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Reaction between Criegee intermediates and hydroxyacetonitrile: Reaction mechanisms, kinetics, and atmospheric implications

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Abstract. Hydroxyacetonitrile ($HOCH_2CN$) is released from wildfires and bleach cleaning environments, which is harmful to the environment and human health. However, its atmospheric lifetime remains unclear. Here, we theoretically investigate the reactions of Criegee intermediates (CH_2OO and *syn*-CH_3CHOO) with $HOCH_2CN$ to explore their reaction mechanisms and obtain their quantitative kinetics. Specifically, we design specific computational strategies and methods close to the CCSDT(Q)/CBS accuracy and use a dual-level strategy for kinetics to elucidate different factors affecting kinetics. We find an unprecedentedly low enthalpy of activation of –5.61 kcal/mol at 0 K for CH_2OO + $HOCH_2CN$ among CH_2OO reaction with atmospheric species containing C≡N group. Furthermore, we also find that the low enthalpy of activation is caused by hydrogen bonding interactions. Moreover, the present findings reveal the rate constant of CH_2OO + $HOCH_2CN$ determined by loose and tight transition states has a significantly negative temperature dependence, reaching 10^{-10} cm^3 molecule^{-1} s^{-1} close to the collisional limit at below 220 K. In addition, our findings also reveal that the rate constants of CH_2OO + $HOCH_2CN$ is 10^3-10^2 times faster than that of OH + $HOCH_2CN$ at below 260 K. The calculated kinetics in combination with data based on global atmospheric chemical transport model suggest that the CH_2OO + $HOCH_2CN$ reaction dominates over the sink of $HOCH_2CN$ at southeast China, northern India at 1 km and in the Indonesian and Malaysian regions at 5 and 10 km.

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1 Introduction

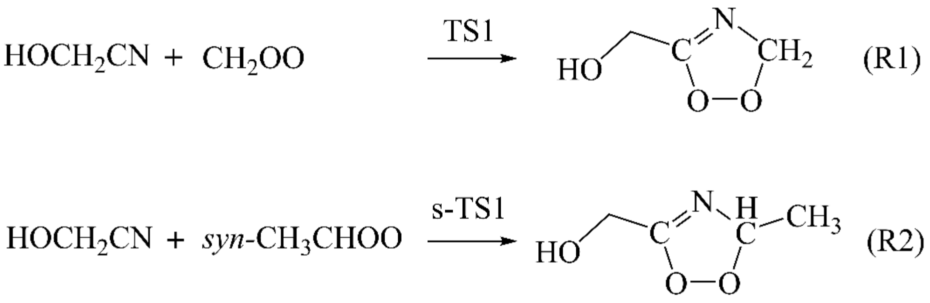
As a reactive nitrogen-containing compound, hydroxyacetonitrile ($HOCH_2CN$) has been recently identified as a C_2H_3NO isomer by using I^- chemical ionization mass spectrometry (I-CIMS) instrument detection. However, previously several field studies had misattributed the C_2H_3NO signal to methyl isocyanate (CH_3NCO) (Finewax et al., 2024) by using CIMS. CIMS is insensitive to the detection of isomers, and thus cannot differentiate between the isomers of CH_3NCO and $HOCH_2CN$. CH_3NCO had been detected in chemicals released from biomass burning, such as wildfires and agricultural fires, as well as in bleach cleaning environments (Mattila et al., 2020; Priestley et al., 2018; Wang et al., 2022a; Koss et al., 2018; Papanastasiou et al., 2020). Therefore, the atmospheric sources of CH_3NCO from previous investigations are actually the sources of $HOCH_2CN$.

Previous studies have demonstrated that $HOCH_2CN$ is secondary pollutant with negative impacts on the environment and human health (Worthy, 1985; Etz et al., 2024; Zhang et al., 2025). Specifically, smoke with $HOCH_2CN$ can be injected into the stratosphere through pyrocumulonimbus clouds, altering the composition of stratospheric aerosols, depleting the ozone layer, and affecting the Earth's radiation balance (Bernath et al., 2022; Ma et al.; Katich et al., 2023). Additionally, $HOCH_2CN$ is harmful to human health, including damage to the respiratory system and skin (Ganguly et al., 2017; Bucher, 1987). Therefore, understanding the chemical processes of $HOCH_2CN$ is important in the atmosphere.

The atmospheric lifetimes of $HOCH_2CN$ in the gas phase are not well understood. Hydroxyl radical (OH) is the most prevalent oxidant in the atmosphere (Wang et al., 2021). The generally considered removal for this species is through the reaction with hydroxyl radical (OH). However, the rate constant of OH + $HOCH_2CN$ is very slow, about 2.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Marshall and Burkholder, 2024). This leads to that OH makes limited contribution to the sinks of $HOCH_2CN$ in the atmosphere. Therefore, it is necessary to explore the other removal routes for $HOCH_2CN$ in the atmosphere.

Criegee intermediates are crucial compounds, resulting from the ozonolysis of unsaturated compounds in the atmosphere (Criegee, 1975; Osborn and Taatjes, 2015; Chhantyal-Pun et al., 2020a; Bunnelle, 1991). Criegee intermediate is considered to be a key intermediate due to its effect on the atmosphere (Chhantyal-Pun et al., 2020b). They play key roles in the chemical processes of atmosphere because they significantly contribute to the formation of hydroxyl radical (OH) and sulfuric acid during the nighttime (Novelli et al., 2014; Lester and Klippenstein, 2018; Kroll et al., 2002; Newland et al., 2018; Kukui et al., 2021). Additionally, they can form secondary organic aerosols via the formation of low-volatile organic compound percussors (Khan et al., 2018; Inomata et al., 2014; Docherty et al., 2005; Chhantyal-Pun et al., 2018). In particular, Criegee intermediates can initiate atmospheric reactions, resulting in additional sinks for atmospheric species such as the reactions of Criegee intermediates with formic acid, nitric acid, hydrochloric acid, and formaldehyde and so on (Khan et al., 2018; Peltola et al., 2020; Long et al., 2009; Chung et al., 2019; Foreman et al., 2016; Luo et al., 2023). While reaction kinetics of Criegee intermediates are prerequisite for elucidating their chemical processes and finding new sink pathways in the atmosphere, their kinetics are very limited and even unknown.

