Unimolecular Degradation of the Criegee Intermediates Derived from Ozonolysis of Isoprene

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Abstract

We have made computational studies on the various unimolecular degradation pathways of the Criegee Intermediates (CIs) derived from the ozonolysis of isoprene which is one of the most abundant alkenes release by plants in nature[1]. These CIs play a significant role in atmospheric chemistry, influencing processes such as aerosol formation, which can reflect sunlight and impact climate[2]. The potential energy profiles for these pathways were mapped with high-level electronic structure calculation. Variational transition state theory with multidimensional tunneling (VTST/MT) was applied to calculate the unimolecular rate constants. The efficiencies of the various degradation pathways, the effects and quantum mechanical tunneling are discussed.

Motivation

The reaction between isoprene and ozone generates multiple Criegee intermediates (CIs). Among them, we specifically introduce methyl vinyl ketone oxide (MVKO) because it is relatively abundant among four-carbon CIs[3]. We employ more accurate Dual-level VTST[4] calculations to investigate the kinetics of MVKO, including rate constant calculations at different temperatures while accounting for tunneling effects. We aim to more accurately identify the kinetically favorable routes, enabling us to model the formation of climate-controlling atmospheric aerosols and assess their potential occurrence.

Methods

Molecular structures and vibrational frequencies were calculated using MP2 theory with the 6-31+G(d,p) basis set. The intrinsic reaction coordinate (IRC) was calculated for every transition states located. Coupled-cluster CCSD(T)[5] energies were calculated at MP2/6-31+G(d,p) geometry with the aug-cc-pVTZ basis set to take the high-level correlation effects into account. Electronic calculations were performed using the Gaussian 16 programs. Dual-level VTST calculations including tunneling correction have been performed to predict the gas-phase molecular rate constants in the temperature range of 150-600 K using the Gaussrate 17-B software.

