

Criegee + HONO reaction: the dominant sink of Criegee, and the missing non-photolytic source of OH•

Pradeep Kumar¹, Vishva Jeet Anand¹, and Philips Kumar Rai¹

¹Department of Chemistry, Malaviya National Institute of Technology Jaipur, Jaipur, 302017, India

Correspondence: Pradeep Kumar (pradeep.chy@mnit.ac.in)

Abstract. One of the most important puzzles in atmospheric chemistry is a mismatch between observed and modelled concentrations of OH•/HO₂• in the presence of high concentration of volatile organic compounds. It is now well established that to fulfill this gap, one needs a reaction that is not only capable of producing OH• but also able to act as a sink of HO₂•. In the present work, we are proposing the Criegee + HONO reaction as a possible solution of this puzzle. Our quantum chemical and kinetic calculations clearly suggest that this reaction can not only be an important source of OH radical but can also act as a sink of HO₂ radical. Our study also suggests that HONO has the potential to become the most dominant sink of certain Criegee intermediates, surpassing SO₂ and water dimer, even in high humid conditions.

1 Introduction

It is well-known that the atmospheric chemistry is mainly dominated by the radicals (Anderson, 1987; Monks, 2005). Particularly in the troposphere, these radicals are key in degrading various pollutants, a phenomenon as important as the ozone layer for the existence of life (Weinstock, 1969; Lelieveld et al., 2004). The primary radicals responsible for the oxidative power of troposphere come from the HO_X (OH•, HO₂•, RO•, RO₂• etc.) family (Prinn, 2003; Ehhalt, 1987; Khan et al., 2018). Among them, OH• is considered as the most important oxidant in the troposphere (Lelieveld et al., 2002, 2016). Although OH• is the most studied radical in the atmosphere, there are still open questions regarding its sources in the atmosphere (Heald and Kroll, 2021; Yang et al., 2024). For a long time, it was believed that OH radicals are mainly formed in daytime via photolysis of tropospheric ozone (O₃), and nitrous acid (HONO) (Calvert et al., 1994; Alicke et al., 2003; Griffith et al., 2016; Aumont et al., 2003). But now, with various on-field measurements (Geyer et al., 2003; Ren et al., 2003; Emmerson and Carslaw, 2009), it is well established that OH radicals are also present at night in sufficient amounts. In fact, average nighttime concentration of OH• ($\sim 2.6 \times 10^5$ molecule cm⁻³) is only one order of magnitude lower than its average daytime concentration ($\sim 1.9 \times 10^6$ molecule cm⁻³) (Emmerson and Carslaw, 2009). As the lifetime of OH• is only ~ 1 second, this much concentration of OH• during night indicates its *in situ* generation via non-photolytic sources. The major non-photolytic source of OH• is the recycling of HO₂• radicals (Whalley et al., 2011; Stone et al., 2012; Hofzumahaus et al., 2009; Smith et al., 2006; Hens et al., 2013). Specifically, during the daytime, the primary reaction contributing to this recycling process is NO• + HO₂•, whereas at night, the key reaction is NO₃• + HO₂• (Hall et al., 1988; Mellouki et al., 1988, 1993; Rai and Kumar, 2024). However, compared to photolytic sources, non-photolytic sources of OH• remain less understood in atmospheric chemistry (Brown and Stutz, 2012; Emmerson and Carslaw, 2009). This is evidenced by the fact that, in the atmosphere with a high concentration of volatile organic compounds (VOCs), atmospheric models consistently under-predict the concentration of OH• compared to

the observed value (Emmerson and Carslaw, 2009; Stone et al., 2012). This discrepancy is especially pronounced in winter (Harrison et al., 2006; Heard et al., 2004; Slater et al., 2020) and indoor environments (Østerstrøm et al., 2025; Gomez Alvarez et al., 2013; Reidy et al., 2023), where light plays a minimal role. In addition, the discrepancy between measured and observed value of OH• was also found to depend upon NO_X concentration. Both under low NO_X (Carslaw et al., 2001; Tan et al., 2001; Lelieveld et al., 2008; Tan et al., 2017) as well as high NO_X (above 6 ppbv) (Slater et al., 2020), the discrepancy was found to be quite significant. As the primary recycling of HO₂• to OH• occurs via NO_X, the under-prediction of OH• by models under low NO_X conditions suggests either the presence of another route for recycling or some new non-photolytic source of OH•. This hypothesis is further strengthened by a few combined experimental and modelling studies. For example, Lu et al. (Lu et al., 2012) have to introduce an artificial source of OH• ↔ HO₂• inter-conversion ($\text{RO}_2 + \text{X} \longrightarrow \text{HO}_2\bullet, \text{HO}_2\bullet + \text{X} \longrightarrow \text{OH}\bullet$) in their atmospheric model to match the experimental concentration profile. In another study, to match the experimental OH concentration with models, Whalley et al. (Whalley et al., 2011) increased the concentration of VOCs in their model. Although their computed OH• concentration becomes closer to experimental value, the mismatch between observed and measured concentration of HO₂• becomes worse. There have been various attempts to identify the missing source of OH• in the atmosphere (Paulot et al., 2009; Peeters et al., 2014; Sander et al., 2019). For example, Peeters et al. (Peeters et al., 2009; Peeters and Müller, 2010; Peeters et al., 2014) suggested that the oxidation of isoprene can regenerate HO_X radicals in the presence of light via isoprene-peroxy radical interconversion and isomerisation pathways (Leuven Isoprene Mechanism (LIM)). Although the introduction of LIM into chemical models were found to improve the value of modelled OH• concentration, the modelled values still remain under-predicted (Crounse et al., 2011; Teng et al., 2017; Berndt et al., 2019; Novelli et al., 2020; J. Medeiros et al., 2022). Particularly, the LIM is more effective in regions where biogenic volatile organic compounds (BVOCs) dominate and NO_X concentration is ultra low, e.g. rain forest regions (Whalley et al., 2011; Feiner et al., 2016; Lew et al., 2020). In contrast, in regions where sufficient anthropogenic sources of VOCs are present, e.g. in polluted areas, LIM is not effective. In addition, LIM is not fundamentally a HO₂• to OH• interconversion process, rather it is the recycling of VOCs to OH•. In a recent study, Yang et al. (Yang et al., 2024) suggested that aldehyde could be an additional source of OH•. Authors proposed that the autoxidation of carbonyl organic peroxy radicals (R(CO)O₂) derived from higher aldehydes, can produce OH• through photolysis (RAM mechanism). Though RAM mechanism efficiently predicts OH• production at low NO_X concentrations, it still under-predicts the same at high NO_X concentrations. Interestingly, when both LIM and RAM are incorporated into a base model in the presence of moderate concentration of NO_X, OH• concentration improves significantly, but the discrepancy in the modelled and observed HO₂• remains unresolved. It is also worth mentioning that photolysis is an important part of both, LIM and RAM, and hence, both of these mechanism do not offer any help in improving the model OH• concentration in nocturnal environment. Furthermore, both LIM and RAM are also not directly involved in recycling of HO₂• to OH•. The discrepancy in the model occurs during both day and night (Faloona et al., 2001; Hens et al., 2013; Geyer et al., 2003), and is associated with HO₂• to OH conversion (Whalley et al., 2011; Hofzumahaus et al., 2009). In light of these studies, we believe that the puzzle of missing OH• source is very much alive and the key to this puzzle may be a non-photolytic source capable of HO₂• ↔ OH• recycling.

In the present work, we are proposing reaction of Criegee intermediate with HONO as a source of OH•. Criegee Intermediates

(CIs) are formed during the ozonolysis of alkenes (Criegee, 1975; Johnson and Marston, 2008; Taatjes, 2017). In fact, alkene ozonolysis is a highly exothermic reaction produces energized CIs. Some of the energized CIs readily convert into OH• via unimolecular decomposition, while the remaining CIs get collisionally stabilized (sCI) (Horie and Moortgat, 1991; Donahue et al., 2011; Novelli et al., 2014; Alam et al., 2011). sCIs can undergo either a thermal unimolecular dissociation or a bimolecular reaction. Depending upon concentration of the co-reactant and rate constant of such bimolecular reaction, the bimolecular reaction paths can be the main sink of sCI (Osborn and Taatjes, 2015; Lin et al., 2015; Sheps et al., 2014; Vereecken and Francisco, 2012). There are several studies in the literature that suggest CI reacts rapidly with the trace gases present in the atmosphere (Cox et al., 2020; Mallick and Kumar, 2020; Vereecken et al., 2015). In this work, we are suggesting HONO as a new partner for the bimolecular reaction of Criegee intermediates as a possible source of OH•. The concentration of CI ($\sim 10^4 - 10^5$ molecule cm^{-3}) in the atmosphere is comparable with $\text{Cl}^\bullet$ ($\sim 5.0 \times 10^4 - 3.0 \times 10^5$ molecule cm^{-3}) and OH• ($\sim 1.0 \times 10^5 - 4.0 \times 10^6$ molecule cm^{-3}) (Khan et al., 2018; Novelli et al., 2017). Similarly, nitrous acid (HONO) is also an important trace gas present in the nighttime atmosphere in a considerable amount (Li et al., 2021; Song et al., 2023). The average concentration of HONO is $\sim 8.9 \times 10^{10}$ molecule cm^{-3} , which can reach as high as $\sim 6.9 \times 10^{11}$ molecule cm^{-3} during the fog event (Pawar et al., 2024). Although a general wisdom about HONO is, its concentration builds up in nighttime, and in daytime, it decomposes via photolysis to give OH•, HONO itself is a highly reactive molecule and can participate in various bimolecular chemical reactions during night (Anglada and Sole, 2017; Lu et al., 2000; Wallington and Japar, 1989). Moreover, in indoor environments, high concentrations of OH• have been found to strongly correlate with high concentrations of HONO (Gomez Alvarez et al., 2013). It is important to mention that, the reaction of HONO with the simple Criegee intermediate (CH_2OO) has already been investigated theoretically (Kumar et al., 2022). In that investigation, the major product was predicted to be hydroperoxymethyl nitrite (HPMN). We will show in the present work that the main product of this reaction is OH• and this path is the dominant path of the title reaction.