In this article, we have investigated the reactions of Criegee intermediates (CH_2OO and *syn*-CH_3CHOO) with $HOCH_2CN$ by designing specific computational strategies and methods to obtain quantitative enthalpies of activation at 0 K for R1 and R2 (See Scheme 1). Then, we used a dual-level strategy to obtain their quantitative rate constants under atmospheric conditions. In dual delve strategy, the quantitative enthalpy of activation at 0 K acted as high level is used to calculate the rate constant by using conventional transition state theory without tunnelling, while the validated density functional methods are used to obtain recrossing effects and tunnelling by using canonical variational transition state theory involving small curvature tunnelling. Additionally, torsional anharmonicity and harmonicity are considered in kinetics calculations. We also considered the decomposition process of the intermediate product formed in R1. Finally, we discuss the importance of these reactions investigated here by comparing with the corresponding OH radical combined with the atmospheric concentrations of these species based on global atmospheric chemistry transport model GEOS-Chem.



Scheme 1. The reaction route for CH_2OO/*syn*-CH_3CHOO) + $HOCH_2CN$

2 Computational methods and strategies

2.1 Electronic structure methods and strategies

Morden quantum chemical methods and reaction rate theory can be used to obtain quantitative kinetics for atmosphere reactions (Long et al., 2018). However, the calculated processes are very complex, where error bars are controlled by multiple parameters. Furthermore, the parameters are correlated with each other. The basic requirement in kinetics calculations is the quantitative enthalpy of activation that is determined by optimized geometries, zero-point vibrational energies, and single point energies in electronic structure methods (Long et al., 2019a).

Our previous investigations have shown that W3X-L (Chan and Radom, 2015)//DF-CCSD(T)-F12b/jun-cc-pVDZ (Győrffy and Werner, 2018; Parker et al., 2014) can be utilized to obtain quantitative enthalpies of activation at 0 K for the bimolecular reactions containing Criegee intermediate (Wang et al., 2022b; Long et al., 2021; Xie et al., 2024; Zhang et al., 2024). Here, we used W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ to investigate the CH_2OO + $HOCH_2CN$ reaction. Additionally, CCSD(T)-F12a/cc-pVDZ-F12 was used to validate the reliability of DF-CCSD(T)-F12b/jun-cc-pVDZ for optimized geometries and calculated frequencies in the CH_2OO + $HOCH_2CN$ reaction. Thus, with respect to *syn*-CH_3CHOO + $HOCH_2CN$, the validated DF-CCSD(T)-F12b/jun-cc-pVDZ method was used to do geometrical optimization and frequency calculations. In single point energy calculations, it is noted that W3X-L is equal to W2X and post-CCSD(T) components (Chan and Radom, 2015). Here, we assume that post-CCSD(T) contribution of *syn*-CH_3CHOO + $HOCH_2CN$ approximately equates to the contribution from CH_2OO + $HOCH_2CN$. We designed an approximation strategy to obtain accuracy close to W3X-L in equation (1) for *syn*-CH_3CHOO + $HOCH_2CN$ to save computational costs.

$$\Delta E_{\mathrm{BE}}^{\ddagger,\mathrm{s-TS1}} = \Delta E_{\mathrm{W2X}}^{\ddagger,\mathrm{s-TS1}} + \Delta E_{\mathrm{W3X-L-W2X}}^{\ddagger,\mathrm{TS1}} \quad (1)$$

Here, $\Delta E_{\mathrm{BE}}^{\ddagger,\mathrm{s-TS1}}$ is the barrier height for the transition state s-TS1 (See Scheme 1). $\Delta E_{\mathrm{W2X}}^{\ddagger,\mathrm{s-TS1}}$ is the barrier height for s-TS1 calculated by W2X. $\Delta E_{\mathrm{W3X-L-W2X}}^{\ddagger,\mathrm{TS1}}$ is post-CCSD(T) contribution that comes from the difference between W3X-L and W2X in TS1 (See Fig. 1 and 2). The benchmark methods are called higher level (HL) structure methods; this helps to clearly illustrate the dual-level strategy for kinetics calculations discussed below.

The reliable density functional method was chosen in comparison to the benchmark results to perform direct kinetics calculations. Here, we chose M06-CR (Long et al., 2016)/MG3S (Zhao et al., 2005) and M11-L (Peverati and Truhlar, 2012) /MG3S functional method for the reactions of CH_2OO and *syn*-CH_3CHOO with $HOCH_2CN$ due to the mean unsigned error (MUD) of 0.23 kcal/mol and 0.72 kcal/mol as listed in Table 1, respectively. M06CR/MG3S and M11-L/MG3S are called lower level (LL) electronic structure method in the present work.

Table 1. The enthalpies of activation at 0 K for the transition states of the CH_2OO/*syn*-CH_3CHOO + $HOCH_2CN$ reactions by various theoretical methods (in kcal/mol).

Methods	$\Delta H_0^{\ddagger}$	MUD
	TS1	
CH_2OO + $HOCH_2CN$		
W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ	–5.61	0.00
M06CR/MG3S	–5.38	0.23
W2X//CCSD(T)-F12a/cc-pVDZ-F12	–6.16	0.55
W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	–6.19	0.58
CCSD(T)-F12a/cc-pVDZ-F12	–5.98	0.37
DF-CCSD(T)-F12b/jun-cc-pVDZ	–6.77	1.16
M11-L/MG3S	–7.52	1.91
syn-CH_3CHOO + $HOCH_2CN$		
$\Delta E_{\mathrm{BE}}^{\ddagger,\mathrm{s-TS1}}$//DF-CCSD(T)-F12b/jun-cc-pVDZ	–1.39	0.00
W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ	–1.97	0.58
M11-L/MG3S	–2.11	0.72
DF-CCSD(T)-F12b/jun-cc-pVDZ	–3.13	1.74
M06-CR/MG3S	0.47	1.86

2.2 Scale factors for calculated frequencies

Previous studies have verified that the standard scale (See Table S1) is suitable for reactants and some transition states (Bao et al., 2016b; Zhang et al., 2017). In order to further explore the effect of anharmonicity on the zero-point vibrational energy, the calculation of the specific reaction scale factors was carried out. The results in Tables S2 and S4 show that the anharmonicity can be neglected in calculating enthalpy of activation. Details of the calculations can be found in previous work of Long et al (Long et al., 2023). Therefore, we used standard scale factor in this work.