Results and Discussion

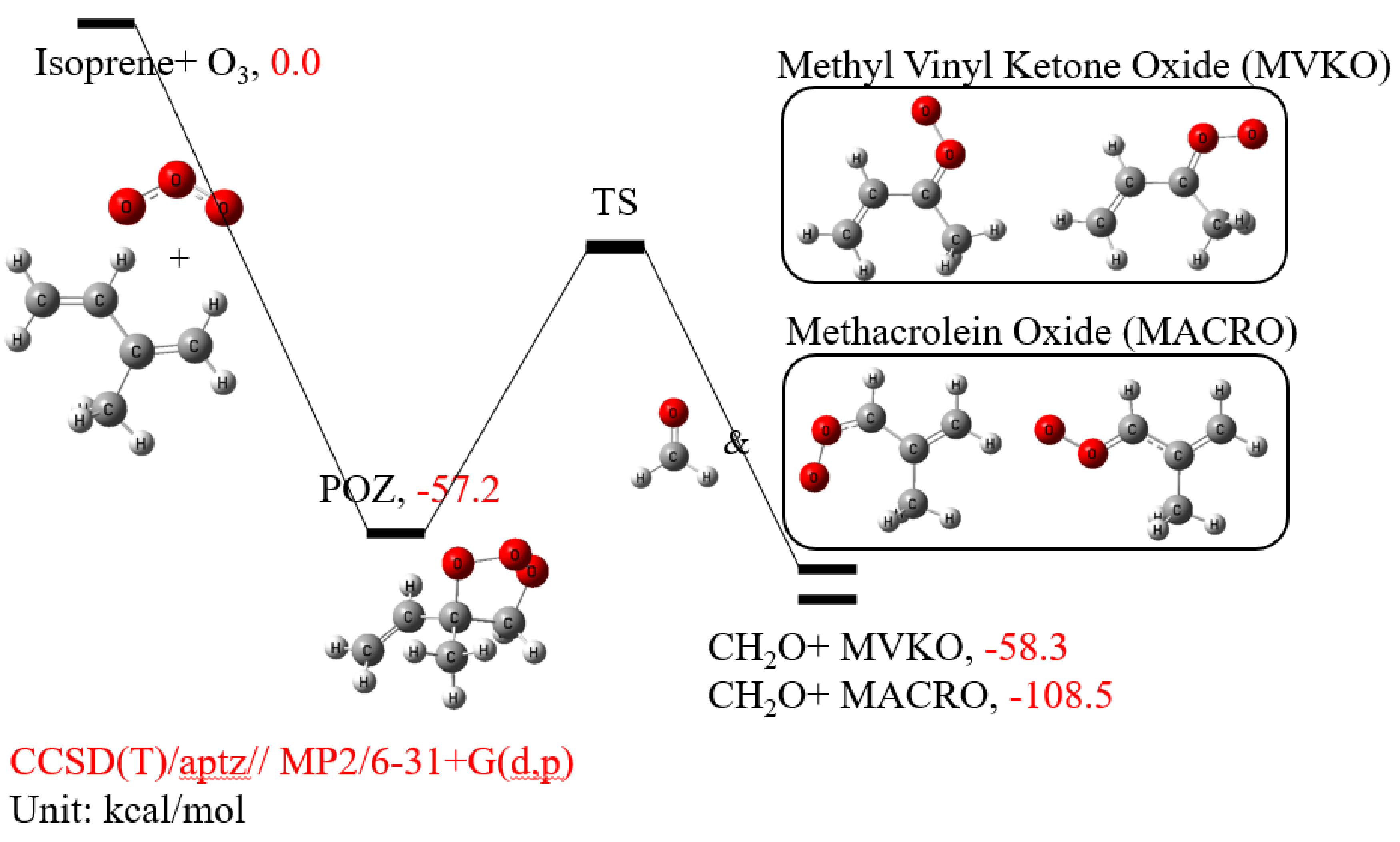

Figure 1. Potential energy diagram of Ozonolysis reaction from isoprene to CIs.