2 Methodology

2.1 Electronic structure theory

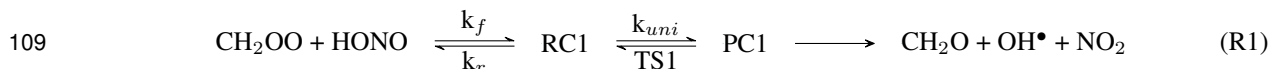
There are two parts of electronic structure theory; optimization and subsequent single-point energy calculations. The criteria behind choosing a method for optimization is; it should be computationally not very demanding and at the same time, it should accurately predict the geometries and frequencies of the species involved in the reaction. Based on these criteria, all the geometries have been optimized using M06-2X functional in conjunction with aug-cc-pVTZ basis set using Gaussian16 software package (Frisch et al., 2016). We have compared the geometrical parameters of the isolated species obtained at M06-2X/aug-cc-pVTZ level of theory with the experimental (Johnson III, 2013; Ruscic et al., 2004) values available in the literature in Figure S1 of the ESI. It is evident from Figure S1 that the maximum deviation in bond lengths at M06-2X/aug-cc-pVTZ level of theory from the experiment was only ~ 0.04 Å, whereas the maximum deviation in bond angles from the experiment was $\sim 1^\circ$. It clearly suggests that M06-2X/aug-cc-pVTZ level of theory is providing accurate geometries of the isolated species. In addition, we have also compared the frequencies of the isolated species obtained at M06-2X/aug-cc-pVTZ level of theory

with the experimental values in Table S2 of the ESI. The maximum deviation in frequency from experiment was $\sim 250\text{ cm}^{-1}$. Therefore, we believe that M06-2X/aug-cc-pVTZ level of theory is appropriate for optimization and frequency calculations. This conclusion is also consistent with the previous work (Kumar et al., 2022) where M06-2X/aug-cc-pVTZ level of theory was found to be adequate for the title reaction. For the second part, we carried out single-point energy calculations for the optimized geometries at CCSD(T) level of theory in complete basis set limit (CBS). To estimate energies at CCSD(T)/CBS level of theory, first, we calculated the single point energies at CCSD(T)/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVTZ level of theory, and then extrapolated these energies to corresponding CBS limit using the method of Varandas and Pansini (Varandas and Pansini, 2014; Pansini et al., 2016) (see ESI for the details).

2.2 Kinetics

Energetics calculations shed light only on enthalpic requirement of the reaction, for a barrierless process, entropy is an equally important factor. Therefore, to account for both, enthalpy and entropy, we have estimated the rate constant for $\text{CH}_2\text{OO} + \text{HONO}$ reaction within a temperature range of 213–320 K.

The mechanism of $\text{CH}_2\text{OO} + \text{HONO}$ reaction can be represented by following reaction:



To calculate the overall rate constant of the title reaction, we have used the master equation approach as implemented in the MESMER software package. It is evident that reaction R1 proceeds in three steps. In the first step, the formation of RC occurs via a barrierless association of isolated reactants. MESMER uses the inverse Laplace transform (ILT) method to estimate the energy-dependent rate constant, $k(E)$, for this step. This, in turn, requires fitted Arrhenius parameters as input to MESMER, which are obtained using KTOOLS code as implemented in the MultiWell suite of programs (Barker et al., 2021). KTOOLS uses variational transition state theory (VTST) for the barrierless reaction. The inputs for KTOOLS are potential energy surface (PES) scans along the coordinate describing the dissociation of RC into isolated reactants. Each point on the PES serves as a trial transition state; KTOOLS searches for the transition state for which the reaction flux is minimized. In the next step, RC undergoes unimolecular dissociation to PC via a transition state. MESMER applies Rice-Ramsperger-Kassel-Marcus (RRKM) theory, including tunneling contributions via an unsymmetrical Eckart barrier. In the final step, PC spontaneously dissociates to form isolated products. It is important to mention that we do not find a tight transition state for product formation from PC; therefore, we have treated this step also using ILT. It is worth noting that the reactant complex (RC) and the transition state (TS) exhibit hindered rotational motions, and multiple conformations may exist due to different torsional angles. To account for this, we have used the HinderedRotorQM1D model in MESMER to compute rate constants. Specifically, we performed a one-dimensional potential energy scan of OH torsion along the N–O bond in both RC and TS, covering the full 0° to 360° range. The resulting energy profiles are used to calculate the hindered rotor partition functions. During this scan, we found local minima in both RC and TS, suggesting that our originally optimized structures correspond to the global minimum conformers. The Lennard-Jones (L-J) model is used to calculate the collision frequency between reactants and the bath gas. Air is used as

the bath gas, with L-J parameters $\sigma = 3.68 \text{ \AA}$ and $\epsilon/kT = 86.2 \text{ K}$. The L-J parameters for RC are not known; therefore, they are estimated using the L-J parameters of CI and HONO via the combining rule (Schnabel et al., 2007).

$$\sigma_{RC} = \frac{1}{2}(\sigma_{CH_2OO} + \sigma_{HONO})$$

$$(\epsilon/k_B)_{RC} = [(\epsilon/k_B)_{CH_2OO}(\epsilon/k_B)_{HONO}]^{1/2}$$

The L-J parameters for RC using above equations turn out to be, $\sigma=4.68$ and $\epsilon=246.15 \text{ K}$. A single-exponential down model is used to describe the collisional energy transfer probability with a maximum energy grain size of 100 cm^{-1} and $\Delta E_{down} = 150 \text{ cm}^{-1}$.

3 Results and discussion

In the present work, we have investigated the reactions of Criegee intermediates (CIs) with nitrous acid (HONO). It is known that the reactivity of CI is greatly influenced by the substitution group present on carbon center of the CI. Therefore, to account for it, we have studied two types of CIs; the simplest Criegee intermediate (CH_2OO) and the dimethyl-substituted Criegee intermediate ($(CH_3)_2COO$). Another motivation for choosing $(CH_3)_2COO$ comes from the fact that in contrast to simple Criegee which is formed only from the ozonolysis of ethene, the dimethyl-substituted Criegee intermediate can be generated from the ozonolysis of many highly abundant alkenes, such as terpenes and myrcene, and hence, the concentration of $(CH_3)_2COO$ is significantly higher in the atmosphere. In this section, we will first discuss the energetics and kinetics of $CH_2OO + HONO$ reaction, followed by $(CH_3)_2COO + HONO$ reaction.

The potential energy surface for $CH_2OO + HONO$ reaction is depicted in Figure 1. It is evident from Figure 1 that reaction occurs in two steps; in the first step, CH_2OO interacts with H atom of HONO via hydrogen bonding and forms a stable reactant-complex (RC1), which is $\sim 10.1 \text{ kcal mol}^{-1}$ stable than isolated reactants. In the next step, RC undergoes a unimolecular transformation to form final products, i.e., CH_2O , $OH^\bullet$, and NO_2 . This happens via a transition-state (TS1) that is effectively $\sim 8.0 \text{ kcal mol}^{-1}$ below the isolated reactants. It suggests that the formation of $OH^\bullet$ via $CH_2OO + HONO$ reaction is a barrierless process. Prior to the formation of the isolated products, a product complex (PC1) is formed which is $\sim 44.7 \text{ kcal mol}^{-1}$ stable than isolated reactants. The overall reaction was found to be exothermic by $\sim 17.3 \text{ kcal mol}^{-1}$ that lies close to the experimental value of $\sim 16.9 \text{ kcal mol}^{-1}$ (Ruscic et al., 2004), again confirming the adequacy of the methodology used. The computed bimolecular rate constant values ($k_{bi}^{CH_2OO}$) for $CH_2OO + HONO$ reaction in the temperature range 213–320 K are given in Table 1. It is evident from Table 1 that the values of $k_{bi}^{CH_2OO}$ slightly decrease with temperature increasing, a typical character of a barrierless process. For example, at 213 K, values of $k_{bi}^{CH_2OO}$ is $1.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ which becomes $\sim 6.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 320 K.

Figure 2 depicts the potential energy surface of $(CH_3)_2COO + HONO$ reaction. It is evident from Figure 2 that $(CH_3)_2COO + HONO$ reaction also proceeds in two steps; in the first step, $(CH_3)_2COO$ associates with HONO to form a stable reactant-complex (RC2) that is $\sim 14.2 \text{ kcal mol}^{-1}$ more stable than isolated reactants. Finally, RC transforms into isolated products, i.e., $(CH_3)_2CO$, $OH^\bullet$, and NO_2 . This transformation occurs through a transition state that lies $\sim 10.1 \text{ kcal mol}^{-1}$ below the

isolated reactants, making the overall reaction barrierless. Here also product complex (PC2) is formed before isolated product with stabilization energy ~ -36.2 kcal mol $^{-1}$ with respect to isolated reactant.

Using the energetics, we have also computed the rate constant for (CH₃)₂COO + HONO reaction employing master equation in the same 213–320 K temperature range. The calculated bimolecular rate constants ($k_{bi}^{(CH_3)_2COO}$) are listed in Table 1. It is evident from Table 1 that similar to CH₂OO + HONO reaction, here also the values of $k_{bi}^{(CH_3)_2COO}$ slightly decrease with increasing temperature within whole range of temperature. But the bimolecular rate constant of (CH₃)₂COO + HONO reaction becomes ~ 2.6 to 3.6 times higher compared to the same for CH₂COO + HONO reaction at all temperatures considered in the present work. For example, at 298 K, the value of $k_{bi}^{(CH_3)_2COO}$ is $\sim 2.03 \times 10^{-11}$ cm³ molecule $^{-1}$ sec $^{-1}$, whereas the value of $k_{bi}^{CH_2OO}$ is only $\sim 7.2 \times 10^{-12}$ cm³ molecule $^{-1}$ sec $^{-1}$. In the bimolecular rate constant, the capture rates of both the reactions are almost same, given in Table S3 of the ESI. The difference in the rate values of the two reactions depends on whether the reactant complex will proceed forward or backward, which further depends on the forward and backward Gibbs free energy barriers of the reactant complex. The Gibbs free energy profile at 298 K is shown in Figure S2 of the ESI. It is evident from Figure S2 that due to the higher stabilization of RC2, its reverse free energy barrier is high (~ 2.9 kcal mol $^{-1}$), while the same is very low for RC1 (~ -1.3 kcal mol $^{-1}$). Consequently, the relative yields of product are higher for the (CH₃)₂COO + HONO reaction compared to CH₂COO + HONO reaction.

