Reaction Dynamics Study on the Unimolecular decay of Methacrolein Oxide (MACRO)

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Abstract

Isoprene is the most abundantly emitted biogenic volatile organic compound in the atmosphere[1], and methacrolein oxide (MACRO) is one of the key Criegee intermediates formed during the ozonolysis of isoprene, playing a crucial role in atmospheric oxidation processes[2]. MACRO can exist in four distinct conformational isomers with different activities. [3] In this study, the unimolecular decay dynamics of MACRO are systematically investigated by theoretical calculations. High-level electronic structure methods are employed to construct the corresponding potential energy surfaces (PESs). Dual-level variational transition-state theory with multidimensional tunneling (VTST/MT) [4] is applied to calculate unimolecular rate constants.

Motivation

The ozonolysis of isoprene produces several Criegee intermediates (CIs), including methyl vinyl ketone oxide (MVKO) and methacrolein oxide (MACRO), which play important roles in atmospheric oxidation processes. In our previous work, the unimolecular decay of syn-MVKO was investigated using dual-level variational transition state theory (VTST) with tunneling corrections, showing that quantum tunneling significantly affects its reaction kinetics.[5] Experimental studies have detected anti-MACRO and shown that it has a relatively long lifetime. [6] In addition, isoprene-derived CIs such as MACRO may undergo unimolecular decay through pathways such as dioxole formation. [7]

Methods

Molecular structures and vibrational frequencies were calculated using M06-2X theory with the 6-31+G(d,p) basis set. Coupled-cluster CCSD(T) [8] energies were calculated at M06-2X/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

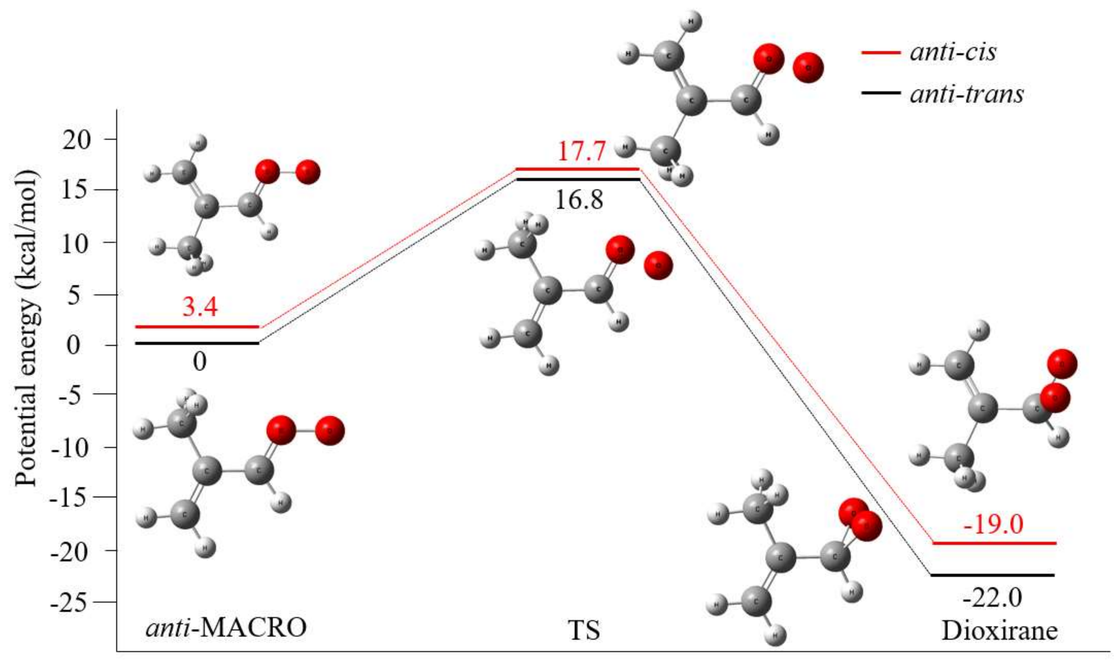

Figure 1. Calculated Potential Energy Profile from *anti*-MACRO to Dioxirane.