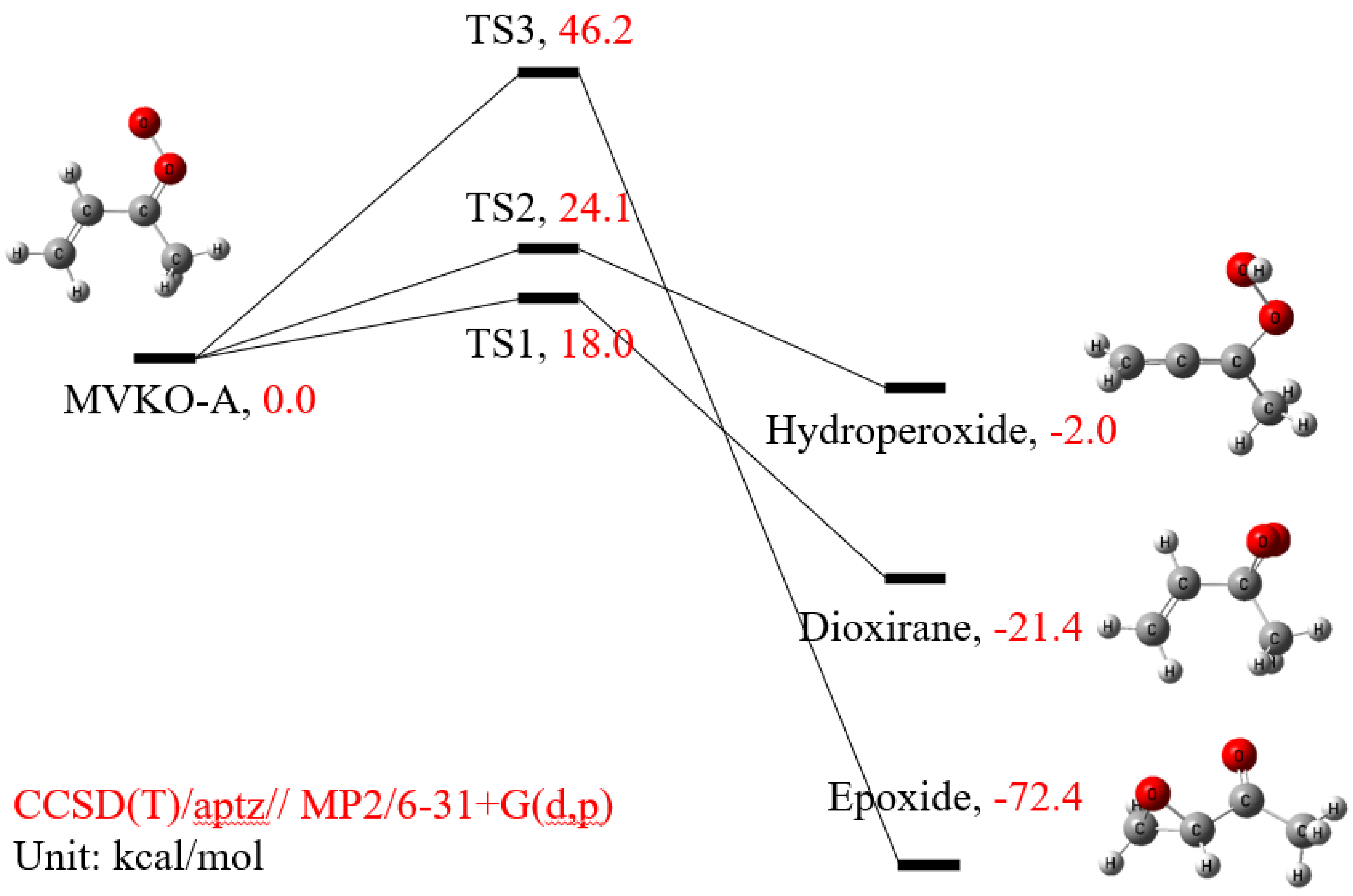

Figure 2. Potential energy diagram of MVKO-A reaction. MVKO-A undergoes three unimolecular reactions, producing hydroperoxide, dioxirane, and epoxide.