2.3 Kinetics methods

The rate constants of the reaction (R1) are calculated by considering the tight and loose transition states because of its low-temperature close-to-collision-limit rate constant. Here, the loose transition state refers to the process from the reactants to the pre-reaction complexes, while the tight transition state is the process from the reactants to the products via the transition state TS1 in Figure 1. The steady state approximation based on the unified statistical theory (CUS) (Garrett and Truhlar, 1982; Bao and Truhlar, 2017; Zhang et al., 2020; Long et al., 2024) is used to calculate the total rate constant by simultaneously considering both transition states by

$$k_{CUS}(T) = \frac{k_{tight}k_{loose}}{k_{tight}+k_{loose}} \tag{1}$$

where k_{tight} was calculated by using a dual-level strategy discussed below, while k_{loose} was calculated by variable-reaction-coordinate variational transition state theory (VRC-TST) (Zheng et al., 2008; Bao et al., 2016a; Georgievskii and Klippenstein, 2003). In VRC-TST calculation, the reaction coordinate *s* is obtained by defining the distance between one pivot point on one reactant and the other pivot point on the other, and the dividing surface is defined by the pivot point connected to each reactant. The distance *s* between the pivot points was varied between 2.6 and 10 Å in steps of 0.1 Å to find the optimum value. Simultaneously, 500 Monte Carlo sampling points were used to sample single-faceted dividing surfaces. The VRC-TST calculation were performed by minimizing the rate constant by changing the distance between two pivot points and the location of the pivot points. The VRC-TST were performed by M06-CR/MG3S for reaction R1. However, the high-pressure-limited rate constants of the reaction (R2) were calculated only by considering tight transition state s-TS1.

The dual-level strategy has been put forward and used in previous works (Long et al., 2022; Long et al., 2018, 2019b; Xia et al., 2022; Gao et al., 2024; Long et al., 2016; Sun et al., 2023). The strategy combines the theory of conventional transition states (Haring, 1942) on the HL with the theory of canonical variational transition states (Garrett and Truhlar, 1979; Truhlar et al., 1982) on the LL and takes into account the small curvature tunnelling effect (Liu et al., 1993). In addition, the torsional anharmonicity factor is considered in our strategy (Long et al., 2023; Zhang et al., 2024; Sun et al., 2023; Li and Long, 2024; Xie et al., 2024; Jiang et al., 2025). The rate constant is given by eqn (2),

$$k = k(T)_{\text{HL}}^{\text{TST}}\, \kappa_{LL}^{SCT}(T)\, \Gamma_{LL}(T)\, \text{F}_{fwd,LL}^{\text{MS-T}} \tag{2}$$

where $k(T)_{\text{HL}}^{\text{TST}}$ is the rate constant without recrossing and tunneling effects calculated at HL. $\kappa_{LL}^{SCT}(T)$ and $\Gamma_{LL}(T)$ is referred to tunneling transmission coefficient and recrossing transmission coefficient calculated by LL, respectively. $\text{F}_{fwd,LL}^{\text{MS-T}}$ is torsional anharmonicity factor calculated by using multi-structural method with coupled torsional potential and delocalized torsions (MS-T(CD) method) (Zheng and Truhlar, 2013; Chen et al., 2022). Three factors were calculated at the validated density functional methods at LL. More details were provided in Tables S4 and S5.

2.4 Software

All density functional calculations were performed by using Gaussian 16 (Frisch et al., 2016) and MN-GFM (Zhao et al., 2015) for geometry optimization and frequency calculations and all coupled cluster calculations by using Molpro 2022 (Werner et al., 2012) and MRCC code (Kállay et al., 2020). Direct kinetics calculations were performed using Polyrate 2017 (Zheng et al., 2017b) and Gaussrate 2017-C (Zheng et al., 2017a). Torsional anharmonicity factor was calculated by using MSTor 2022 code (Zheng et al., 2012). And rate constants were calculated by Kisthelp program package (Canneaux et al., 2014).

3 Results and Discussion

3.1 Electronic Structure calculation results

3.1.1 The reaction of CH_2OO + $HOCH_2CN$

The reaction of CH_2OO + $HOCH_2CN$ has not been reported in the literature. It is noted that there are three different H-O, C≡N, and CH_2 groups in $HOCH_2CN$. Therefore, we explored four different mechanisms of CH_2OO + $HOCH_2CN$ as described in Fig. 1. Three of them is similar to the CH_2OO + CH_3CN reaction, as they contain the same C-H and C≡N bonds (Zhang et al., 2022).