Lastly, it is important to discuss the uncertainties associated with the computed rate constant due to limitations in the methodology used for the energetics calculations. For example, a major source of uncertainty can originate from the fact that Criegee intermediates are known to possess moderate multireference character, and CCSD(T)/CBS sometimes fails in accurately predicting the energetics of such reactions (Rai and Kumar, 2022; Mallick et al., 2019; Mallick and Kumar, 2018). It is worth mentioning that for multireference systems, incorporating higher-level excitations at the coupled-cluster level yield energetics within chemical accuracy (Tajti et al., 2004; Misiewicz et al., 2018; Nguyen et al., 2013; Anand and Kumar, 2023; Rai and Kumar, 2023). To assess the uncertainty in the energetics arising from the multireference character, we have carried out CCSDT(Q)/CBS calculations for the smaller Criegee intermediate reaction, i.e., CH₂OO + HONO. We focused on key stationary points; the reactant complex (RC) and the transition state (TS). The various components of the post-CCSD(T) corrections (δ_T and $\delta_{T(Q)}$) are provided in Table S7 of the ESI. It is evident from Table S7 that post-CCSD(T) corrections lead to only minor changes in the calculated energetics of CH₂OO + HONO reaction. Quantitatively, these corrections reduce the stabilization energy of RC by ~ 0.54 kcal mol $^{-1}$, while increasing the barrier height by a similar ~ 0.67 kcal mol $^{-1}$. Both variations fall well within the range of chemical accuracy. This supports the reliability and computational efficiency of our chosen level of theory, CCSD(T)/CBS//M06-2X/aug-cc-pVTZ, for studying the title reaction. Another source of uncertainty in the computed rate constant may arise from the error in estimation of frequency. The maximum deviation in frequency is 250 cm $^{-1}$, which corresponds to ~ 0.7 kcal mol $^{-1}$ in the reaction energetics. To account for this, we have assumed an uncertainty of ± 1 kcal mol $^{-1}$ in both well depths and reaction barriers. Using this assumption, we estimated the resulting uncertainty in the rate constants at 298 K for the model reaction CH₂OO + HONO. Due to ± 1 kcal mol $^{-1}$ uncertainty in the reaction barriers and well depths, the deviation in the rate constant is $\sim 7.21^{+4.67}_{-3.65} \times 10^{-12}$ cm³ molecule $^{-1}$ sec $^{-1}$ (± 1 reaction barriers) and $\sim 7.21^{+0.45}_{-0.45} \times 10^{-12}$ cm³ molecule $^{-1}$ sec $^{-1}$ (± 1 well depths), respectively.

196 After estimating the energetics and kinetics of title reaction, it is important to discuss the impact of title reaction in the atmo-
 197 spheric chemistry. The importance of title reaction in the atmosphere critically depends on how it competes with other known
 198 sinks of Criegee intermediate, i.e., H_2O , $(\text{H}_2\text{O})_2$, NO_2 , NO , CO , and SO_2 . The efficiency of a chemical reaction in the atmo-
 199 sphere depends upon two factors; rate of reaction and concentration of co-reactants. The effective rate constant (k_{eff}) captures
 200 both of these factors as it is defined as the multiplication of bimolecular rate and concentration of co-reactants. Therefore,
 201 we have used k_{eff} to compare the effectiveness of title reaction compared to other sinks of Criegee intermediates. A list of
 202 effective rates for the reaction of CI with H_2O , $(\text{H}_2\text{O})_2$, NO_2 , NO , CO , and SO_2 at 298 K are provided in Table S4 of the ESI.
 203 To compute k_{eff} , the average concentrations of all the sinks have been taken from polluted urban environments. The corre-
 204 sponding rate coefficients of all the sinks are taken from experimental measurements. One can see from Table S4, the effective
 205 rate coefficients (k_{eff}) of CO , NO , and NO_2 are lower compared to those of SO_2 , H_2O , and $(\text{H}_2\text{O})_2$. For example, k_{eff} for the
 206 reaction of CI with SO_2 is 3.35 sec^{-1} , while that for NO_2 is only 0.9 sec^{-1} . Therefore, in the present work, we have focused
 207 our attention on a detailed comparison of the title reaction with SO_2 , H_2O , and $(\text{H}_2\text{O})_2$. The stabilized Criegee such as un-
 208 substituted and disubstituted Criegee intermediates can dissociate via bimolecular reactions with radicals, depending upon the
 209 concentration of their co-reactant in the atmosphere. As far as abundance of HONO is concerned, it is found in both regions;
 210 forested as well as polluted in significant amounts (Kim et al., 2015; Acker et al., 2006; Ren et al., 2010; Zhang et al., 2012;
 211 He et al., 2006; Su et al., 2008; Ren et al., 2006; Rondon and Sanhueza, 1989; Zhou et al., 2011; Pawar et al., 2024; Vereecken
 212 et al., 2012). Among the two, HONO concentrations are comparatively higher in polluted urban areas, such as megacities.
 213 Therefore, we expect HONO to play a more effective role as a sink for Criegee intermediates in such regions. Hence, we have
 214 used representative concentrations of HONO and SO_2 in urban areas for the primary comparison. The concentration of water
 215 varies greatly in the atmosphere depending upon saturation vapour pressure and relative humidity (RH) (Anglada et al., 2013;
 216 Rai and Kumar, 2025). Therefore, in the case of H_2O and $(\text{H}_2\text{O})_2$, we have taken two concentrations; one calculated at 20%
 217 RH, and the other calculated at 100% RH. The former serves as lower limits of H_2O and $(\text{H}_2\text{O})_2$ concentrations, whereas the
 218 latter serves as the upper limits of H_2O and $(\text{H}_2\text{O})_2$ concentrations.

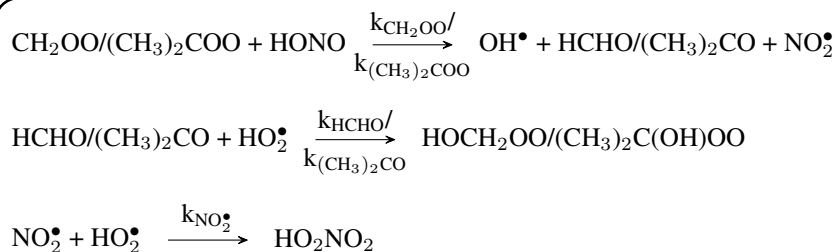
219 In Figure 3, we have compared the k_{eff} of $\text{CH}_2\text{OO} + \text{HONO}$ with the k_{eff} of $\text{CH}_2\text{OO} + \text{H}_2\text{O}/(\text{H}_2\text{O})_2/\text{SO}_2$ reactions. Figure 3
 220 shows, at 100% RH, k_{eff} of $\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2$ is the dominant reaction across the entire temperature range (213–320 K) (Lin
 221 et al., 2016). At 20% RH, k_{eff} for $\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2$ and $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ remain dominant at higher temperatures, specifically
 222 within 235–320 K and 260–320 K, respectively. However, at lower temperatures, k_{eff} of $\text{CH}_2\text{OO} + \text{HONO}$ becomes domi-
 223 nant, surpassing both, $\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2$ and $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ in the range of 213–235 K and 213–260 K, respectively. As far
 224 as $\text{CH}_2\text{OO} + \text{SO}_2$ reaction is concerned (Onel et al., 2021), its k_{eff} values are ~ 5 times higher than that of $\text{CH}_2\text{OO} + \text{HONO}$
 225 reaction within the whole temperature range, indicating that $\text{CH}_2\text{OO} + \text{HONO}$ reaction is a minor contributor compared to
 226 $\text{CH}_2\text{OO} + \text{SO}_2$.

227 Similarly, we have compared our dimethyl substituted Criegee reaction ($(\text{CH}_3)_2\text{COO} + \text{HONO}$) with other known bimolec-
 228 ular reactions of $(\text{CH}_3)_2\text{COO}$. Here also, we have computed k_{eff} for the comparison (see Figure 4). The rate constants of

229 $(\text{CH}_3)_2\text{COO} + \text{SO}_2$ reaction (Smith et al., 2016) is known in the range of 283–303 K, and hence, we have compared its k_{eff}
 230 in this temperature range with dimethyl substituted $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction. Figure 4 shows that unlike $\text{CH}_2\text{OO} +$
 231 HONO reaction, here k_{eff} of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ is 2 times higher than the same for $(\text{CH}_3)_2\text{COO} + \text{SO}_2$ reaction within
 232 283–303 K. In addition, it is worth mentioning that under certain atmospheric conditions, concentration of HONO can be quite
 233 high compared to SO_2 . For example, during fog events, it is well known that concentration of SO_2 drops significantly (Zhang
 234 et al., 2013) while concentration of HONO increases (Pawar et al., 2024), making HONO a potentially major sink of Criegee
 235 intermediates in fog-like environments. In addition, as SO_2 mainly comes from human activities, its concentrations are high
 236 in polluted areas and become quite very low in tropical forests and rural areas. In fact, its concentrations fall below detection
 237 limits in tropical forest regions (Vereecken et al., 2012). In contrast, although HONO concentration is also high in polluted
 238 regions compared to a clean environment, due to the various *in situ* sources, HONO is present in reasonable amounts even in
 239 tropical forest areas (Zhang et al., 2012). Therefore, in this region also, HONO is a more effective sink of CI compared to SO_2 .
 240 Moreover, CI + HONO reaction is a hydrogen atom transfer (HAT) process, and hence, the presence of water can effectively
 241 catalyze this reaction (Buszek et al., 2012; Viegas and Varandas, 2012; Rai and Kumar, 2025). In contrast, the presence of water,
 242 particularly droplets and aerosols, can act as a sink for SO_2 (Zhang et al., 2013), and hence, in the presence of water, Criegee
 243 + SO_2 reaction should be less important compared to CI + HONO reaction. After establishing that compared to SO_2 , HONO
 244 is a more effective sink for $(\text{CH}_3)_2\text{COO}$ under most of the conditions, at last, it is important to compare it with $(\text{CH}_3)_2\text{COO}$
 245 + $\text{H}_2\text{O}/(\text{H}_2\text{O})_2$ reactions (Vereecken et al., 2017). It is evident from Figure 4 that at 100% RH, k_{eff} of $(\text{CH}_3)_2\text{COO} + \text{HONO}$
 246 can dominate over k_{eff} of $(\text{CH}_3)_2\text{COO} + \text{H}_2\text{O}$ and $(\text{CH}_3)_2\text{COO} + (\text{H}_2\text{O})_2$ for a relatively wider range of temperatures. For
 247 example, the dominant temperature range of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ is, 213–275 K for $(\text{CH}_3)_2\text{COO} + (\text{H}_2\text{O})_2$ and 213–290
 248 K for $(\text{CH}_3)_2\text{COO} + \text{H}_2\text{O}$. At 20% RH, k_{eff} of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ becomes dominant over k_{eff} of both, $(\text{CH}_3)_2\text{COO} +$
 249 H_2O and $(\text{CH}_3)_2\text{COO} + (\text{H}_2\text{O})_2$ in almost whole temperature range (213–310 K). For example, at 298 K, k_{eff} of $(\text{CH}_3)_2\text{COO}$
 250 + HONO is $\sim 1.8 \text{ sec}^{-1}$, which is 1.6 times and 2.2 times higher than the same for $(\text{CH}_3)_2\text{COO} + \text{H}_2\text{O}$ and $(\text{CH}_3)_2\text{COO} +$
 251 $(\text{H}_2\text{O})_2$, respectively. This suggests that the major sink of substituted CI can be its reaction with HONO in the atmosphere
 252 even in the presence of high humidity and SO_2 . It is important to mention that although substituted CI undergoes a bimolecular
 253 reaction with HONO, it is still primarily removed by its unimolecular dissociation, particularly at room temperature. For exam-
 254 ple, the unimolecular dissociation rate of $(\text{CH}_3)_2\text{COO}$ is $\sim 276 \text{ sec}^{-1}$ at room temperature. Interestingly, the unimolecular rate
 255 increases rapidly with temperature, whereas for the bimolecular reaction $(\text{CH}_3)_2\text{COO} + \text{HONO}$, k_{eff} increases only slightly.
 256 As a result, at lower temperatures, k_{eff} may become comparable to the unimolecular dissociation rate of $(\text{CH}_3)_2\text{COO}$. For ex-
 257 ample, at 213 K, k_{eff} and the unimolecular rate constants are 3.80 sec^{-1} and 1.82 sec^{-1} , respectively. A comparison between
 258 k_{eff} and the unimolecular dissociation rate constant of $(\text{CH}_3)_2\text{COO}$ within 213–320 K is provided in Table S6 of the ESI. It
 259 is evident from Table S6 that under conditions of high HONO concentration and low temperature, the bimolecular reaction of
 260 $(\text{CH}_3)_2\text{COO}$ with HONO competes well with its unimolecular dissociation.
 261 Finally, it is important to assess the extent to which the title reaction can contribute in resolving the puzzle of mismatch be-
 262 tween measured and modelled $\text{OH}^\bullet/\text{HO}_2^\bullet$ concentrations. It is important to mention that during daytime, HONO undergoes
 263 rapid photolysis; therefore, its concentration is higher in the absence of light, e.g. at night, indoors, in winter, etc. For example,

