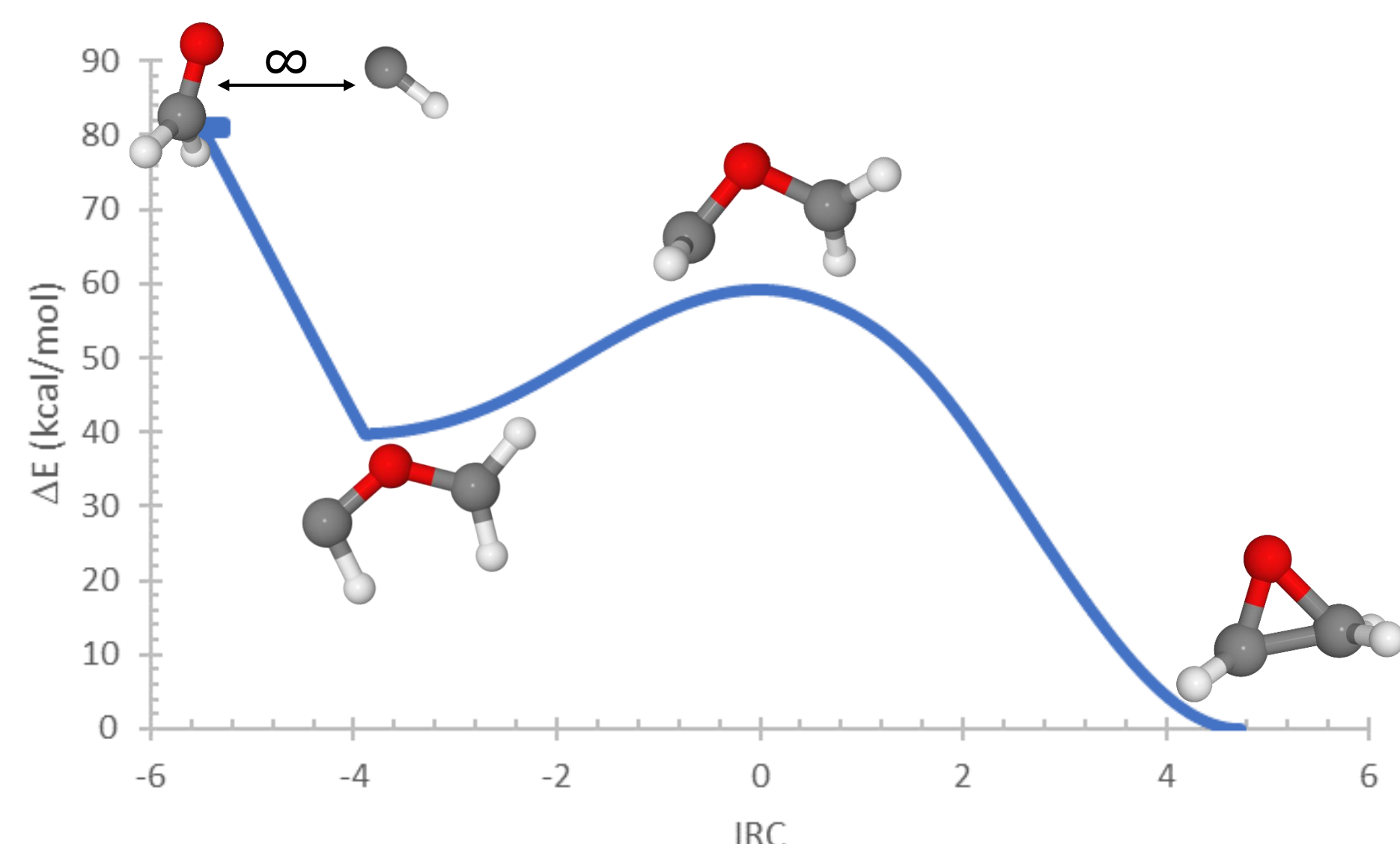
Open-shell Reactions

Open-shell reactions involve electrons that are unpaired. Unpaired electrons often yield interesting reaction dynamics because singly-occupied orbitals can simultaneously act as *electron donor* for alpha-spin density and *electron acceptor* for beta-spin density. In our open-shell reactions, we focus the CH_3 and CH radicals, both of which are doublet.