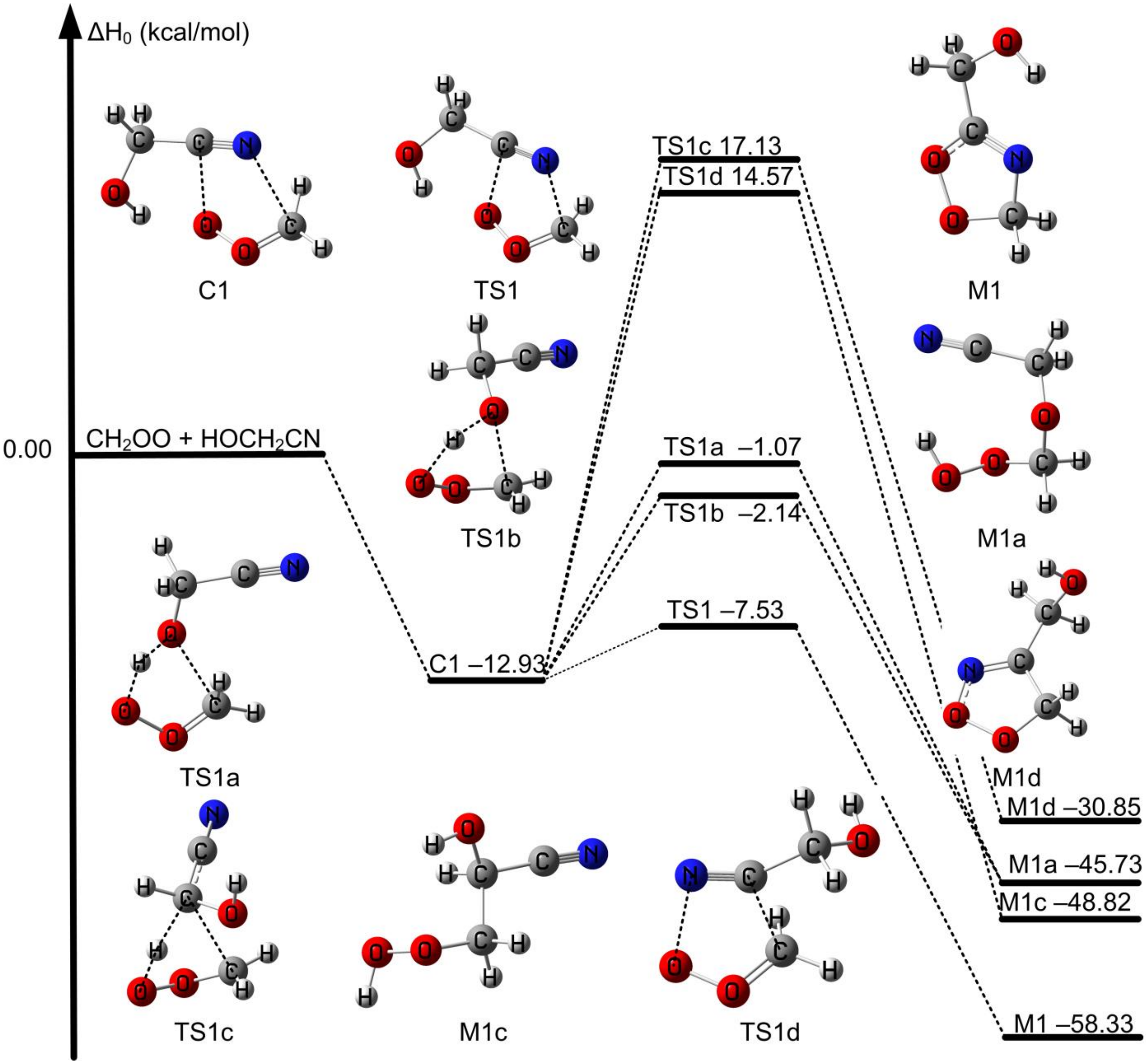


Figure 1: The relative enthalpies at 0 K for the reaction of CH_2OO + $HOCH_2CN$. Values are given for all species as calculated by M11-L/MG3S.

The most feasible (first) mechanism leads to the formation of five-membered cyclic intermediate M1 via C≡N group addition to COO group in Fig. 1. Specifically, the addition of carbon atom of C≡N group in $HOCH_2CN$ is added to the terminal oxygen atom of CH_2OO and the addition of N atom of C≡N group in $HOCH_2CN$ is added to the central carbon of CH_2OO by the transition state TS1 (See Fig. 1). This mechanism is the same as CH_2OO + CH_3CN and is like that of the reaction between CH_2OO and carbonyl group (Long et al., 2021; Luo et al., 2023; Chhantyal-Pun et al., 2018; Chung et al., 2019). We called

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the mechanism as carbon-oxygen addition coupled carbon-nitrogen addition mechanism. The second mechanism still occurs via five-membered cyclic transition states TS1a and TS1b responsible for the formation of M1a in Fig. 1. The H atom of the OH group in $HOCH_2CN$ is migrated to the terminal oxygen atom of CH_2OO, and simultaneously the oxygen atom of OH group in $HOCH_2CN$ is added to the central carbon atom of CH_2OO by TS1a and TS1b, which is similar to the reaction of CH_2OO with molecules containing OH group such as H_2O/H_2O_2/$HOOCH_2SCHO$/$CH_3C(O)OOH$/HOCl (Long et al., 2016; Zhao et al., 2022; Long et al., 2024; Zhang et al., 2024; Xie et al., 2024). The third mechanism is the addition of C atom on the C≡N group in $HOCH_2CN$ to the central C atom of CH_2OO and the N atom of C≡N group in $HOCH_2CN$ to the terminal O of CH_2OO by TS1d. The last mechanism is that the H atom on the central CH_2 group in $HOCH_2CN$ shifts to the terminal O atom of CH_2OO and the C atom is added to the central C atom of CH_2OO via TS1c, which leads to the formation of a peroxide. We mainly consider the most feasible mechanism in detail in this work because the enthalpy of activation via TS1 at 0 K is at least 5 kcal/mol lower than those of other reaction pathways by M11-L/MG3S (See Fig. 1). Moreover, the intermediate product M1 formed has a larger enthalpy of activation of –58.33 kcal/mol in Fig.1.

We previously showed that CCSD(T)-F12a/cc-pVDZ-F12 can reach the accuracy of CCSD(T)-F12a/cc-pVTZ-F12 for geometrical optimization and frequency calculations for reactions containing C≡N groups (Long et al., 2021; Zhang et al., 2024; Zhang et al., 2022). Therefore, we further show the reliability of DF-CCSD(T)-F12b/jun-cc-pVDZ by using CCSD(T)-F12a/cc-pVDZ-F12. As a result, the difference between W2X//CCSD(T)-F12a/cc-pVDZ-F12 and W2X//DF-CCSD(T)-F12b/jun-cc-pVDZ shows that DF-CCSD(T)-F12b/jun-cc-pVDZ is only 0.03 kcal/mol for the enthalpy of activation of TS1 at 0 K (See Table 1); this further shows that DF-CCSD(T)-F12b/jun-cc-pVDZ is quantitatively reliable for geometrical optimizations and frequency calculations in the preset investigations.

The enthalpy of activation at 0 K of R1 via TS1 is computed to be –5.61 kcal/mol calculated by W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ-F12, which is 5.25 lower than that of CH_2OO + CH_3CN (Zhang et al., 2022) calculated by W3X-L//CCSD(T)-F12a/cc-pVTZ-F12. The much lower enthalpy of activation at 0 K via TS1 in R1 leads to much faster rate constant of R1, comparing with the CH_2OO + CH_3CN reaction. Simultaneously, we also found that the activation enthalpy is 2.05 kcal/mol lower than that of the $(CF_3)_2CFCN$ + CH_2OO reaction calculated using the best estimate (Jiang et al., 2025). From geometrical point of view, the much lower enthalpy of activation at 0 K via TS1 is due to the introduction of HO group in $HOCH_2CN$, comparing with CH_3CN; this remarkably change the reactivity of $HOCH_2CN$ toward CH_2OO. We note that the introduction of OH in $HOCH_2CN$ results in the formation of hydrogen bonding in TS1. The hydrogen bonding is formed via the interaction OH group in $HOCH_2CN$ with the terminal oxygen atom in CH_2OO in TS1. The bond distance between the hydrogen atom of HO group in $HOCH_2CN$ and the terminal oxygen atom of CH_2OO in TS1 is computed to be 1.942 Å by DF-CCSD(T)-F12b/jun-cc-pVDZ (See Fig. 2); this shows the formation of hydrogen boning from geometrical point of view (Kar and Scheiner, 2004). The present results reveal that the hydrogen bonding interaction opens a way for decreasing the enthalpy of activation at 0 K.