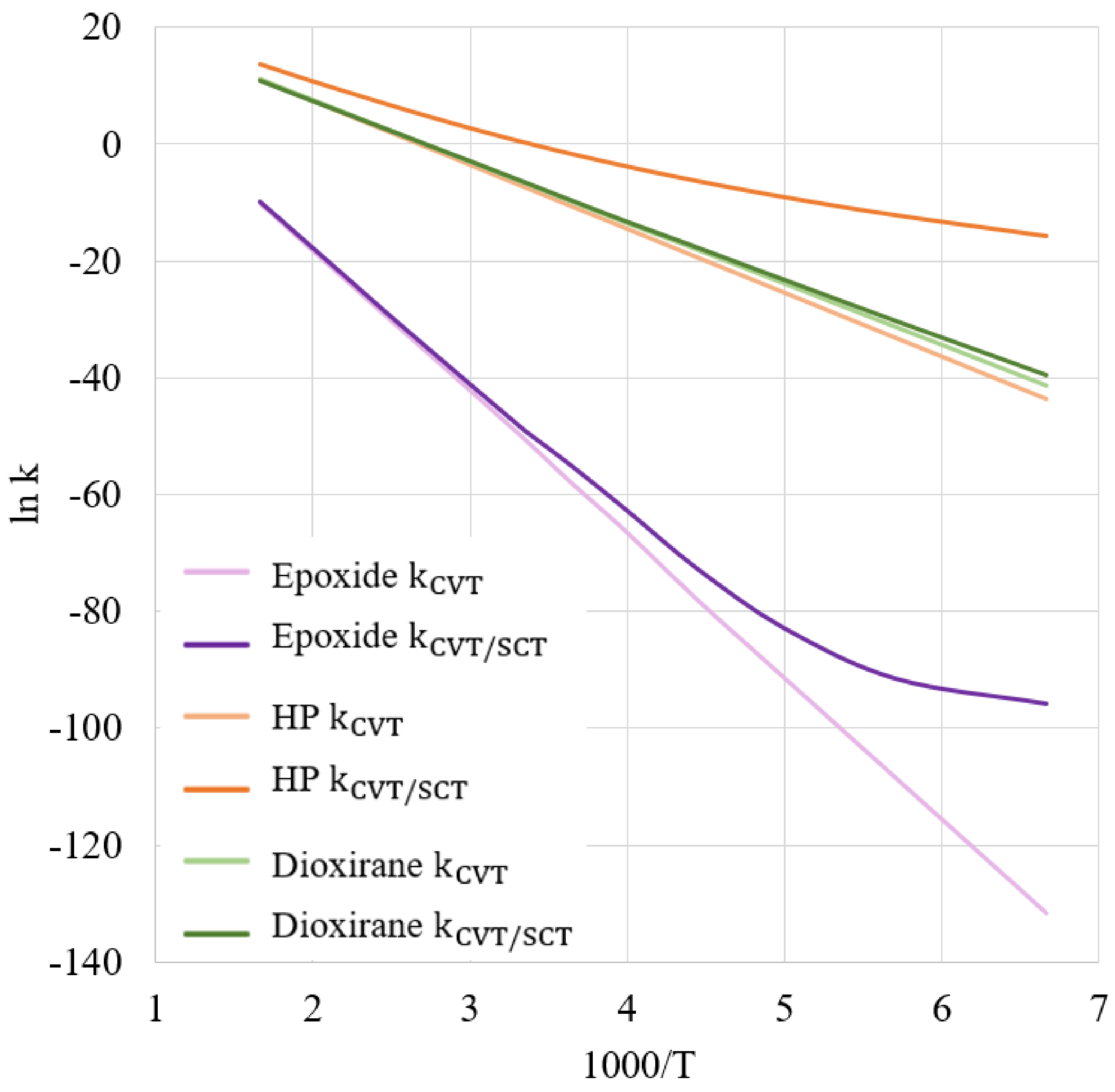

Figure 3. The Arrhenius plot of the three unimolecular reactions of MVKO-A.

The ozonolysis reaction of isoprene first forms POZ. Due to the significant decrease in potential energy, approximately 57.2 kcal, the system gains internal energy, allowing the reaction to proceed further.

POZ overcomes an energy barrier of approximately 25.0 kcal (calculated using M06-2X/6-31+G(d,p)) to form various CIs, including one-carbon formaldehyde oxide and four-carbon species such as MVKO and MACRO. Due to differences in the orientation of their terminal oxygen atoms and the rotation of single bonds, these CIs also exist in multiple isomeric forms. Owing to space limitations, we select a MVKO that can generate a greater variety of products for further discussion and designate it as MVKO-A. MVKO-A undergoes unimolecular reactions to form HP, dioxirane, and epoxide, with reaction barriers of 24.1, 18.0, and 46.2 kcal/mol, respectively. For the rate constant $k_{CVT/SCT}$ calculated with tunneling effects, as shown in Figure 3, we observe that the formation of HP has the highest rate constant, despite not having the lowest energy barrier. This is because HP undergoes a hydrogen transfer reaction, where the significant tunneling effect allows its $k_{CVT/SCT}$ to surpass that of dioxirane, which has a lower energy barrier. On the other hand, epoxide, which has the highest energy barrier, consistently exhibits extremely low $k_{CVT/SCT}$ values across the temperature range. The calculated results provide an estimated half-life of 0.6 s for MVKO-A at room temperature.

Conculsion

In this study, we have calculated three unimolecular degradation pathways of MVKO-A for three different unimolecular reactions, producing HP, dioxirane, and epoxide, with energy barriers of 24.1, 18.0, and 46.2 kcal/mol, respectively. Although the reaction barrier for dioxirane formation is the lowest, HP has the highest reaction rate constant because the hydrogen transfer reaction exhibits very significant tunneling effects. The half-life of MVKO-A due to the formation of HP was estimated to be 0.6 s at room temperature.

References

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