the photolysis rate of HONO is known to be $\sim 10^{-3} \text{ sec}^{-1}$, which is several orders of magnitude higher than the effective rate constant of its reaction with Criegee intermediates ($\sim 10^{-7} - 10^{-6} \text{ sec}^{-1}$, computed using maximum Criegee concentration of $\sim 10^5 \text{ molecule cm}^{-3}$) (Shabin et al., 2023). Therefore, during the peak of daytime, title reaction does not contribute much to $\text{OH}^\bullet$ production; rather, it can play a key role in nocturnal atmospheric chemistry, specifically at times when both, concentrations of HONO and CI are high, and, at the same time, the presence of light is minimal. To understand the efficiency of the title reaction in affecting $\text{OH}^\bullet$ concentration in a nocturnal environment, we can compare it with $\text{NO}_3^\bullet + \text{HO}_2^\bullet$ reaction, which is a well-known source of $\text{OH}^\bullet$ at nighttime. The rate constants for $\text{CH}_2\text{OO} + \text{HONO}$ reaction are ~ 2 times higher compared to $\text{NO}_3^\bullet + \text{HO}_2^\bullet$. For example, at 298 K, the rate value for $\text{CH}_2\text{OO} + \text{HONO}$ is $\sim 7.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, which is almost double compared to the rate value (Rai and Kumar, 2024) for $\text{NO}_3^\bullet + \text{HO}_2^\bullet$, i.e., $\sim 3.36 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. In the atmosphere, average concentration of both $\text{NO}_3^\bullet$ and $\text{HO}_2^\bullet$ are $\sim 10^8 \text{ molecule cm}^{-3}$ (Bottorff et al., 2023; Brown and Stutz, 2012), thus combined concentration turns out to be $\sim 10^{16} \text{ molecule}^2 \text{ cm}^{-6}$. Similarly, the combined concentration will be $\sim 10^{15} \text{ molecule}^2 \text{ cm}^{-6}$ for $\text{CH}_2\text{OO} + \text{HONO}$ under high concentrations of CI ($\sim 10^5 \text{ molecule cm}^{-3}$) (Khan et al., 2018) and HONO ($\sim 10^{10} \text{ molecule cm}^{-3}$) (Pawar et al., 2024). It suggests that $\text{CH}_2\text{OO} + \text{HONO}$ reaction may be somewhat slower in producing $\text{OH}^\bullet$. However, since the rate of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction is one order of magnitude higher compared to $\text{NO}_3^\bullet + \text{HO}_2^\bullet$, we believe both $\text{NO}_3^\bullet + \text{HO}_2^\bullet$ and title reactions should be of similar importance as far as the production of nighttime $\text{OH}^\bullet$ is concerned. In other words, title reaction has the potential to serve as a significant contributor to $\text{OH}^\bullet$ production in nighttime atmospheric chemistry.

Another factor worth noting is, besides $\text{OH}^\bullet$, the title reaction produces $\text{HCHO}/(\text{CH}_3)_2\text{CO}$, and $\text{NO}_2^\bullet$ as products. It is well known that both $\text{HCHO}/(\text{CH}_3)_2\text{CO}$ (Gao et al., 2024; Long et al., 2022; Hermans et al., 2004) and $\text{NO}_2^\bullet$ (Christensen et al., 2004) can act as sinks for HO_2 radicals (corresponding reactions are listed in the box below). It suggests that title reaction has the potential for recycling of $\text{HO}_2^\bullet \leftrightarrow \text{OH}^\bullet$ process. To illustrate the ability of title reaction in recycling $\text{HO}_2^\bullet \leftrightarrow \text{OH}^\bullet$ process, we have developed a kinetic model consisting of the following reactions (see ESI for the details):



This model requires two key components: first, the rate coefficients of the relevant reactions, which have been taken from the recommended literature values (Gao et al., 2024; Hermans et al., 2004; Long et al., 2022; Christensen et al., 2004), and second, a list of realistic initial concentrations of the reactive species involved in $\text{HO}_2^\bullet \leftrightarrow \text{OH}^\bullet$ recycling process (Table S5 of the ESI). We first tracked the change in concentration of $\text{OH}^\bullet$ and $\text{HO}_2^\bullet$ using the first kinetic model consisting of $\text{CH}_2\text{OO} + \text{HONO}$ reaction, followed by second model consisting of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction. Initial concentrations of relevant species (HCHO, HONO, $(\text{CH}_3)_2\text{CO}$, and $\text{HO}_2^\bullet$) are chosen based on literature values representing polluted urban conditions

293 (Vereecken et al., 2012; Pawar et al., 2024). Although the average concentration of $\text{OH}^\bullet$ can vary within $\sim 10^4$ – 10^6 molecules
 294 cm^{-3} in the atmosphere, we have used a modelled value of it in the present work. In $\text{CH}_2\text{OO} + \text{HONO}$ reaction model,
 295 the initial $\text{OH}^\bullet$ concentration was set to $\sim 10^4$ molecules cm^{-3} , while in $(\text{CH}_3)_2\text{COO} + \text{HONO}$ model, it was set to $\sim 10^5$
 296 molecules cm^{-3} . This difference was chosen based on how much OH each reaction is expected to produce when no *in situ*
 297 reactions are taking place from the byproducts of the title reaction. Since $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction can generate more
 298 OH, starting with a higher initial concentration helps one observe a noticeable change in $\text{OH}^\bullet$ levels during the simulation.
 299 This makes it easier to observe and compare the effect of $\text{OH}^\bullet$ production between the two reactions. It is important to mention
 300 that the maximum concentration of $\text{OH}^\bullet$ can be taken as $\sim 10^5$ molecules cm^{-3} in the kinetic model. This is because the
 301 production of $\text{OH}^\bullet$ is limited by the available concentration of CI which can be as high as $\sim 10^5$ molecules cm^{-3} . Therefore,
 302 taking $\text{OH}^\bullet$ concentration more than $\sim 10^5$ molecules cm^{-3} would produce no effect on the concentration of $\text{OH}^\bullet$. This also
 303 reveals the fact that the title reaction is capable of producing $\text{OH}^\bullet$ in regions where the concentration of $\text{OH}^\bullet$ is already low.
 304 Similarly, the concentration of NO_2 can vary within $\sim 10^{10}$ – 10^{12} molecules cm^{-3} in polluted urban regions. However, in the
 305 present model, we have kept it at $\sim 10^{10}$ molecules cm^{-3} in order to observe a clear numerical change in the values of $\text{HO}_2^\bullet$.
 306 Taking a high concentration of NO_2 ($\sim 10^{12}$ molecules cm^{-3}) would drastically consume $\text{HO}_2^\bullet$, and a gradual change would
 307 not be observed.
 308 We have divided the simulation results into two parts; first we will discuss $\text{CH}_2\text{OO} + \text{HONO}$ reaction followed by $(\text{CH}_3)_2\text{COO}$
 309 + HONO. The model results have been shown in Figure 5. It is evident from Figure 5 that $\text{CH}_2\text{OO} + \text{HONO}$ reaction increases
 310 $\text{OH}^\bullet$ concentration while simultaneously reducing $\text{HO}_2^\bullet$ concentration. Quantitatively, this reaction increases $\text{OH}^\bullet$ production
 311 by five times its initial value while decreasing $\text{HO}_2^\bullet$ production by more than one order of magnitude. Furthermore, when
 312 we consider dimethyl-substituted Criegee intermediate reaction ($(\text{CH}_3)_2\text{COO} + \text{HONO}$), $\text{OH}^\bullet$ production has been found to
 313 increase by only two times compared to its initial concentration, while $\text{HO}_2^\bullet$ production again decreases by the same one order
 314 of magnitude (Figure 5). The difference in $\text{OH}^\bullet$ production can be attributed to the fact that, in case of $(\text{CH}_3)_2\text{COO} + \text{HONO}$,
 315 the initial $\text{OH}^\bullet$ concentration was taken to be $\sim 10^5$ molecules cm^{-3} compared to $\sim 10^4$ molecules cm^{-3} in case of CH_2OO
 316 + HONO. This further strengthens the fact that the effect of title reaction on $\text{OH}^\bullet$ production will be more pronounced in
 317 the conditions where $\text{OH}^\bullet$ concentration is lower in the atmosphere, e.g., at night. The overall simulation results suggest that
 318 incorporating title reaction into atmospheric models can improve their accuracy in predicting $\text{OH}^\bullet$ and $\text{HO}_2^\bullet$ concentrations.
 319 It is important to note that the kinetics model used in the present work is preliminary. However, a more realistic impact of the
 320 title reaction on the budget of both $\text{OH}^\bullet$ and $\text{HO}_2^\bullet$, requires a more complete modeling. In order to do so, one needs accurate
 321 estimation of the rate constants for the reaction of HONO with various important Criegee intermediates. For bigger Criegee
 322 intermediates, computation will be more costly and require a separate study. In addition, being a HAT reaction, the effect of
 323 humidity on the title reaction is also important to build a complete model.