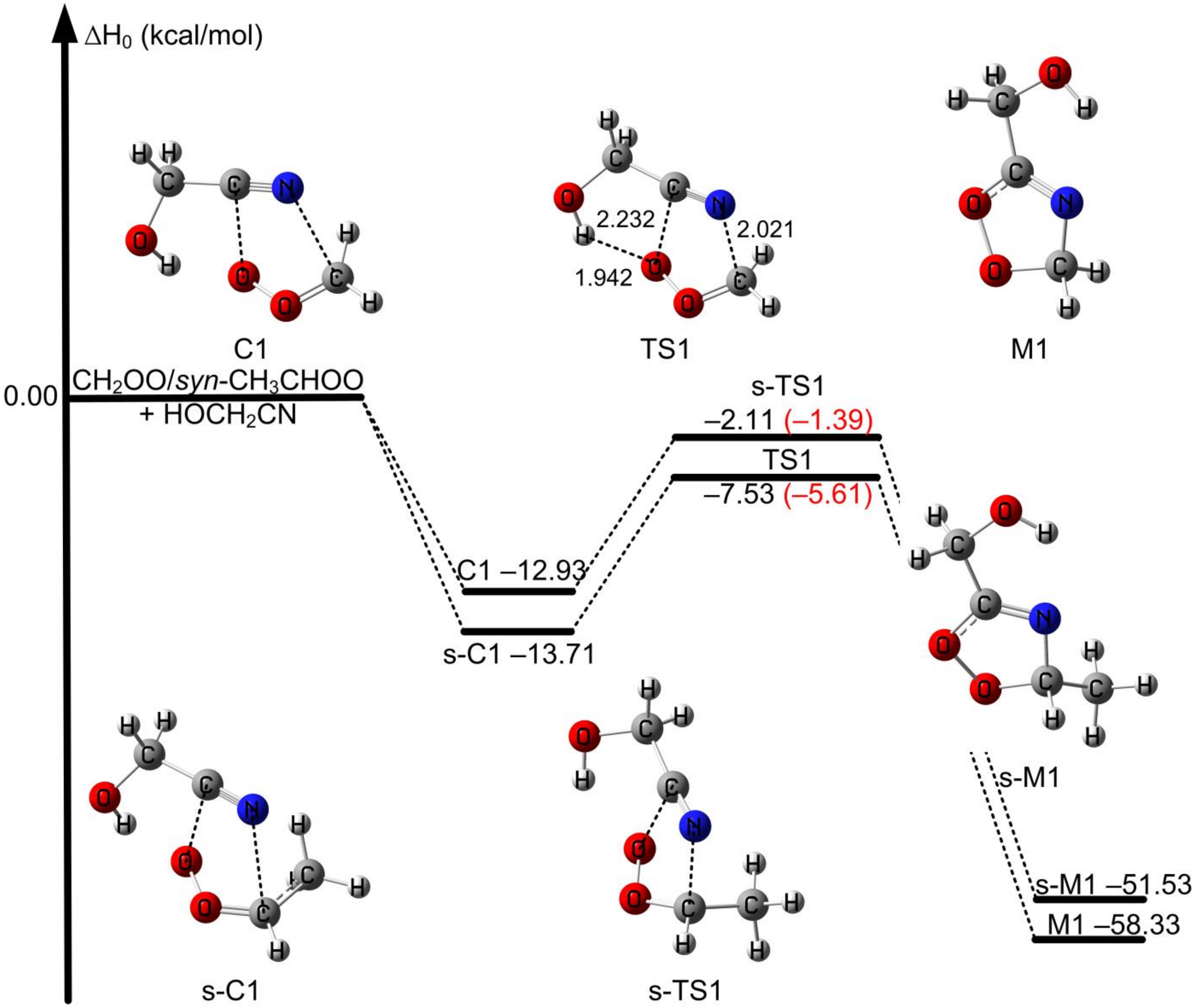

Figure 2: The relative enthalpies at 0 K for the reaction of CH_2OO/*syn*-CH_3CHOO + $HOCH_2CN$ for R1 and R2. Values are given for all species as calculated by M11-L/MG3S, and in small parentheses and brackets, values are given for the transition state TS path as calculated by W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ. The bond length in TS1 is in units of Å.

CCSD(T) has been considered as "gold standard" in the quantum chemical calculations. However, the previous investigations have shown that post-CCSD(T) is necessary to obtain quantitative reaction energy barriers for atmospheric reactions (Long et al., 2019b, 2016; Hansen et al., 2022; Xia et al., 2024). Here, we discuss the contribution of post-CCSD(T) calculations. The contribution of post-CCSD(T) is 0.58 kcal/mol from the difference between W3X-L and W2X of TS1, which is the same as the result of the reaction of CH_2OO with CH_3CN (0.58 kcal/mol) (Zhang et al., 2022) and our previous estimated

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value (0.50 kcal/mol) (Zhang et al., 2022; Zhao et al., 2022). This shows that post-CCSD(T) calculations are necessary for obtaining quantitative enthalpies of activation for the reaction of Criegee intermediate with $HOCH_2CN$. The MUD of M06-CR/MG3S is 0.23 kcal/mol for CH_2OO and $HOCH_2CN$ in Table 1. Therefore, M06-CR/MG3S was chosen to perform direct kinetics calculation for the reaction of CH_2OO with $HOCH_2CN$.

Decomposition pathways for the formed product M1 have also been investigated at the M11-L/MG3S level; this is similar to the product decomposition pathway in the CH_2OO + CH_3CN reaction (Zhang et al., 2022). Firstly, the product M1 undergoes oxygen-oxygen bond cleavage via M1-TSa to result in forming a singlet biradical intermediate M2, which is similar to the reaction of CH_2OO + HCHO (Jalan et al., 2013). Subsequently, the intermediate M2 undergoes the formation of carbon-nitrogen bonding to form a three-member ring with the enthalpy of activation of 21.76 kcal/mol relative to M1 via the transition state M2-TSb. Then, the three-member ring intermediate then undergoes an open-ring coupled hydrogen shift process to form M4 via the transition state M3-TSc. Eventually, the H atom of the intermediate OH on intermediate M4 is transferred to the N atom to yield the final product P1. The process was depicted in Fig. 3. The calculated enthalpy of activation at 0 K of P1 is –86.55 kcal/mol, indicating the unimolecular isomerization is –5.61 thermodynamically driven.