The stability of CH_3 contributes to a very high barrier of 60 kcal/mol, which makes it unlikely that this radical will add to formaldehyde in an energy-deficient cloud.



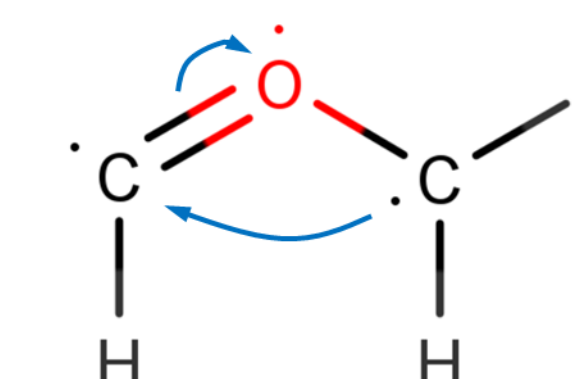
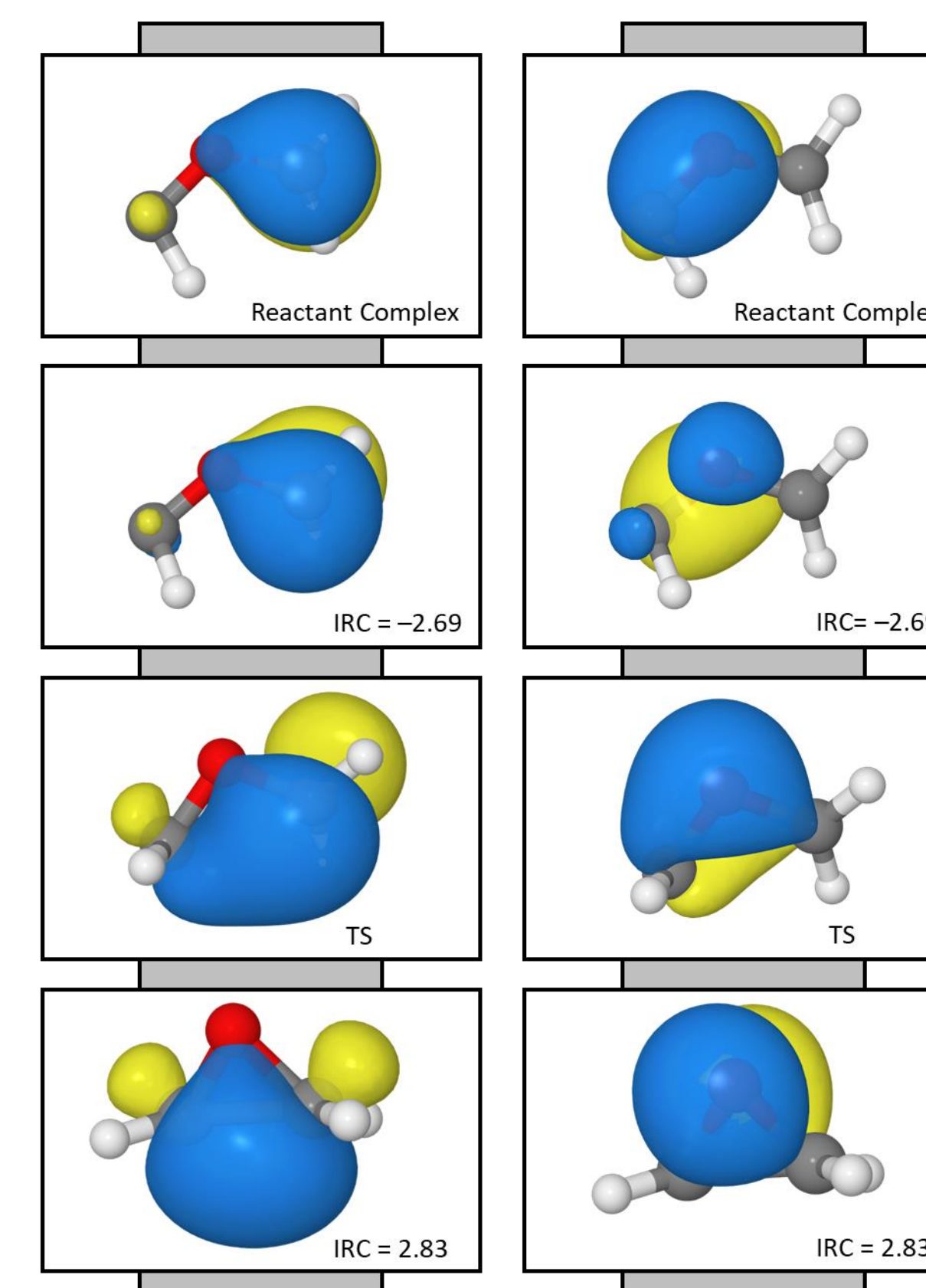
The CH radical is much less stable than the CH_3 radical. This makes the CH radical and formaldehyde much better candidates for causing the formation of oxirane (by first forming a hydrogen deficient oxirane).



