Reaction dynamics of Criegee intermediates with alkanes

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Abstract

We have performed the reaction dynamics study of CH_2OO, CF_2OO, and CCl_2OO with alkanes (CH_4, C_2H_6) to form alcohols and aldehydes. The potential energy surfaces (PES) have been mapped with high-level electronic structure calculation. Dual-level VTST/MT calculation have been carried out to evaluate the rate constants and kinetic isotope effects from 150 K to 600 K. The results showed that the halogen substituted Criegee intermediates can significantly reduce the energy barriers. Reactions with ethane have slightly lower barrier heights (2-3 kcal/mol) and thus higher rate constants. The tunneling and kinetic isotope effects are significant below 250 K.

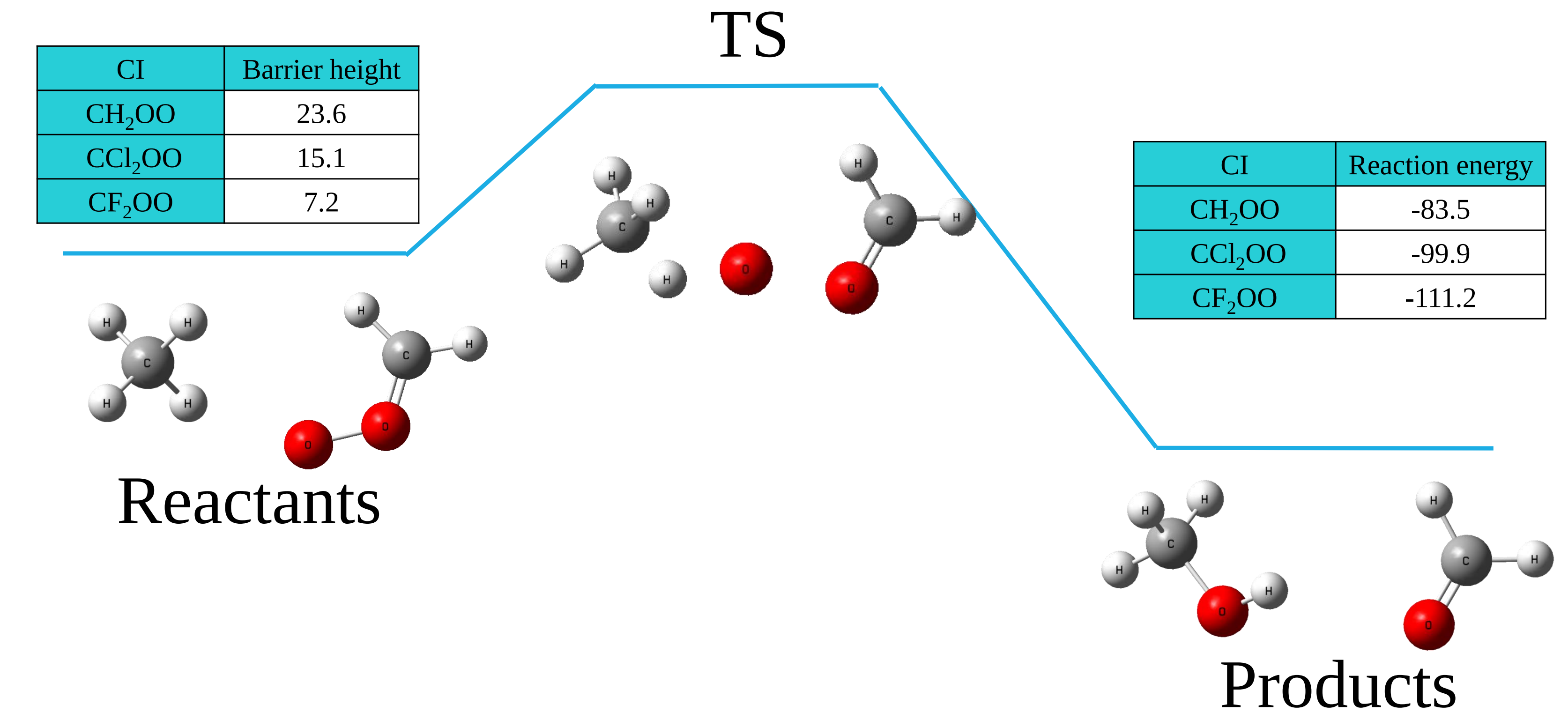
Motivation

Criegee intermediates (CIs) are a class of highly reactive intermediates[1] containing the peroxide functional group (R_1R_2COO), where R_1 and R_2 can be alkyl or other organic groups. The simplest CI is the methylene carbonyl oxide radical (CH_2OO). These intermediates were first proposed by the German chemist Rudolf Criegee in the 1950s[1] and play an important role in atmospheric chemistry and organic synthesis. The primary formation pathway of CI is the ozonolysis of alkenes, where peroxide intermediates formed then subsequently decompose to generate CIs and byproducts. In the atmosphere, CIs undergo oxidation reactions with various organic and inorganic substances, influencing ozone layer dynamics and climate change. In organic synthesis, these intermediates can selectively oxidize alkanes (such as CH_4 and C_2H_6) and cyclic alkenes to produce specific alcohol and aldehyde products. To model the efficiency of the hydrocarbon removal by CIs in the atmosphere, the current research focuses on the reactions of two simplest alkanes with the simplest CI and two halogen substituted CIs (e.g., CH_2OO, CF_2OO, CCl_2OO) with high-level VTST/MT calculation.