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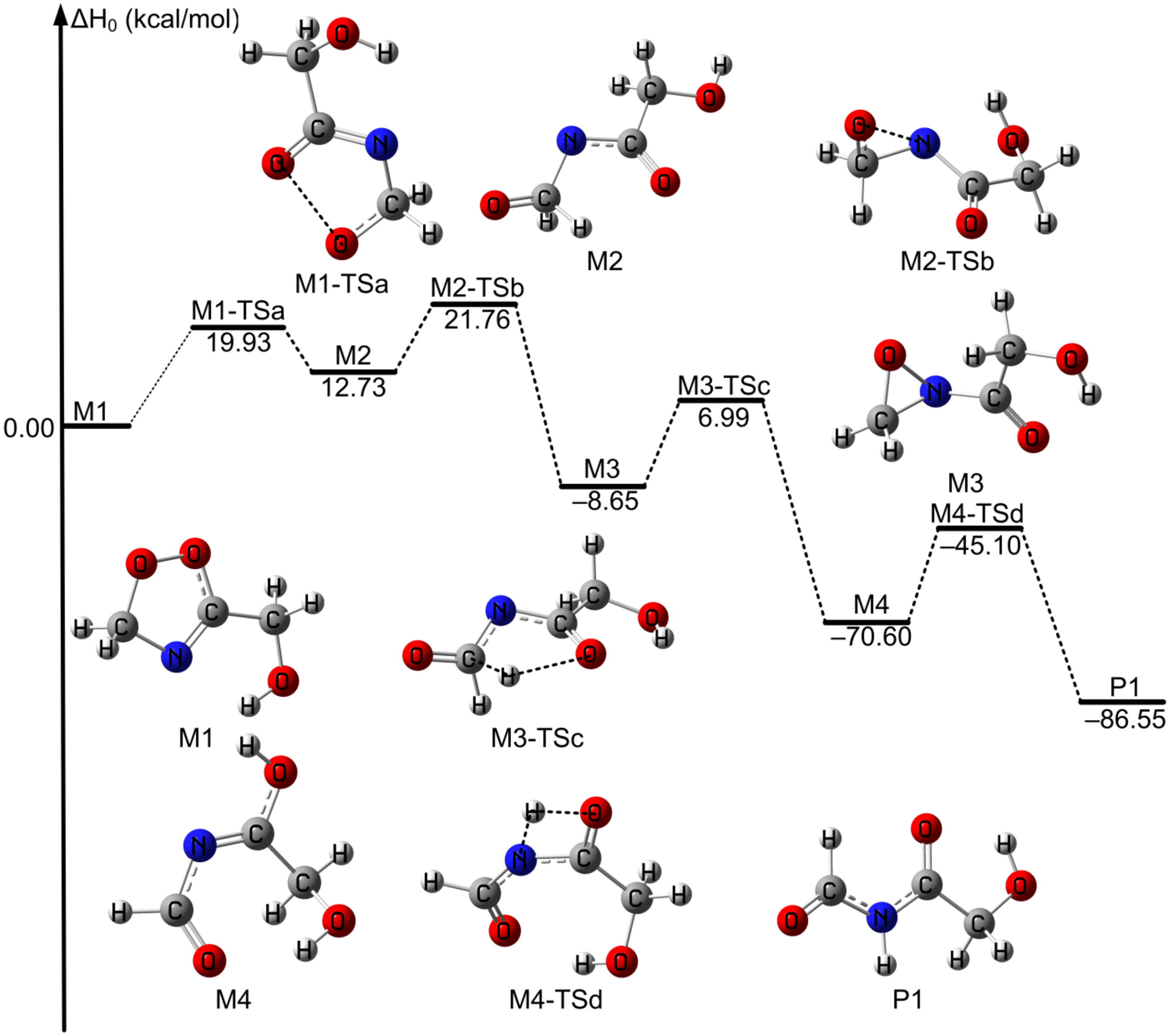

Figure 3: The relative enthalpies at 0 K for the decomposition reactions of the intermediate product M1 formed in the CH_2OO + $HOCH_2CN$ reaction. Values are given for all species as calculated by M11-L/MG3S.

3.1.2 The reaction of syn-CH_3CHOO + $HOCH_2CN$

210 The reaction of *syn*-CH_3CHOO with $HOCH_2CN$ has been also studied by considering similar mechanisms for the reaction of CH_2OO + $HOCH_2CN$. The HL calculation of the enthalpy of activation at 0 K of s-TS1 was performed by employing an approximation method, as listed in eqn (1), which is discussed in method section. The lowest energy route is depicted in Fig. 2 and details can be found in Fig. S1. The enthalpy of activation of s-TS1 at 0 K is –1.39 kcal/mol calculated by HL calculation,

which is 4.22 kcal/mol higher than that of TS1. The lower reactivity of *syn*-CH_3CHOO than CH_2OO results in the much slower reaction of *yn*-CH_3CHOO with $HOCH_2CN$. However, the enthalpy of activation for s-TS1 is 5.45 kcal/mol lower than the reaction of *syn*-CH_3CHOO + CH_3CN calculated by W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ (Zhang et al., 2022); this again shows that the introduction of OH group in $HOCH_2CN$ can significantly reduce the enthalpy of activation at 0 K toward Criegee intermediates. However, the decrease in value of 5.45 kcal/mol between *syn*-CH_3CHOO + $HOCH_2CN$ and *syn*-CH_3CHOO + CH_3CN is different from the corresponding value of 5.25 between CH_2OO + $HOCH_2CN$ and CH_2OO + CH_3CN; this indicates that the change in the enthalpy of activation at 0 K is not only determined by the change from CH_3CN to $HOCH_2CN$, but also determined by the change from CH_2OO to *syn*-CH_3CHOO. Therefore, the enthalpy of activation at 0 K for every reaction can only be quantitively obtained by specific calculations. We also found that the MUD between the HL result and M11-L/MG3S is only 0.72 kcal/mol. Therefore, the combination of M11-L functional method with MG3S basis set was chose to perform direct kinetics calculations.