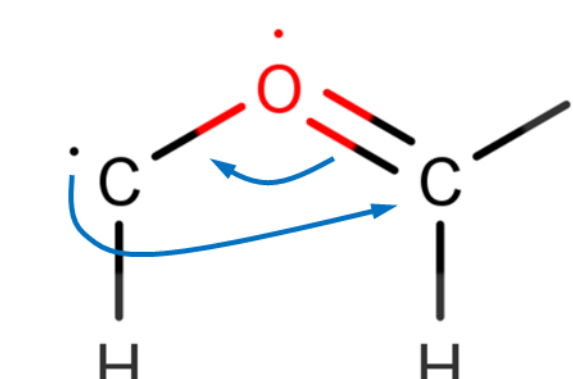
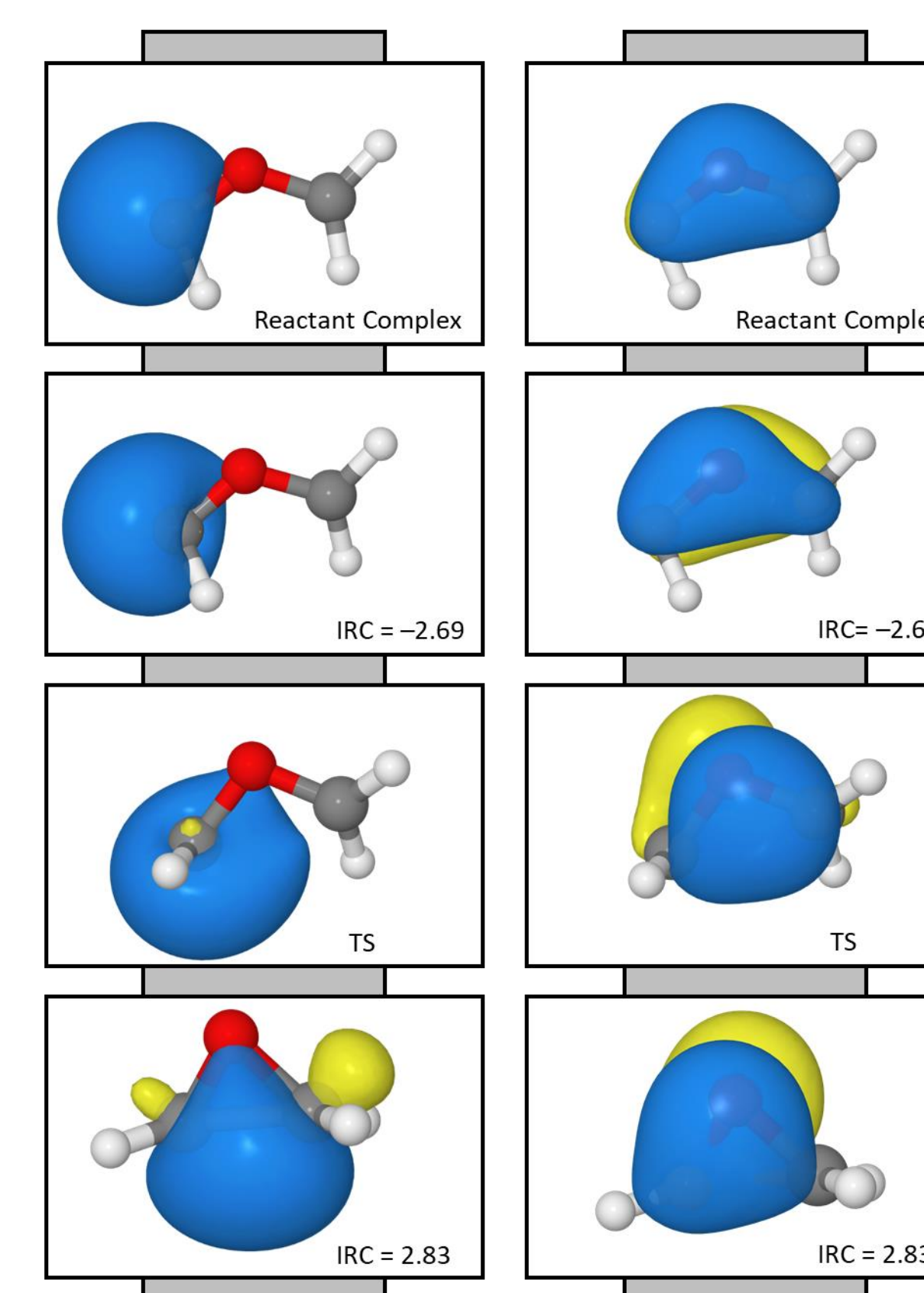
The high energy of separated formaldehyde and CH radical allows the reaction to overcome the high (~20 kcal/mol) reaction barrier to become the more stable hydrogen deficient oxirane.