Methods

Dual-level VTST/MT calculation[2] was performed to predict gas-phase bimolecular reaction rate constants at 50 K ~ 600 K. The level of VTST applied was the canonical variational theory (CVT)[3] and the tunneling correction applied was the small-curvature tunneling (SCT)[4] method. Low-level PES is calculated with M06-2X/6-31+G method and high-level PES is corrected with CCSD(T)/aug-cc-pVTZ method. The gradient and hessian step sizes used in calculating the PES were 0.002 and 0.010 bohr, respectively. The calculated MEP ranges are mostly in the range -5.0 to 4.0 bohr, which differs subtly from each reaction. For The electronic structure calculation was performed using the Gaussian 16 program and the dual-level VTST/MT calculation was performed using the Polyrate 17 program.**

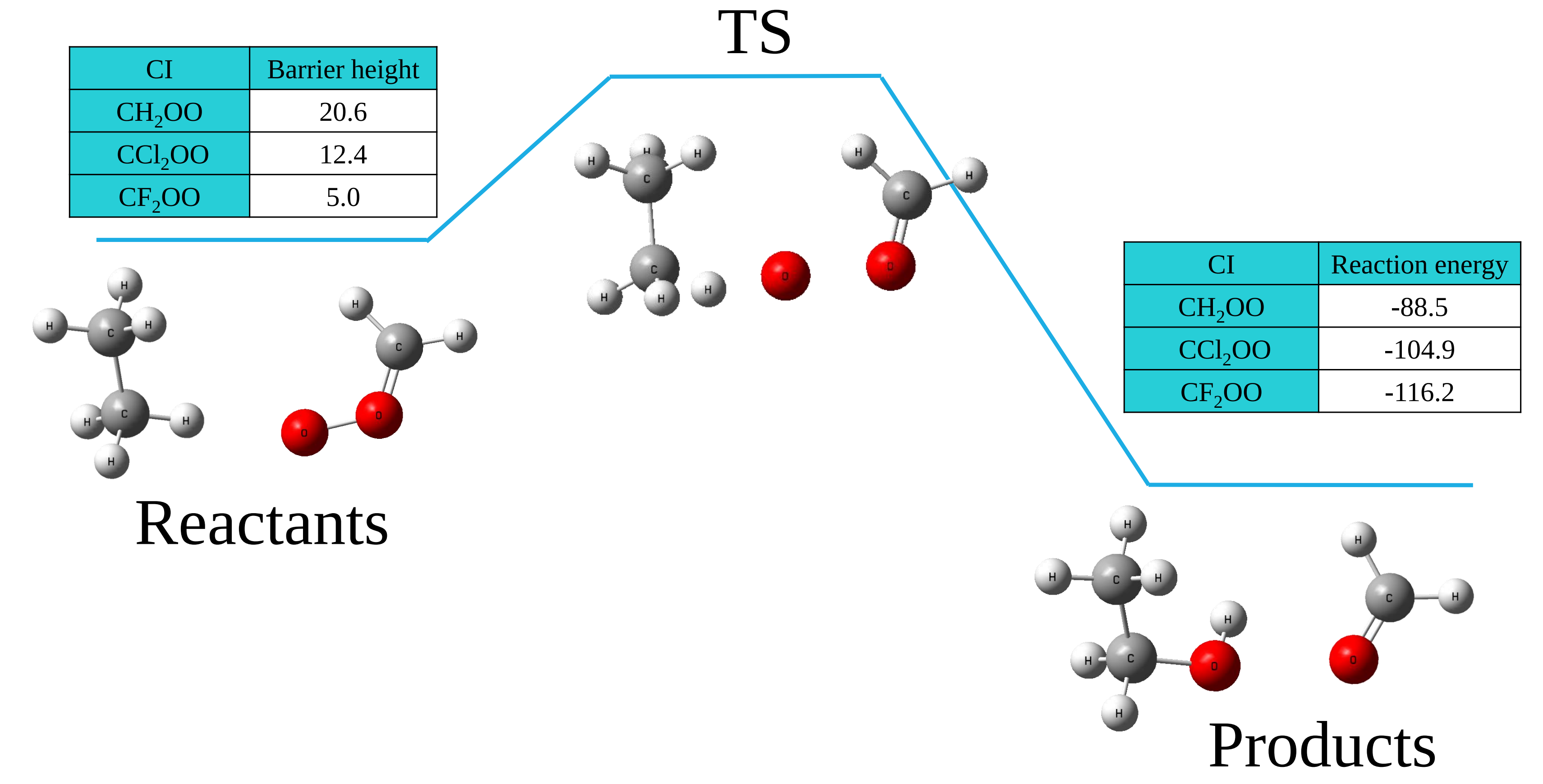
Results & discussion



CI	Barrier height
CH_2OO	23.6
CCl_2OO	15.1
CF_2OO	7.2

CI	Reaction energy
CH_2OO	-83.5
CCl_2OO	-99.9
CF_2OO	-111.2

Figure 1. Calculated Potential Energy Profile of CI + CH4 Unit : kcal/mol



CI	Barrier height
CH_2OO	20.6
CCl_2OO	12.4
CF_2OO	5.0

CI	Reaction energy
CH_2OO	-88.5
CCl_2OO	-104.9
CF_2OO	-116.2

Figure 2. Calculated Potential Energy Profile of CI + C2H6 Unit : kcal/mol

We focus on the simplest form of CI but there are lots of possible candidates e.g., syn-CH_3CHOO and anti-CH_3CHOO and so on. Previous study by Xu et al.[5], the energy barriers are 24.1 and 20.6 kcal/mol respectively. The order of rate constant is anti-CH_3CHOO > CH_2OO > syn-CH_3CHOO and the range is from 10^{-27} to 10^{-30} cm^3 $molecule^{-1}$ s^{-1}.