324 5 Conclusions

325 In this work, we have studied the energetics and kinetics of bimolecular reaction of simple and dimethyl-substituted Criegee
326 with HONO using high-level electronic structure theory and chemical kinetics. Our quantum chemical calculations suggest
327 that both of the reactions are barrierless and kinetic calculations reveal that reaction of substituted Criegee with HONO is $\sim$
328 2.6–3.6 times faster than simple Criegee + HONO reaction. By comparing it with other known sinks of CI, we have shown that
329 this reaction can serve as a major sink for Criegee intermediates in most of the atmospheric conditions, even in the presence of
330 high humidity and SO₂. In addition, we have also shown that title reaction can be one of the most important source of OH[•] in
331 nocturnal atmosphere. In addition, the products of CI + HONO reaction can be a sink for HO₂ radicals, and hence this reaction
332 is capable of HO₂[•] $\leftrightarrow$ OH[•] recycling. Consequently, this reaction can be key in fulfilling the gap between the observed OH
333 radicals and modelled values. Although in urban areas, HONO can be the dominant sink of certain CIs. But it is important
334 to notice that larger Criegee intermediates predominantly originate from biogenic volatile organic compounds (BVOCs). On
335 the other hand, HONO concentrations in forested regions are also found to be moderate ($\sim 10^8$ to 10^{10} molecules cm⁻³).
336 Therefore, we believe a separate study is required to understand the fate of larger Criegee intermediates in the presence of
337 HONO. At last, we look forward to the experimental verification of our results.

338 *Author contributions.* VJA: Conducted the investigation, Writing–original draft, Formal analysis, curated the data. PKR: Contributed to par-
339 tial formal analysis, writing, reviewing, and editing the manuscript. PK: Provided supervision, resources, and methodology; conceptualized
340 the study; acquired funding; and contributed to the review and editing of the manuscript.

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

342 *Acknowledgements.* V.J.A. and P.K.R acknowledge MNIT Jaipur for financial assistance. P.K. acknowledges DST, Govt. of India, for the
343 financial support through the sanctioned project No. EEQ/2023/000351.

344 References

- 345 Acker, K., Möller, D., Wieprecht, W., Meixner, F. X., Bohn, B., Gilge, S., Plass-Dülmer, C., and Berresheim, H.: Strong daytime production
346 of OH from HNO₂ at a rural mountain site, *Geophys. Res. Lett.*, 33, 2006.
- 347 Alam, M. S., Camredon, M., Rickard, A. R., Carr, T., Wyche, K. P., Hornsby, K. E., Monks, P. S., and Bloss, W. J.: Total radical yields from
348 tropospheric ethene ozonolysis, *Phys. Chem. Chem. Phys.*, 13, 11 002–11 015, 2011.
- 349 Aliche, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Pätz, H., Schäfer, J., Stutz, J., Volz-Thomas, A., and Platt, U.: OH formation
350 by HONO photolysis during the BERLIOZ experiment, *J. Geophys. Res.*, 108, PHO–3, 2003.
- 351 Anand, V. J. and Kumar, P.: Mechanistic insight into the N₂O + O(¹D, ³P) reaction: role of post-CCSD (T) corrections and non-adiabatic
352 effects, *Phys. Chem. Chem. Phys.*, 25, 33 119–33 129, 2023.
- 353 Anderson, J. G.: Free Radicals in the Earth’s Atmosphere: Their Measurement and Interpretation, *Annu. Rev. Phys. Chem.*, 38, 489–520,
354 1987.
- 355 Anglada, J. M. and Sole, A.: The atmospheric oxidation of HONO by OH, Cl, and ClO radicals, *J. Phys. Chem. A*, 121, 9698–9707, 2017.
- 356 Anglada, J. M., Hoffman, G. J., Slipchenko, L. V., M. Costa, M., Ruiz-Lopez, M. F., and Francisco, J. S.: Atmospheric significance of water
357 clusters and ozone–water complexes, *J. Phys. Chem. A*, 117, 10 381–10 396, 2013.
- 358 Aumont, B., Chervier, F., and Laval, S.: Contribution of HONO sources to the NO_x/HO_x/O₃ chemistry in the polluted boundary layer,
359 *Atmos. Environ.*, 37, 487–498, 2003.
- 360 Barker, J., Nguyen, T., Stanton, J., Aieta, C., Ceotto, M., Gabas, F., Kumar, T., Li, C., Lohr, L., Maranzana, A., et al.: MultiWell-2021 Software
361 Suite; J. R. Barker, University of Michigan, Ann Arbor, Michigan, USA, <http://claspresearch.engin.umich.edu/multiwell/> (accessed march
362 5, 2025), 2021.
- 363 Berndt, T., Hyttinen, N., Herrmann, H., and Hansel, A.: First oxidation products from the reaction of hydroxyl radicals with isoprene for
364 pristine environmental conditions, *Commun. Chem.*, 2, 21, 2019.
- 365 Bottorff, B., Lew, M. M., Woo, Y., Rickly, P., Rollings, M. D., Deming, B., Anderson, D. C., Wood, E., Alwe, H. D., Millet, D. B., et al.: OH,
366 HO₂, and RO₂ radical chemistry in a rural forest environment: measurements, model comparisons, and evidence of a missing radical
367 sink, *Atmos. Chem. Phys.*, 23, 10 287–10 311, 2023.
- 368 Brown, S. S. and Stutz, J.: Nighttime radical observations and chemistry, *Chem. Soc. Rev.*, 41, 6405–6447, 2012.
- 369 Buszek, R. J., Barker, J. R., and Francisco, J. S.: Water effect on the OH + HCl reaction, *J. Phys. Chem. A*, 116, 4712–4719, 2012.
- 370 Calvert, J., Yarwood, G., and Dunker, A.: An evaluation of the mechanism of nitrous acid formation in the urban atmosphere, *Res. Chem.*
371 *Intermed.*, 20, 463–502, 1994.
- 372 Carslaw, N., Creasey, D., Harrison, D., Heard, D., Hunter, M., Jacobs, P., Jenkin, M., Lee, J., Lewis, A., Pilling, M., et al.: OH and HO₂
373 radical chemistry in a forested region of north-western Greece, *Atmos. Environ.*, 35, 4725–4737, 2001.
- 374 Christensen, L. E., Okumura, M., Sander, S. P., Friedl, R. R., Miller, C. E., and Sloan, J. J.: Measurements of the Rate Constant of HO₂ +
375 NO₂ + N₂ → HO₂NO₂ + N₂ Using Near-Infrared Wavelength-Modulation Spectroscopy and UV- Visible Absorption Spectroscopy, *J.*
376 *Phys. Chem. A*, 108, 80–91, 2004.
- 377 Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Troe, J., and Wallington, T. J.: Evaluated
378 kinetic and photochemical data for atmospheric chemistry: Volume VII–Criegee intermediates, *Atmos. Chem. Phys.*, 20, 13 497–13 519,
379 2020.
- 380 Criegee, R.: Mechanism of ozonolysis, *Angew. Chem. internat. Edit.*, 14, 745–752, 1975.

381 Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Phys. Chem.*
382 *Chem. Phys.*, 13, 13 607–13 613, 2011.

383 Donahue, N. M., Drozd, G. T., Epstein, S. A., Presto, A. A., and Kroll, J. H.: Adventures in ozoneland: down the rabbit-hole, *Phys. Chem.*
384 *Chem. Phys.*, 13, 10 848–10 857, 2011.

385 Ehhalt, D.: Free Radicals in the Atmosphere, *Free Radic. Res. Commun.*, 3, 153–164, 1987.

386 Emmerson, K. and Carslaw, N.: Night-time radical chemistry during the TORCH campaign, *Atmos. Environ.*, 43, 3220–3226, 2009.

387 Faloona, I., Tan, D., Brune, W., Hurst, J., Barket Jr, D., Couch, T. L., Shepson, P., Apel, E., Riemer, D., Thornberry, T., et al.: Nighttime
388 observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, *J. Geophys. Res. Atmos.*, 106, 24 315–
389 24 333, 2001.

390 Feiner, P. A., Brune, W. H., Miller, D. O., Zhang, L., Cohen, R. C., Romer, P. S., Goldstein, A. H., Keutsch, F. N., Skog, K. M., Wennberg,
391 P. O., et al.: Testing atmospheric oxidation in an Alabama forest, *J. Atmos. Sci.*, 73, 4699–4710, 2016.

392 Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A.,
393 Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V.,
394 Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson,
395 T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa,
396 J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, Jr., J. A., Peralta, J. E., Ogliaro, F.,
397 Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari,
398 K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W.,
399 Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B., and Fox, D. J.: Gaussian~16 Revision C.01, gaussian Inc. Wallingford CT,
400 2016.

401 Gao, Q., Shen, C., Zhang, H., Long, B., and Truhlar, D. G.: Quantitative kinetics reveal that reactions of HO₂ are a significant sink for
402 aldehydes in the atmosphere and may initiate the formation of highly oxygenated molecules via autoxidation, *Phys. Chem. Chem. Phys.*,
403 26, 16 160–16 174, 2024.

404 Geyer, A., Bächmann, K., Hofzumahaus, A., Holland, F., Konrad, S., Klüpfel, T., Pätz, H.-W., Perner, D., Mihelcic, D., Schäfer, H.-J., et al.:
405 Nighttime formation of peroxy and hydroxyl radicals during the BERLIOZ campaign: Observations and modeling studies, *J. Geophys.*
406 *Res. Atmos.*, 108, 2003.

407 Gomez Alvarez, E., Amedro, D., Afif, C., Gligorovski, S., Schoemaeker, C., Fittschen, C., Doussin, J.-F., and Wortham, H.: Unexpectedly
408 high indoor hydroxyl radical concentrations associated with nitrous acid, *Proc. Natl. Acad. Sci.*, 110, 13 294–13 299, 2013.

409 Griffith, S. M., Hansen, R., Dusanter, S., Michoud, V., Gilman, J., Kuster, W., Veres, P., Graus, M., De Gouw, J., Roberts, J., et al.: Mea-
410 surements of hydroxyl and hydroperoxy radicals during CalNex-LA: Model comparisons and radical budgets, *J. Geophys. Res.*, 121,
411 4211–4232, 2016.

412 Hall, I. W., Wayne, R. P., Cox, R. A., Jenkin, M. E., and Hayman, G. D.: Kinetics of the reaction of nitrate radical with hydroperoxo, *J. Phys.*
413 *Chem.*, 92, 5049–5054, 1988.

414 Harrison, R., Yin, J., Tilling, R., Cai, X., Seakins, P., Hopkins, J., Lansley, D., Lewis, A., Hunter, M., Heard, D., et al.: Measurement and
415 modelling of air pollution and atmospheric chemistry in the UK West Midlands conurbation: Overview of the PUMA Consortium project,
416 *Sci. Total Environ.*, 360, 5–25, 2006.