3.2 Kinetics

The rate constants for the reaction of R1 and R2 have been calculated and listed in Table 3. The details are listed in Table S5 and S6. We have fitted the calculated rate constants by eqn (3).

$$k_{\infty} = A\left(\frac{T+T_0}{300}\right)^n \exp\left[-\frac{E(T+T_0)}{R(T^2+T_0{}^2)}\right] \tag{3}$$

Here, T is temperature in Kelvin and R is ideal gas constant (0.0019872 kcal mol^{-1} K^{-1}). The fitting parameters A, n, E, and T_0 were listed in Table S7. The temperature-dependent Arrhenius activation energies also have been fitted by using eqn (4) as listed in Table 3.

$$E_a = -R\frac{d\, In\, k}{d\,(1/T)} \tag{4}$$

The calculated rate constants for k_1 are decreased from 2.64 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} to 1.83 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 200 - 340 K in Table 2, which shows significant negative temperature dependence. The temperature dependent activation energies are decreased from –3.45 to –5.32 kcal/mol, which provides the evidence for the negative temperature dependence of the rate constants of R1. The rate constant for the reaction of CH_2OO + $HOCH_2CN$ is 5.79 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, which is 24 times larger than the rate constant for the reaction of OH + $HOCH_2CN$ at 298 K (Marshall and Burkholder, 2024). In particular, we have found that the rate constants of reaction R1 is two magnitude order faster than the reaction of OH + $HOCH_2CN$ when temperature below 260 K (See Table 2).

The rate constant of the reaction R2 ranges from 3.00 × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} to 2.03 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} in the temperature range 200 – 340 K, which exhibits weak negative temperature dependence. As a result, we found that *syn*-CH_3CHOO make a minor contribution for the sink of $HOCH_2CN$ because the rate constants of *syn*-CH_3CHOO + $HOCH_2CN$ are always lower than those of the reaction of OH + $HOCH_2CN$ at 200 – 340 K. However, the rate constant of reaction of R2 is 2.69 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1}, which is two orders of magnitude slower than the rate constant of the reaction of OH + $HOCH_2CN$ and two orders of magnitude larger than that of the reaction of *syn*-CH_3CHOO + CH_3CN, suggesting that the contribution of *syn*-CH_3CHOO to the sink of $HOCH_2CN$ is small, yet this reaction is more favourable than that for the reaction of *syn*-CH_3CHOO + CH_3CN in the atmosphere (Zhang et al., 2022). Therefore, we do not consider the contribution of *syn*-CH_3CHOO to $HOCH_2CN$ in the atmosphere. Additionally, we have found that recrossing, tunneling transmission, and torsional anharmonicity effects for the reaction of R1 and R2 can be negligible because they are close to unit, as listed in Table S5 and S6.

Table 2. The rate constants (cm^3 molecule^{-1} s^{-1}) and activation energies (kcal mol^{-1}) for the CH_2OO/syn-CH_3CHOO + $HOCH_2CN$ reactions at different temperatures.

T/K	k_1[a]	Ea_1[a]	k_2[b]	Ea_2[b]	k_{OH}	k_1/k_{OH}
200	2.64×10^{-10}	–3.45	3.00×10^{-14}	–7.65	1.06×10^{-13}	2495.80
220	1.32×10^{-10}	–4.33	8.16×10^{-15}	–3.54	1.25×10^{-13}	1056.27
240	5.26×10^{-11}	–4.93	5.20×10^{-15}	–2.55	1.48×10^{-13}	354.83
250	3.39×10^{-11}	–5.14	4.46×10^{-15}	–2.33	1.61×10^{-13}	210.30
260	2.25×10^{-11}	–5.31	3.92×10^{-15}	–2.18	1.76×10^{-13}	127.83
270	1.52×10^{-11}	–5.43	3.16×10^{-15}	–2.02	1.91×10^{-13}	79.59
280	1.05×10^{-12}	–5.52	3.16×10^{-15}	–2.02	2.07×10^{-13}	50.90
298	5.79×10^{-12}	–5.59	2.69×10^{-15}	–1.98	2.39×10^{-13}	24.26
300	5.44×10^{-12}	–5.59	2.65×10^{-15}	–1.98	2.42×10^{-13}	22.45
320	3.04×10^{-12}	–5.55	2.29×10^{-15}	–1.99	2.81×10^{-13}	10.84
340	1.83×10^{-12}	–5.42	2.03×10^{-15}	–2.04	3.22×10^{-13}	5.68

[a] The rate constants and Arrhenius activation energies for the reaction R1.
[b] The rate constants and Arrhenius activation energies for the reaction R2.

3.3 Atmospheric implications

The reaction of OH with $HOCH_2CN$ has been investigated in previous work (Marshall and Burkholder, 2024). Therefore, we considered the competition between the R1 reaction and the OH + $HOCH_2CN$ reaction by comparing with their rate ratios followed by eqn (5),

$$v_1 = \frac{k_1[CH_2OO][HOCH_2CN]}{k_{OH}[OH][HOCH_2CN]} = \frac{k_1[CH_2OO]}{k_{OH}[OH]} \qquad (5)$$

where k_1 is referred to the rate constants of the reaction of CH_2OO + $HOCH_2CN$, k_{OH} is rate constants of the reaction of OH with $HOCH_2CN$ from the literature (Marshall and Burkholder, 2024).

In the atmosphere, Vereecken et al. have evaluated that the concentrations for stabilized Criegee intermediates are in the range between 10^4 and 10^5 molecule cm^{-3}, especially in the Amazon rainforest region, where sCIs could reach a maximum concentration of 10^5 molecule cm^{-3} (Novelli et al., 2017). Typically, the concentration of OH varies between 10^4 and 10^6 molecules cm^{-3} (Ren et al., 2003; Stone et al., 2012; Lelieveld et al., 2016). However, due to the consideration of reactions CH_2OO with H_2O and $(H_2O)_2$, the CH_2OO concentration in the GEOS-Chem model simulations is always an order of magnitude less than the results of Vereecken et al. Therefore, we consider the rate ratios between CH_2OO + $HOCH_2CN$ and OH + $HOCH_2CN$ at different concentrations of CH_2OO and OH at 200-340 K in Table 3, and further discuss the atmospheric implications based on global atmospheric chemistry model GEOS-Chem.

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Table 3. The concentration ratio of CH_2OO to OH at different heights from different region in GEOS-Chem.

Height	T/K	P/mbar	$[CH_2OO]^a$	$[OH]^a$	$[CH_2OO]/[OH]^a$	k_1/k_{OH}	v_1^b
				India			
1	290.2	1013	253.44	1.92×10^4	1.32×10^{-2}	33.27	0.44
5	250.5	495.9	23.10	1.40×10^4	1.65×10^{-3}	203.47	0.34
10	215.6	242.8	20.22	6.24×10^3	3.24×10^{-3}	1262.75	4.09
				the southeast of China			
1	290.2	1013	95.21	1.49×10^4	6.39×10^{-3}	33.27	0.21
5	250.5	495.9	19.22	1.49×10^4	1.29×10^{-3}	203.47	0.26
10	215.6	242.8	11.34	1.08×10^4	1.05×10^{-3}	1262.75	1.33
				Indonesian and Malaysian			
1	290.2	1013	150.42	3.45×10^4	4.36×10^{-3}	33.27	0.15
5	250.5	495.9	79.21	1.38×10^4	5.74×10^{-3}	203.47	1.17
10	215.6	242.8	137.75	5.51×10^3	2.50×10^{-2}	1262.75	31.57

[a] the data were extracted in the work of Long et al.(Long et al., 2024)
[b] the product of rate ratio and concentration ratio.