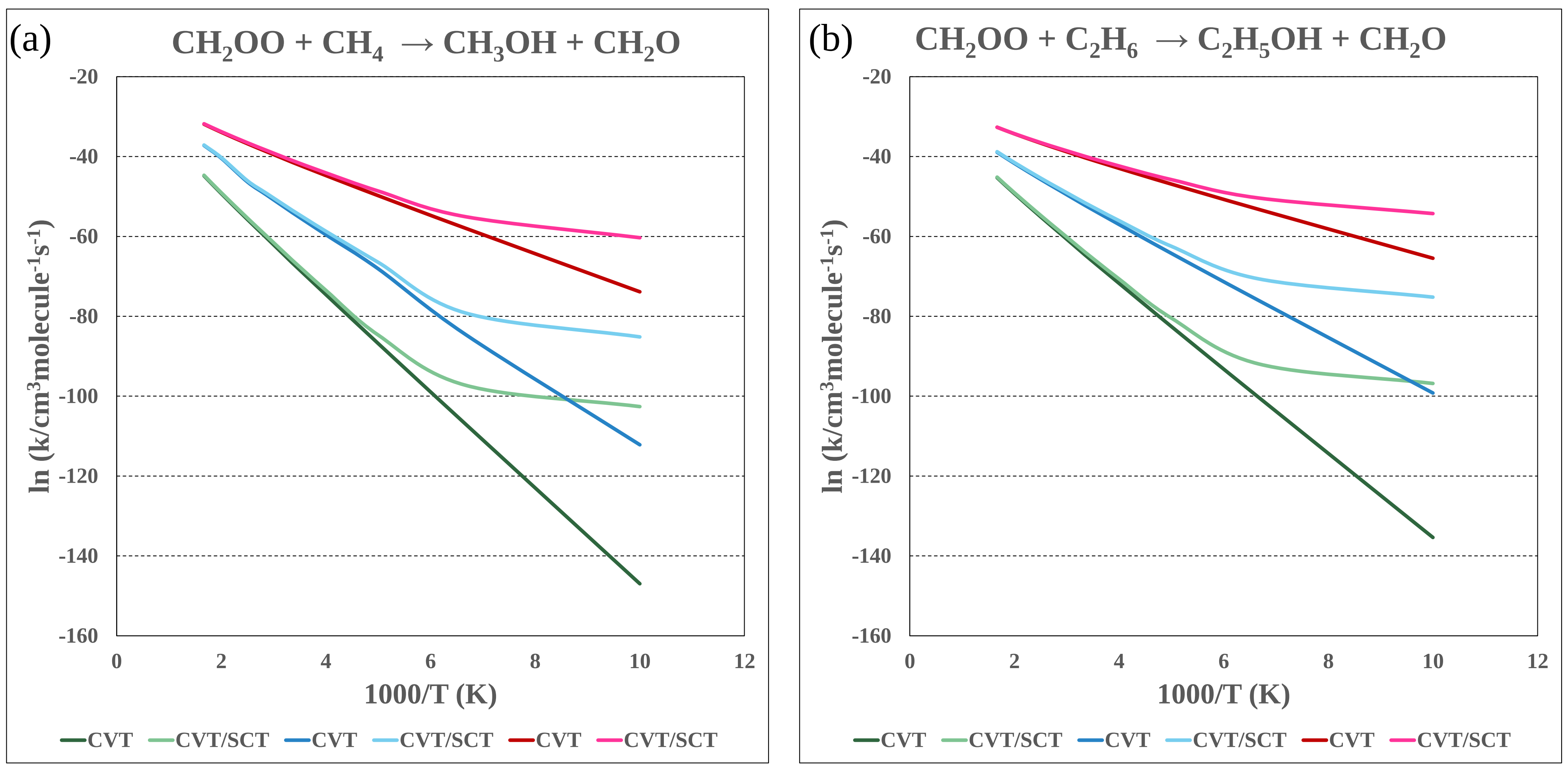


Figure 3. (a) Arrhenius plot of $CX_2OO + CH_4$ bimolecular rate constants (b) Arrhenius plot of $CX_2OO + C_2H_6$ bimolecular rate constants. Green: X = H, Blue: X = Cl, Red: X = F

Table 1. (a) KIEs of CH_2OO reacts with CD_4 between single-level and dual-level correction.
(b) KIEs of CH_2OO reacts with C_2D_6 between single-level and dual-level correction.

(a)	Single-level		Dual-level	
T(K)	CVT	CVT/SCT	CVT	CVT/SCT
50.00	10.1	5480	10.0	5790
100.00	3.98	1590	3.97	1490
150.00	2.82	78.9	2.82	49.8
200.00	2.33	3.64	2.33	3.37
250.00	2.04	2.41	2.04	2.36
298.15	1.86	2.05	1.86	2.02
300.00	1.86	2.04	1.86	2.02
350.00	1.72	1.83	1.72	1.81
400.00	1.62	1.69	1.62	1.68
500.00	1.48	1.51	1.48	1.50
600.00	1.38	1.39	1.38	1.39

(b)	Single-level		Dual-level	
T(K)	CVT	CVT/SCT	CVT	CVT/SCT
50.00	27.1	2170	26.6	1910
100.00	6.17	723	6.13	625
150.00	3.67	41.8	3.65	25.3
200.00	2.79	4.14	2.78	3.84
250.00	2.34	2.76	2.34	2.70
298.15	2.08	2.29	2.07	2.26
300.00	2.07	2.27	2.07	2.25
350.00	1.88	2.01	1.88	1.99
400.00	1.75	1.83	1.75	1.82
500.00	1.58	1.61	1.58	1.61
600.00	1.46	1.48	1.46	1.48

Conclusion

Our results reveal that CF_2OO and CCl_2OO exhibit lower reaction barriers compared to CH_2OO. At 200 K, the temperature where Criegee intermediates are most likely to be stable, the order of rate constants calculated using CVT method follows the trend CF_2OO > CCl_2OO > CH_2OO. The rate constants for each of these intermediates are approximately 10^8 times faster than the next slower one in both methane and ethane reactions. Additionally, reactions with ethane exhibit slightly lower barrier heights compared to methane, leading to a 