The formation of deprotonated oxirane occurs in two electron-spin systems in the reaction of CH radical and formaldehyde. This is due to the differentiation of alpha and beta electrons within the reaction complex.

The first system, the alpha system, reveals two transformation. The first transformation is of a nonbonding electron on the carbon (originating from the formaldehyde) to a bonding electron in a σ_{CC} bond. The second transformation is that of a π_{CO} bonding electron to a nonbonding electron on the oxygen atom.



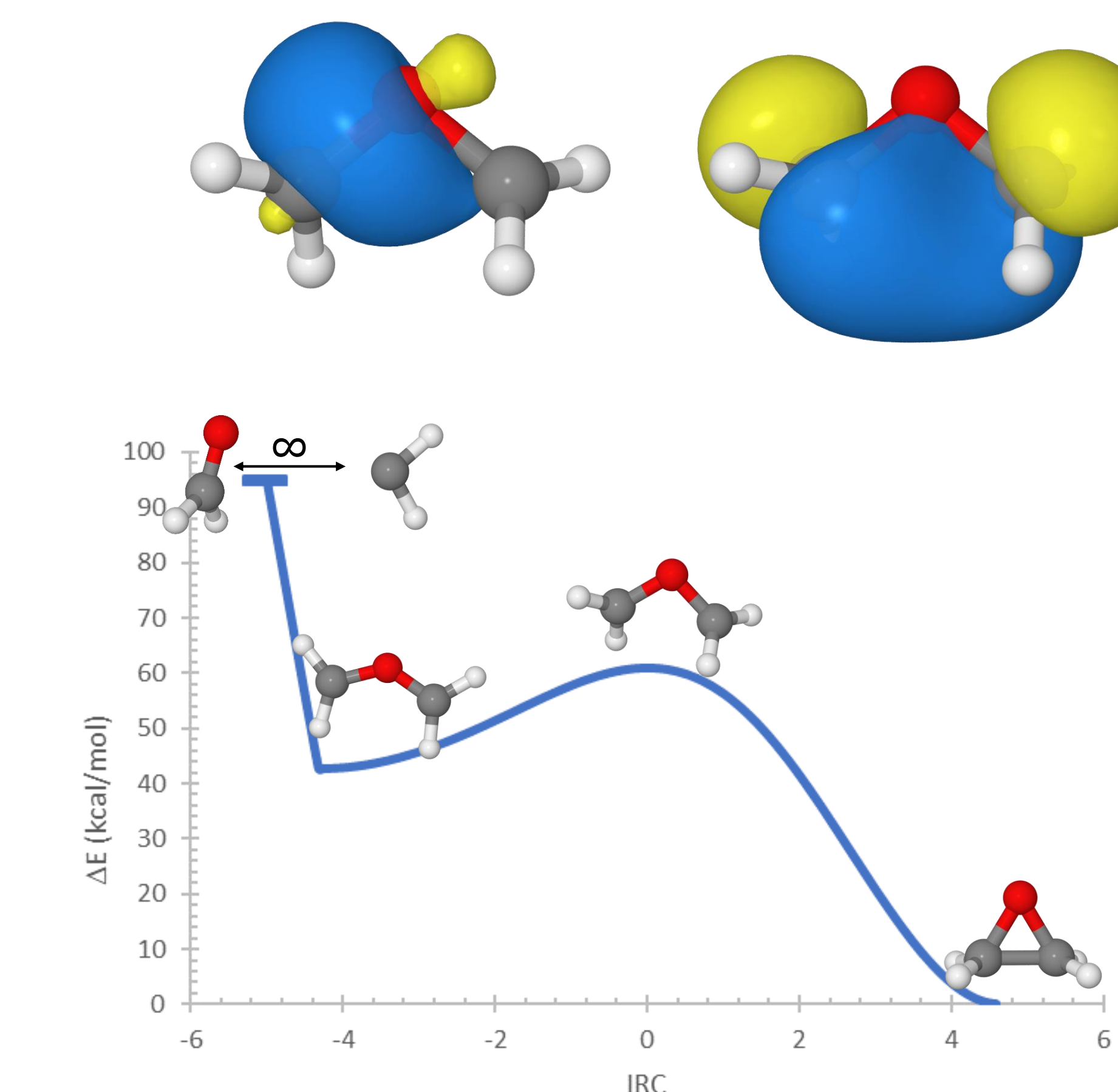
The second system, the beta system, likewise reveals two transformation. The first transformation is of a nonbonding electron on the carbon (originating from the CH radical) to a bonding electron in a σ_{CC} bond. The second transformation is that of a π_{CO} bonding electron to a bonding electron of the other π_{CO} system.



Closed-shell Reactions

The reactions of closed-shell systems involve electrons that are paired. One of the simplest closed-shell reactions that could form oxirane is the addition of singlet CH_2 with formaldehyde.

The singlet CH_2 molecule exists as an excited state of triplet CH_2 . Singlet CH_2 reacts well with formaldehyde in this situation because it has an empty 2p orbital. Thus, the CH_2 donates electron density into the π^* bond of formaldehyde, while the electron density of the dissociated π bond electron fills the empty 2p orbital on CH_2 . The result is σ bonds forming between the formaldehyde C and the new C, and between the O and the new C. These sigma bonds are displayed below as they form at the transition state



Conclusions

The reaction of radical CH and formaldehyde provides an interesting and reasonable pathway to formation of oxirane. The consideration that ought to be carried moving forward is that reactions, beginning with the completely downhill formation of a reaction complex, are key to the formation of oxirane due to the high activation energy associated with creating a three-member ring.

Acknowledgements

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