417 He, Y., Zhou, X., Hou, J., Gao, H., and Bertman, S. B.: Importance of dew in controlling the air-surface exchange of HONO in rural forested
418 environments, *Geophys. Res. Lett.*, 33, 2006.

419 Heald, C. L. and Kroll, J. H.: A radical shift in air pollution, *Science*, 374, 688–689, 2021.

420 Heard, D., Carpenter, L., Creasey, D., Hopkins, J., Lee, J., Lewis, A., Pilling, M., Seakins, P., Carslaw, N., and Emmerson, K.: High levels of
421 the hydroxyl radical in the winter urban troposphere, *Geophys. Res. Lett.*, 31, 2004.

422 Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A., et al.: Observation
423 and modelling of HO_x radicals in a boreal forest., *Atmos. Chem. Phys. Discuss.*, 13, 2013.

424 Hermans, I., Nguyen, T. L., Jacobs, P. A., and Peeters, J.: Tropopause chemistry revisited: HO₂[•]-initiated oxidation as an efficient acetone
425 sink, *J. Am. Chem. Soc.*, 126, 9908–9909, 2004.

426 Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., et al.: Amplified trace
427 gas removal in the troposphere, *science*, 324, 1702–1704, 2009.

428 Horie, O. and Moortgat, G.: Decomposition pathways of the excited Criegee intermediates in the ozonolysis of simple alkenes, *Atmos.*
429 *Environ.*, 25A, 1881–1896, 1991.

430 J. Medeiros, D., Blitz, M. A., Seakins, P. W., and Whalley, L. K.: Direct measurements of isoprene autoxidation: Pinpointing atmospheric
431 oxidation in tropical forests, *JACS Au*, 2, 809–818, 2022.

432 Johnson, D. and Marston, G.: The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere, *Chem. Soc. Rev.*, 37,
433 699–716, 2008.

434 Johnson III, R. D.: NIST computational chemistry comparison and benchmark database, NIST standard reference database number 101,
435 Release 16a <http://cccbdb.nist.gov/> (accessed march 5, 2025), 2013.

436 Khan, M., Percival, C., Caravan, R., Taatjes, C., and Shallcross, D.: Criegee intermediates and their impacts on the troposphere, *Environ.*
437 *Sci.: Process. Impacts*, 20, 437–453, 2018.

438 Kim, S., Kim, S.-Y., Lee, M., Shim, H., Wolfe, G., Guenther, A. B., He, A., Hong, Y., and Han, J.: Impact of isoprene and HONO chemistry
439 on ozone and OVOC formation in a semirural South Korean forest, *Atmos. Chem. Phys.*, 15, 4357–4371, 2015.

440 Kumar, A., Mallick, S., and Kumar, P.: Nitrous acid (HONO) as a sink of the simplest Criegee intermediate in the atmosphere, *Phys. Chem.*
441 *Chem. Phys.*, 24, 7458–7465, 2022.

442 Lelieveld, J., Peters, W., Dentener, F., and Krol, M.: Stability of tropospheric hydroxyl chemistry, *J. Geophys. Res.*, 107, ACH–17, 2002.

443 Lelieveld, J., Dentener, F., Peters, W., and Krol, M.: On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere, *Atmos.*
444 *Chem. Phys.*, 4, 2337–2344, 2004.

445 Lelieveld, J., Gromov, S., Pozzer, A., and Taraborrelli, D.: Global tropospheric hydroxyl distribution, budget and reactivity, *Atmos. Chem.*
446 *Phys.*, 16, 12 477–12 493, 2016.

447 Lelieveld, J. a., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli,
448 D., et al.: Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452, 737–740, 2008.

449 Lew, M. M., Rickly, P. S., Bottorff, B. P., Reidy, E., Sklaveniti, S., Léonardis, T., Locoge, N., Dusanter, S., Kundu, S., Wood, E., et al.: OH
450 and HO₂ radical chemistry in a midlatitude forest: measurements and model comparisons, *Atmos. Chem. Phys.*, 20, 9209–9230, 2020.

451 Li, Y., Wang, X., Wu, Z., Li, L., Wang, C., Li, H., Zhang, X., Zhang, Y., Li, J., Gao, R., et al.: Atmospheric nitrous acid (HONO) in an alternate
452 process of haze pollution and ozone pollution in urban Beijing in summertime: Variations, sources and contribution to atmospheric
453 photochemistry, *Atmos. Res.*, 260, 105 689, 2021.

454 Lin, H.-Y., Huang, Y.-H., Wang, X., Bowman, J. M., Nishimura, Y., Witek, H. A., and Lee, Y.-P.: Infrared identification of the Criegee
455 intermediates syn-and anti-CH₃CHOO, and their distinct conformation-dependent reactivity, *Nat. Commun.*, 6, 7012, 2015.

456 Lin, L.-C., Chang, H.-T., Chang, C.-H., Chao, W., Smith, M. C., Chang, C.-H., Takahashi, K., et al.: Competition between H_2O and $(\text{H}_2\text{O})_2$
 457 reactions with $\text{CH}_2\text{OO}/\text{CH}_3\text{CHOO}$, *Phys. Chem. Chem. Phys.*, 18, 4557–4568, 2016.
 458 Long, B., Xia, Y., and Truhlar, D. G.: Quantitative kinetics of HO_2 reactions with aldehydes in the atmosphere: High-order dynamic corre-
 459 lation, anharmonicity, and falloff effects are all important, *J. Am. Chem. Soc.*, 144, 19 910–19 920, 2022.
 460 Lu, K., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C., Häseler, R., Hu, M., Kita, K., et al.: Observation and modelling
 461 of OH and HO_2 concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, *Atmos. Chem. Phys.*, 12,
 462 1541–1569, 2012.
 463 Lu, X., Park, J., and Lin, M.-C.: Gas phase reactions of HONO with NO_2 , O_3 , and HCl: Ab initio and TST study, *J. Phys. Chem. A*, 104,
 464 8730–8738, 2000.
 465 Mallick, S. and Kumar, P.: Impact of Post-CCSD(T) Corrections on Reaction Energetics and Rate Constants of the $\text{OH}^\bullet + \text{HCl}$ Reaction, *J.*
 466 *Phys. Chem. A*, 122, 7151–7159, 2018.
 467 Mallick, S. and Kumar, P.: The reaction of N_2O with the Criegee intermediate: A theoretical study, *Comput. Theor. Chem.*, 1191, 113 023,
 468 2020.
 469 Mallick, S., Kumar, A., and Kumar, P.: Revisiting the reaction energetics of the $\text{CH}_3\text{O}^\bullet + \text{O}_2$ ($^3\Sigma^-$) reaction: the crucial role of post-
 470 CCSD(T) corrections, *Phys. Chem. Chem. Phys.*, 21, 6559–6565, 2019.
 471 Mellouki, A., Le Bras, G., and Poulet, G.: Kinetics of the reactions of nitrate radical with hydroxyl and hydroperoxo, *J. Phys. Chem. A*, 92,
 472 2229–2234, 1988.
 473 Mellouki, A., Talukdar, R., Bopegedera, A., and Howard, C. J.: Study of the kinetics of the reactions of NO_3 with HO_2 and OH, *Int. J. Chem.*
 474 *Kinet.*, 25, 25–39, 1993.
 475 Misiewicz, J. P., Elliott, S. N., Moore, K. B., and Schaefer, H. F.: Re-examining ammonia addition to the Criegee intermediate: converging
 476 to chemical accuracy, *Phys. Chem. Chem. Phys.*, 20, 7479–7491, 2018.
 477 Monks, P. S.: Gas-phase radical chemistry in the troposphere, *Chem. Soc. Rev.*, 34, 376–395, 2005.
 478 Nguyen, T. L., Li, J., Dawes, R., Stanton, J. F., and Guo, H.: Accurate determination of barrier height and kinetics for the $\text{F} + \text{H}_2 \rightarrow \text{HF} +$
 479 OH reaction, *J. Phys. Chem. A*, 117, 8864–8872, 2013.
 480 Novelli, A., Vereecken, L., Lelieveld, J., and Harder, H.: Direct observation of OH formation from stabilised Criegee intermediates, *Phys.*
 481 *Chem. Chem. Phys.*, 16, 19 941–19 951, 2014.
 482 Novelli, A., Hens, K., Tatum Ernest, C., Martinez, M., Nölscher, A. C., Sinha, V., Paasonen, P., Petäjä, T., Sipilä, M., Elste, T., et al.:
 483 Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument, *Atmos.*
 484 *Chem. Phys.*, 17, 7807–7826, 2017.
 485 Novelli, A., Vereecken, L., Bohn, B., Dorn, H.-P., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Reimer, D., Rohrer, F., Rosanka, S., et al.:
 486 Importance of isomerization reactions for OH radical regeneration from the photo-oxidation of isoprene investigated in the atmospheric
 487 simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 20, 3333–3355, 2020.
 488 Onel, L., Lade, R., Mortiboy, J., Blitz, M. A., Seakins, P. W., Heard, D. E., and Stone, D.: Kinetics of the gas phase reaction of the Criegee
 489 intermediate CH_2OO with SO_2 as a function of temperature, *Phys. Chem. Chem. Phys.*, 23, 19 415–19 423, 2021.
 490 Osborn, D. L. and Taatjes, C. A.: The physical chemistry of Criegee intermediates in the gas phase, *Int. Rev. Phys. Chem.*, 34, 309–360,
 491 2015.
 492 Østerstrøm, F. F., Carter, T. J., Shaw, D. R., Abbatt, J. P., Abeleira, A., Arata, C., Bottorff, B. P., Cardoso-Saldaña, F. J., DeCarlo, P. F.,
 493 Farmer, D. K., et al.: Modelling indoor radical chemistry during the HOMEChem campaign, *Environ. Sci.: Process. Impacts*, 2025.