10^2-fold increase in reaction rates. Compared to the work of Xu et al., our study further clarifies the significant role of tunneling effects and kinetic isotope effects (KIEs), particularly at temperatures below 250 K. The tunneling effect dominates at low temperatures in these reactions, where hydrogen and oxygen atoms undergo transfer and rearrangement. The KIEs observed for hydrogen substitution in alkanes are significantly larger than those for oxygen substitution in formaldehyde oxide, indicating that the reaction rate constants are primarily governed by hydrogen transfer. Moreover, the dual-level VTST/MT approach employed in this work enhances the accuracy of rate constant predictions, outperforming single-level calculations in capturing subtle quantum dynamical effects. Understanding the reaction dynamics of Criegee intermediates with alkanes, which are key greenhouse gases, could contribute to the development of more accurate atmospheric models. Future work will extend this study to investigate the reactions of Criegee intermediates with a broader range of alkanes, further elucidating their role in atmospheric chemistry and hydrocarbon oxidation processes.

References

[1] Criegee, R. *Angew. Chem. Int. Ed*. **1975**, 14, 745–752.

[2] Hu, W.-P.; Liu, Y.-P.; Truhlar, D. G. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 1715.

[3] Truhlar, D. G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, 13, 12, 440–448.

[4] Skodje, R, T; Truhlar, D. G.; Garrett, B. C. *The Journal of Physical Chemistry.* **1981,** 85, 3019-3023.

[5] Xu, K.; Wang, W.; Wei, W.; Feng, W.; Sun, Q.; Li, P. *J. Phys. Chem. A* **2017**, 121 (38), 7236–7245.