The competition between the CH_2OO + $HOCH_2CN$ reaction and the OH + $HOCH_2CN$ reaction is determined by two factors, one is the rate constant ratio and the other is the concentration ratio. The concentration ratio decreases with increasing altitude until two orders of magnitude are observed at 10 km in the Indonesian and Malaysian regions. It is noted that when the altitude increases, the atmospheric temperature is remarkably decreased. The atmospheric temperatures are 250.5-198 K at the altitudes from 5-15 km. The results show that although the concentration ratio of two orders of magnitude, CH_2OO does make some contribution to the sink of $HOCH_2CN$ at 1 km. At 10 km, CH_2OO + $HOCH_2CN$ can completely dominate over the OH + $HOCH_2CN$ reaction in India, southeast China, Indonesia, and Malaysian region (See Table 3 and Figure 4). However, CH_2OO only dominates over the sink of $HOCH_2CN$ in the Indonesian and Malaysian regions due to the relatively large ratio of rate constants and concentration ratios at low temperatures at 5 km. Using the model data, we find that the sink of CH_2OO to $HOCH_2CN$ has strong geographical and sensitivity to altitude (See Fig. 4.).

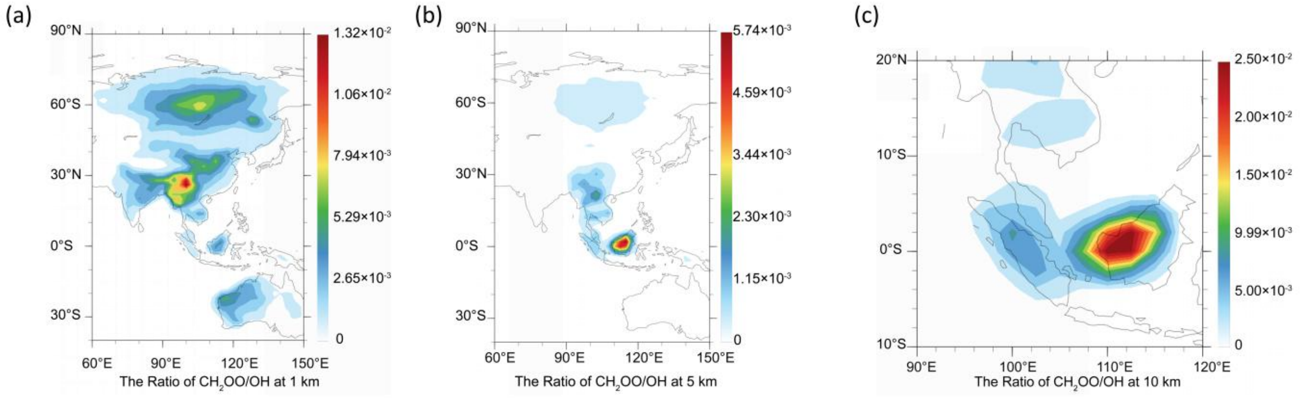

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Figure 4: The ratio of CH_2OO to OH at night from literature.(Long et al., 2024) (a) at 1 km, (b) at 5 km, (c) at 10 km, (d)at 15 km.

4 Conclusions

Wildfires have attracted the attention of researchers due to their impact on aerosols and the ozone layer, which can lead to adverse effects on the environment and human health. $HOCH_2CN$ is a harmful species present in wildfires. Thus, it is necessary to study its atmospheric chemical processes. The quantitative kinetics for reactions of Criegee intermediates with $HOCH_2CN$ have been investigated by using designing specific computational strategies for electronic structure calculations and dual-level strategy for kinetics calculations coupled with atmospheric chemistry transport model analysis. The high-accuracy quantum chemical calculations were performed by using W3X-L//DF-CCSD(T)-F12b/jun-cc-pVDZ-F12 for reaction of R1 close to CCSDT(Q)/CBS accuracy and an approximation strategy to reach W3X-L accuracy for R2. Additionally, CCSD(T)-F12a/cc-pVDZ-F12 was used to verified the reliability of DF-CCSD(T)-F12b/jun-cc-pVDZ-F12 for reaction R1. Four mechanisms were found for the reactions of CH_2OO and $HOCH_2CN$, with the lowest energy pathway route called carbon-oxygen addition coupled carbon-nitrogen addition. We find an unprecedentedly low enthalpy of activation of –5.61 kcal/mol at 0 K for the reactions of CH_2OO with C≡N group of atmospheric species. The present findings uncover that the post-CCSD(T) is necessary to obtain quantitative enthalpy of activation at 0 K because its contribution is 0.58 kcal/mol. However, we also find that all the factors contain anharmonicity, recrossing and tunneling, torsional anharmonicity effects, which are negligible for obtaining quantitative rate constants. The rate constants for the CH_2OO with $HOCH_2CN$ increase from 3.18×10^{-10} to 2.25×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which is two orders of magnitude higher than the reaction of OH + $HOCH_2CN$ below 260 K. Therefore, the reaction of CH_2OO with $HOCH_2CN$ dominates over the sinks of $HOCH_2CN$ in southeast China, northern India at 5 km and in the Indonesian and Malaysian regions at 5 and 10 km. This work provides a new insight into the role of Criegee intermediate in the removal of $HOCH_2CN$.

Supplement. The following information is provided in the Supplement： Standard scale factors and Specific Reaction Scale Factors; The activate enthalpies at 0 K for the CH_2OO + $HOCH_2CN$ reaction at different methods; The anharmonicity effect for the enthalpy of activation; The rate constants of the reaction of R1 and R2; The fitting parameters for k_1 and k_2; The ratio of the rate constants at various temperatures and different concentration; Absolute energies (Hartree) and the Cartesian coordinates (Å) of the optimized geometries; The relative enthalpies at 0 K for the reaction of CH_2OO + $HOCH_2CN$.

Data availability. All raw data can be provided by the corresponding authors upon request.

Author contributions. Chaolu Xie performed the calculations, analysed and interpretation of data, and wrote the manuscript draft. Shunyu Li performed the calculations.   Bo Long designed the project, analysed and interpretation of data, and reviewed and edited the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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