494 Pansini, F., Neto, A., and Varandas, A.: Extrapolation of Hartree–Fock and multiconfiguration self-consistent-field energies to the complete
 495 basis set limit, *Theor. Chem. Acc.*, 135, 1–6, 2016.
 496 Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxide formation
 497 in the gas-phase photooxidation of isoprene, *science*, 325, 730–733, 2009.
 498 Pawar, P. V., Mahajan, A. S., and Ghude, S. D.: HONO chemistry and its impact on the atmospheric oxidizing capacity over the Indo-Gangetic
 499 Plain, *Sci. Total Environ.*, p. 174604, 2024.
 500 Peeters, J. and Müller, J.-F.: HO_X radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence
 501 and global impact, *Phys. Chem. Chem. Phys.*, 12, 14 227–14 235, 2010.
 502 Peeters, J., Nguyen, T. L., and Vereecken, L.: HO_X radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 11, 5935–
 503 5939, 2009.
 504 Peeters, J., Müller, J.-F., Stavrou, T., and Nguyen, V. S.: Hydroxyl radical recycling in isoprene oxidation driven by hydrogen bonding and
 505 hydrogen tunneling: The upgraded LIM1 mechanism, *J. Phys. Chem. A*, 118, 8625–8643, 2014.
 506 Prinn, R. G.: The Cleansing Capacity of the Atmosphere, *Annu. Rev. Environ. Resour.*, 28, 29–57, 2003.
 507 Rai, P. K. and Kumar, P.: Role of post-CCSD (T) corrections in predicting the energetics and kinetics of the OH• + O₃ reaction, *Phys. Chem.*
 508 *Chem. Phys.*, 24, 13 026–13 032, 2022.
 509 Rai, P. K. and Kumar, P.: Accurate determination of reaction energetics and kinetics of HO₂•+O₃ → OH•+2O₂ reaction, *Phys. Chem. Chem.*
 510 *Phys.*, 25, 8153–8160, 2023.
 511 Rai, P. K. and Kumar, P.: Mechanistic Inside into the Gas-Phase NO₃ + HO₂ Reaction, *J. Phys. Chem. A*, 128, 7907–7913, 2024.
 512 Rai, P. K. and Kumar, P.: Influence of Water on the NO₃ + HO₂ Reaction, *J. Phys. Chem. A*, 129, 2067–2076, 2025.
 513 Reidy, E., Bottorff, B. P., Rosales, C. M. F., Cardoso-Saldaña, F. J., Arata, C., Zhou, S., Wang, C., Abeleira, A., Hildebrandt Ruiz, L.,
 514 Goldstein, A. H., et al.: Measurements of hydroxyl radical concentrations during indoor cooking events: Evidence of an unmeasured
 515 photolytic source of radicals, *Environ. Sci. Technol.*, 57, 896–908, 2023.
 516 Ren, X., Harder, H., Martinez, M., Leshner, R. L., Oligier, A., Shirley, T., Adams, J., Simpás, J. B., and Brune, W. H.: HO_X concentrations
 517 and OH reactivity observations in New York City during PMTACS-NY2001, *Atmos. Environ.*, 37, 3627–3637, 2003.
 518 Ren, X., Brune, W. H., Oligier, A., Metcalf, A. R., Simpás, J. B., Shirley, T., Schwab, J. J., Bai, C., Roychowdhury, U., Li, Y., et al.: OH,
 519 HO₂, and OH reactivity during the PMTACS–NY Whiteface Mountain 2002 campaign: Observations and model comparison, *J. Geophys.*
 520 *Res. Atmos.*, 111, 2006.
 521 Ren, X., Gao, H., Zhou, X., Crounse, J., Wennberg, P., Browne, E., LaFranchi, B., Cohen, R., McKay, M., Goldstein, A., et al.: Measurement
 522 of atmospheric nitrous acid at Bodgett Forest during BEARPEX2007, *Atmos. Chem. Phys.*, 10, 6283–6294, 2010.
 523 Rondon, A. and Sanhueza, E.: High HONO atmospheric concentrations during vegetation burning in the tropical savannah, *Tellus B*, 41,
 524 474–477, 1989.
 525 Ruscic, B., Pinzon, R. E., Morton, M. L., von Laszewski, G., Bittner, S. J., Nijssure, S. G., Amin, K. A., Minkoff, M., and Wagner, A. F.:
 526 Introduction to active thermochemical tables: Several “key” enthalpies of formation revisited, *J. Phys. Chem. A*, 108, 9979–9997, 2004.
 527 Sander, R., Baumgaertner, A., Cabrera-Perez, D., Frank, F., Gromov, S., Grooß, J.-U., Harder, H., Huijnen, V., Jöckel, P., Karydis, V. A.,
 528 et al.: The community atmospheric chemistry box model CAABA/MECCA-4.0, *Geosci. Model Dev.*, 12, 1365–1385, 2019.
 529 Schnabel, T., Vrabec, J., and Hasse, H.: Unlike Lennard–Jones parameters for vapor–liquid equilibria, *J. Mol. Liq.*, 135, 170–178, 2007.
 530 Shabin, M., Kumar, A., Hakkim, H., Rudich, Y., and Sinha, V.: Sources, sinks, and chemistry of stabilized Criegee intermediates in the
 531 indo-gangetic plain, *Sci. Total Environ.*, 896, 165 281, 2023.

532 Sheps, L., Scully, A. M., and Au, K.: UV absorption probing of the conformer-dependent reactivity of a Criegee intermediate CH_3CHOO ,
 533 Phys. Chem. Chem. Phys., 16, 26 701–26 706, 2014.
 534 Slater, E. J., Whalley, L. K., Woodward-Massey, R., Ye, C., Lee, J. D., Squires, F., Hopkins, J. R., Dunmore, R. E., Shaw, M., Hamilton, J. F.,
 535 et al.: Elevated levels of OH observed in haze events during wintertime in central Beijing, Atmos. Chem. Phys., 20, 14 847–14 871, 2020.
 536 Smith, M. C., Chao, W., Takahashi, K., Boering, K. A., and Lin, J. J.-M.: Unimolecular decomposition rate of the Criegee intermediate
 537 $(\text{CH}_3)_2\text{COO}$ measured directly with UV absorption spectroscopy, J. Phys. Chem. A, 120, 4789–4798, 2016.
 538 Smith, S., Lee, J., Bloss, W., Johnson, G., Ingham, T., and Heard, D.: Concentrations of OH and HO_2 radicals during NAMBLEX: measure-
 539 ments and steady state analysis, Atmos. Chem. Phys., 6, 1435–1453, 2006.
 540 Song, M., Zhao, X., Liu, P., Mu, J., He, G., Zhang, C., Tong, S., Xue, C., Zhao, X., Ge, M., et al.: Atmospheric NO_x oxidation as major
 541 sources for nitrous acid (HONO), npj clim. atmos. sci., 6, 30, 2023.
 542 Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO_2 radicals: field measurements and model comparisons, Chem. Soc.
 543 Rev., 41, 6348–6404, 2012.
 544 Su, H., Cheng, Y. F., Shao, M., Gao, D. F., Yu, Z. Y., Zeng, L. M., Slanina, J., Zhang, Y. H., and Wiedensohler, A.: Nitrous acid (HONO) and
 545 its daytime sources at a rural site during the 2004 PRIDE-PRD experiment in China, J. Geophys. Res. Atmos., 113, 2008.
 546 Taatjes, C. A.: Criegee intermediates: What direct production and detection can teach us about reactions of carbonyl oxides, Annu. Rev.
 547 Phys. Chem., 68, 183–207, 2017.
 548 Tajti, A., Szalay, P. G., Császár, A. G., Kállay, M., Gauss, J., Valeev, E. F., Flowers, B. A., Vázquez, J., and Stanton, J. F.: HEAT: High
 549 accuracy extrapolated ab initio thermochemistry, J. Chem. Phys., 121, 11 599–11 613, 2004.
 550 Tan, D., Faloon, I., Simpas, J., Brune, W., Shepson, P., Couch, T., Sumner, A., Carroll, M., Thornberry, T., Apel, E., et al.: HO_x budgets in
 551 a deciduous forest: Results from the PROPHET summer 1998 campaign, J. Geophys. Res. Atmos., 106, 24 407–24 427, 2001.
 552 Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häseler, R., He, L., et al.: Radical chemistry at a
 553 rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO_2 and RO_2 radicals, Atmos. Chem. Phys., 17,
 554 663–690, 2017.
 555 Teng, A. P., Crounse, J. D., and Wennberg, P. O.: Isoprene peroxy radical dynamics, J. Am. Chem. Soc., 139, 5367–5377, 2017.
 556 Varandas, A. and Pansini, F.: Narrowing the error in electron correlation calculations by basis set re-hierarchization and use of the unified
 557 singlet and triplet electron-pair extrapolation scheme: Application to a test set of 106 systems, J. Chem. Phys., 141, 224 113, 2014.
 558 Vereecken, L. and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, Chem. Soc. Rev., 41, 6259–
 559 6293, 2012.
 560 Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO_2 , and SO_2 , and their fate in the atmosphere,
 561 Phys. Chem. Chem. Phys., 14, 14 682–14 695, 2012.
 562 Vereecken, L., Rickard, A., Newland, M., and Bloss, W.: Theoretical study of the reactions of Criegee intermediates with ozone, alkylhy-
 563 droperoxides, and carbon monoxide, Phys. Chem. Chem. Phys., 17, 23 847–23 858, 2015.
 564 Vereecken, L., Novelli, A., and Taraborrelli, D.: Unimolecular decay strongly limits the atmospheric impact of Criegee intermediates, Phys.
 565 Chem. Chem. Phys., 19, 31 599–31 612, 2017.
 566 Viegas, L. P. and Varandas, A. J.: Can water be a catalyst on the $\text{HO}_2 + \text{H}_2\text{O} + \text{O}_3$ reactive cluster?, Chem. Phys., 399, 17–22, 2012.
 567 Wallington, T. J. and Japar, S. M.: Fourier transform infrared kinetic studies of the reaction of HONO with HNO_3 , NO_3 and N_2O_5 at 295 K,
 568 J. Atmos. Chem., 9, 399–409, 1989.
 569 Weinstock, B.: Carbon monoxide: Residence time in the atmosphere, Science, 166, 224–225, 1969.

570 Whalley, L., Edwards, P., Furneaux, K., Goddard, A., Ingham, T., Evans, M. J., Stone, D., Hopkins, J., Jones, C. E., Karunaharan, A., et al.:
 571 Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest, *Atmos. Chem. Phys.*, 11, 7223–7233, 2011.
 572 Yang, X., Wang, H., Lu, K., Ma, X., Tan, Z., Long, B., Chen, X., Li, C., Zhai, T., Li, Y., et al.: Reactive aldehyde chemistry explains the
 573 missing source of hydroxyl radicals, *Nat. Commun.*, 15, 1648, 2024.
 574 Zhang, N., Zhou, X., Bertman, S., Tang, D., Alaghmand, M., Shepson, P., and Carroll, M.: Measurements of ambient HONO concentrations
 575 and vertical HONO flux above a northern Michigan forest canopy, *Atmos. Chem. Phys.*, 12, 8285–8296, 2012.
 576 Zhang, Q., Tie, X., Lin, W., Cao, J., Quan, J., Ran, L., and Xu, W.: Variability of SO₂ in an intensive fog in North China Plain: Evidence of
 577 high solubility of SO₂, *Particuology*, 11, 41–47, 2013.
 578 Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., et al.: Nitric
 579 acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, *Nat. Geosci.*, 4, 440–443, 2011.