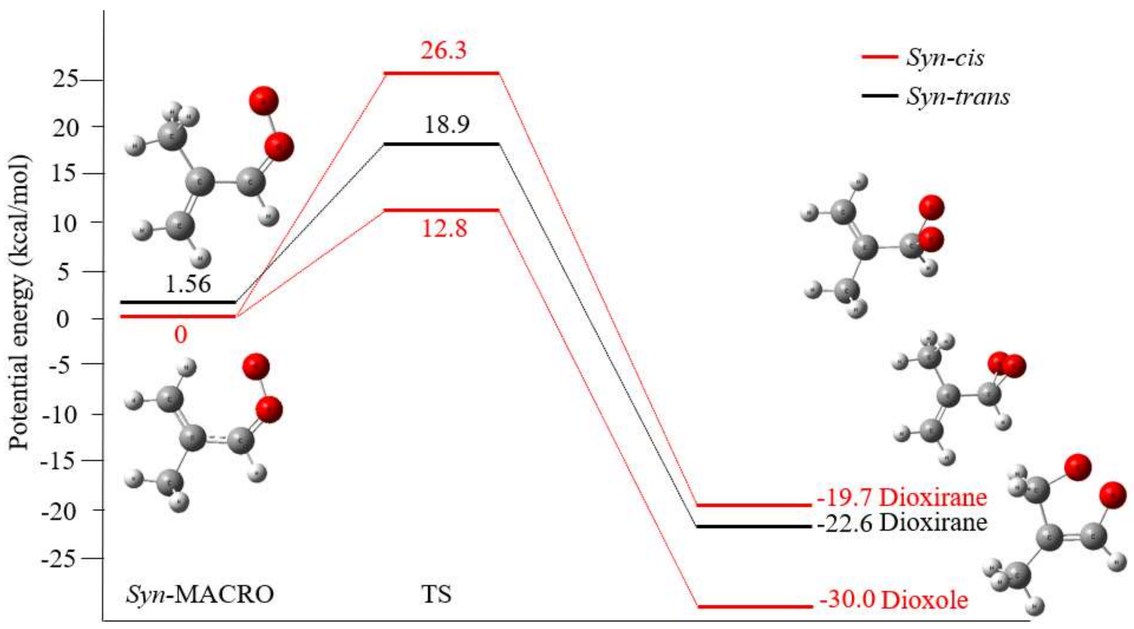

Figure 2. Potential energy diagram of *syn*-MARCO reaction. *syn*-MARCO undergoes two unimolecular reactions, producing dioxirane and dioxole.

The unimolecular reactions of MACRO were investigated for both syn and anti conformers. Among the four conformers, *anti-trans*-MACRO is the most stable structure, while the other conformers lie at slightly higher energies. The unimolecular decay of *anti*-MACRO proceeds through a 1,3-oxygen shift to form dioxirane with calculated barriers of 14.3–16.8 kcal mol^{-1}. In contrast, syn-MACRO can undergo two possible pathways, and the formation of dioxole from *syn-cis*-MACRO has the lowest barrier (12.8 kcal mol^{-1}), indicating that this pathway is kinetically favored.

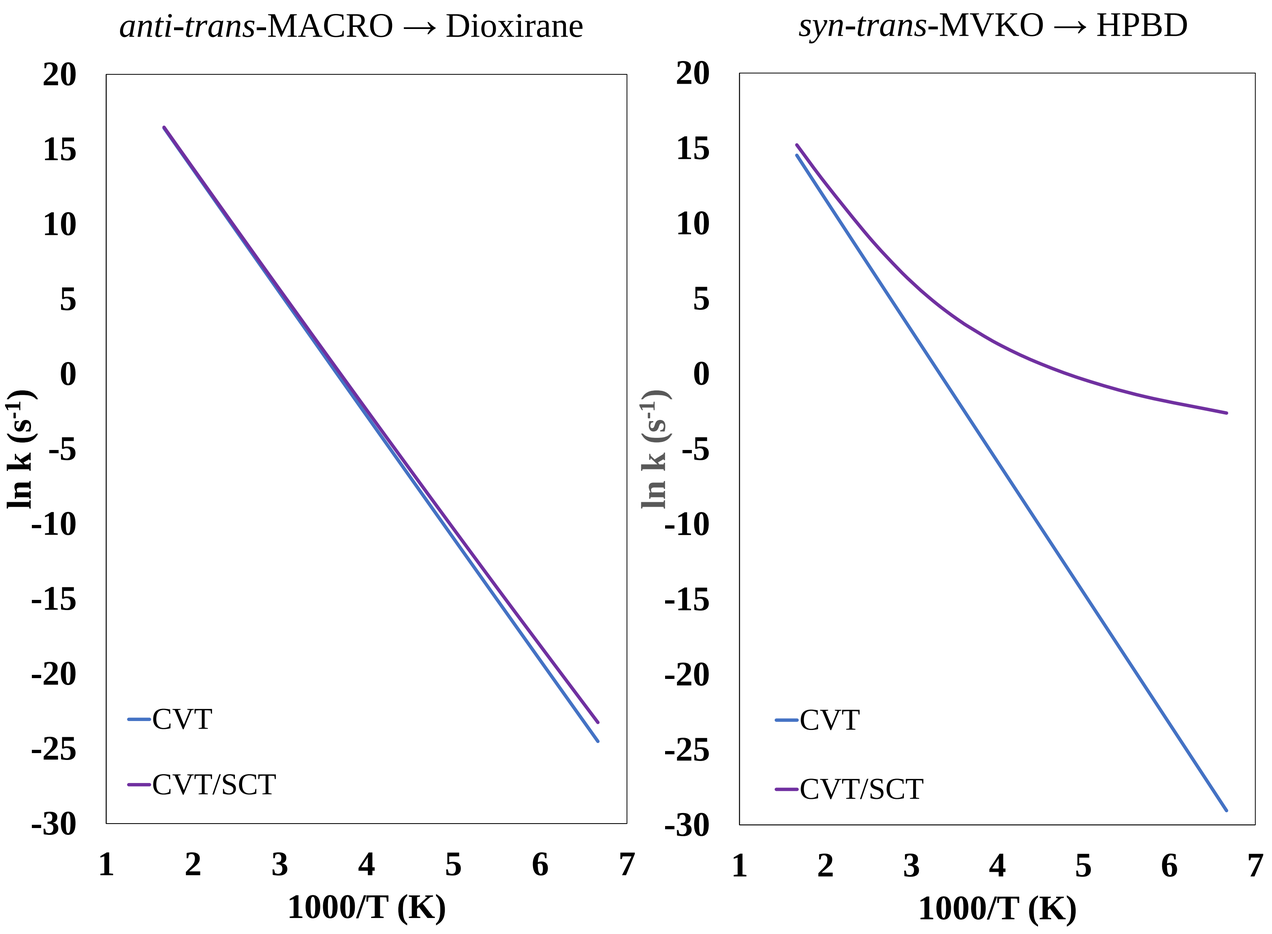

Figure 3. Arrhenius plots for unimolecular reactions of *anti-trans*-MACRO (left) and *syn-trans*-MVKO (right).

The calculated Arrhenius plots show that the rate constants obtained from CVT and CVT/SCT are very similar for the *anti*-MACRO reaction, suggesting that tunneling plays only a minor role. This is consistent with the heavy-atom rearrangement involved in the oxygen-shift mechanism. In contrast, the unimolecular decay of *syn-trans*-MVKO shows a noticeable difference between CVT and CVT/SCT rate constants, indicating a stronger tunneling contribution due to hydrogen transfer.

The calculated lifetimes at 298.15 K further illustrate the difference in reactivity among these species. The lifetime of *anti*-MACRO is predicted to be 16.8 ms, which is much longer than that of *syn-cis*-MACRO (0.27 ms), indicating that the anti conformer is significantly more stable against unimolecular decay. For comparison, *syn-trans*-MVKO has a lifetime of 8.71 ms at the same temperature. Experimental studies suggested that *anti*-MACRO has an atmospheric lifetime of ca. 18 ms at 298 K and RH = 70% [6], which is in good agreement with the present theoretical prediction.

Overall, the unimolecular reactions of MACRO are strongly dependent on conformational structure. Compared with MVKO, MACRO exhibits weaker tunneling effects because its reactions mainly involve heavy-atom rearrangements rather than hydrogen transfer. These findings help clarify the conformer-dependent reactivity of isoprene-derived Criegee intermediates and provide useful kinetic parameters for atmospheric chemistry modeling.

Conclusion

The unimolecular reactions of MACRO conformers were investigated using dual-level VTST calculations with tunneling corrections. *Anti-trans*-MACRO is the most stable conformer and mainly undergoes a 1,3-oxygen shift to form dioxirane, while *syn-cis*-MACRO preferentially forms dioxole due to its lower reaction barrier. The calculated lifetime of *anti*-MACRO at 298.15 K (16.8 ms) agrees well with the experimental atmospheric lifetime of ~18 ms. Compared with MVKO, MACRO exhibits weaker tunneling effects because its reactions involve heavy-atom rearrangements rather than hydrogen transfer.

References

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