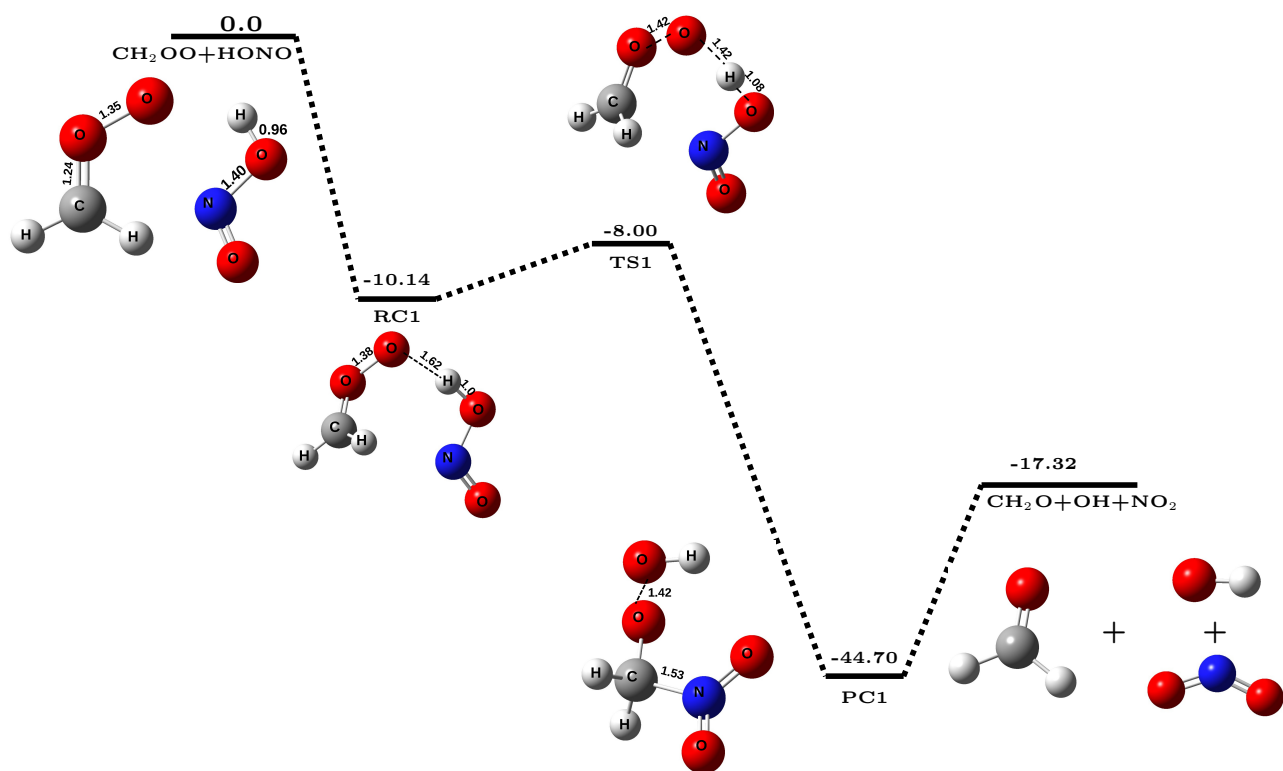


Figure 1. The potential energy surface for CH₂OO + HONO reaction (in kcal mol⁻¹) obtained at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory along with optimized geometries of species involved in the reaction.

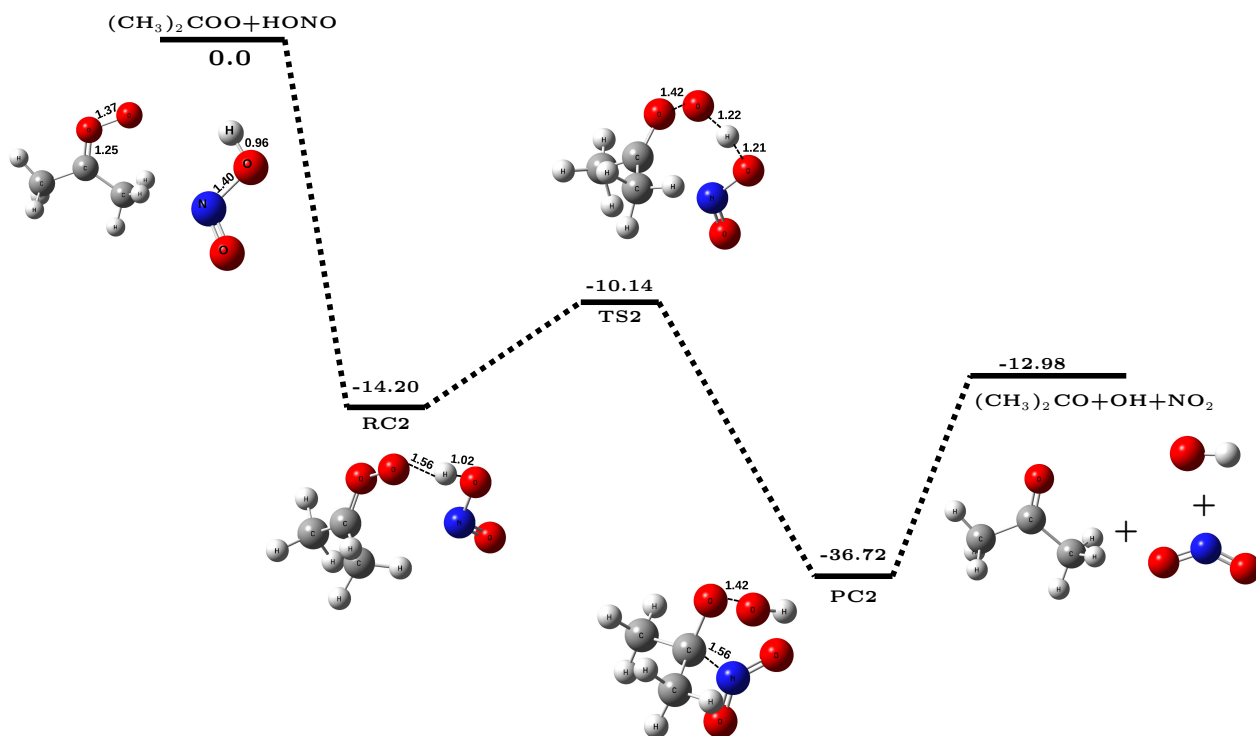


Figure 2. The potential energy surface for $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction (in kcal mol⁻¹) obtained at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory along with optimized geometries of species involved in the reaction.

Table 1. Bimolecular rate constants (k_{bi} , in $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) for $\text{CH}_2\text{OO}/(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction within the temperature range of 213–320 K.

T (K)	$k_{bi}^{\text{CH}_2\text{OO}}$	$k_{bi}^{(\text{CH}_3)_2\text{COO}}$
213	1.17×10^{-11}	4.28×10^{-11}
216	1.15×10^{-11}	4.18×10^{-11}
219	1.13×10^{-11}	4.09×10^{-11}
224	1.11×10^{-11}	3.94×10^{-11}
235	1.04×10^{-11}	3.61×10^{-11}
250	9.58×10^{-12}	3.18×10^{-11}
259	9.10×10^{-12}	2.94×10^{-11}
265	8.79×10^{-12}	2.78×10^{-11}
278	8.14×10^{-12}	2.47×10^{-11}
280	8.04×10^{-12}	2.42×10^{-11}
290	7.57×10^{-12}	2.20×10^{-11}
298	7.21×10^{-12}	2.03×10^{-11}
300	7.13×10^{-12}	1.99×10^{-11}
310	6.70×10^{-12}	1.80×10^{-11}
320	6.30×10^{-12}	1.63×10^{-11}

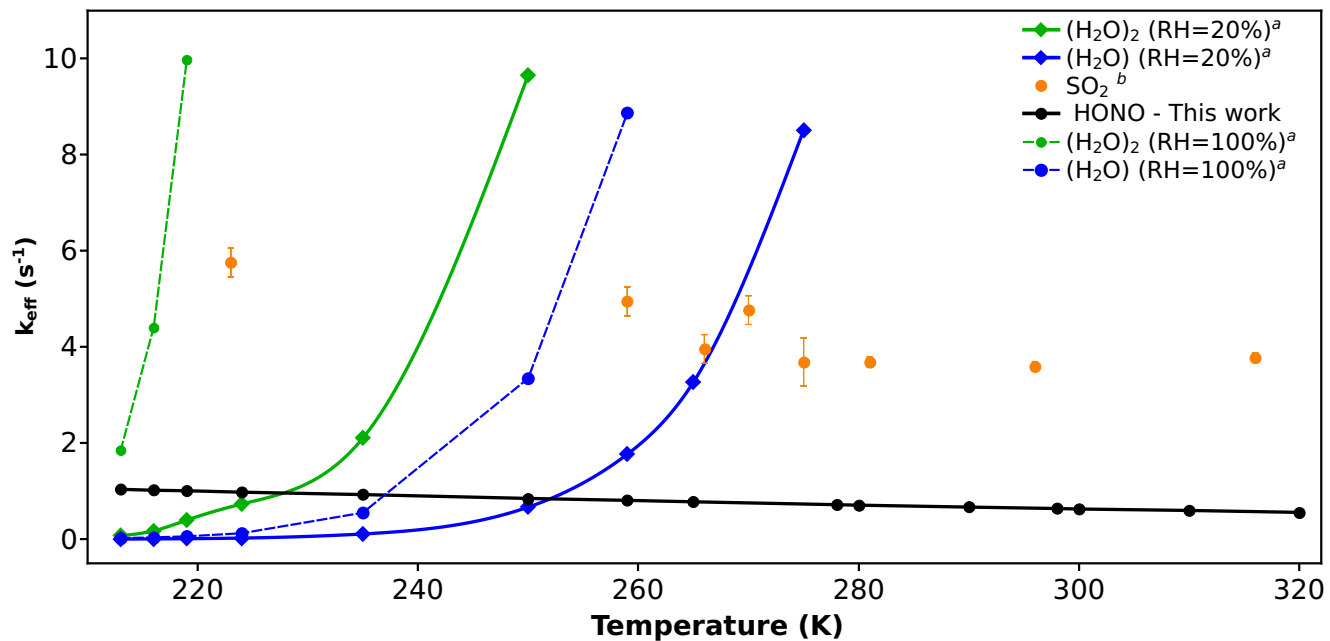


Figure 3. Effective rate constant comparison (k_{eff} , in sec^{-1}) of CH_2OO + HONO with the k_{eff} of previously known sinks of CH_2OO .

a. Values are taken from reference (Lin et al., 2016)

b. Values are taken from reference (Onel et al., 2021)

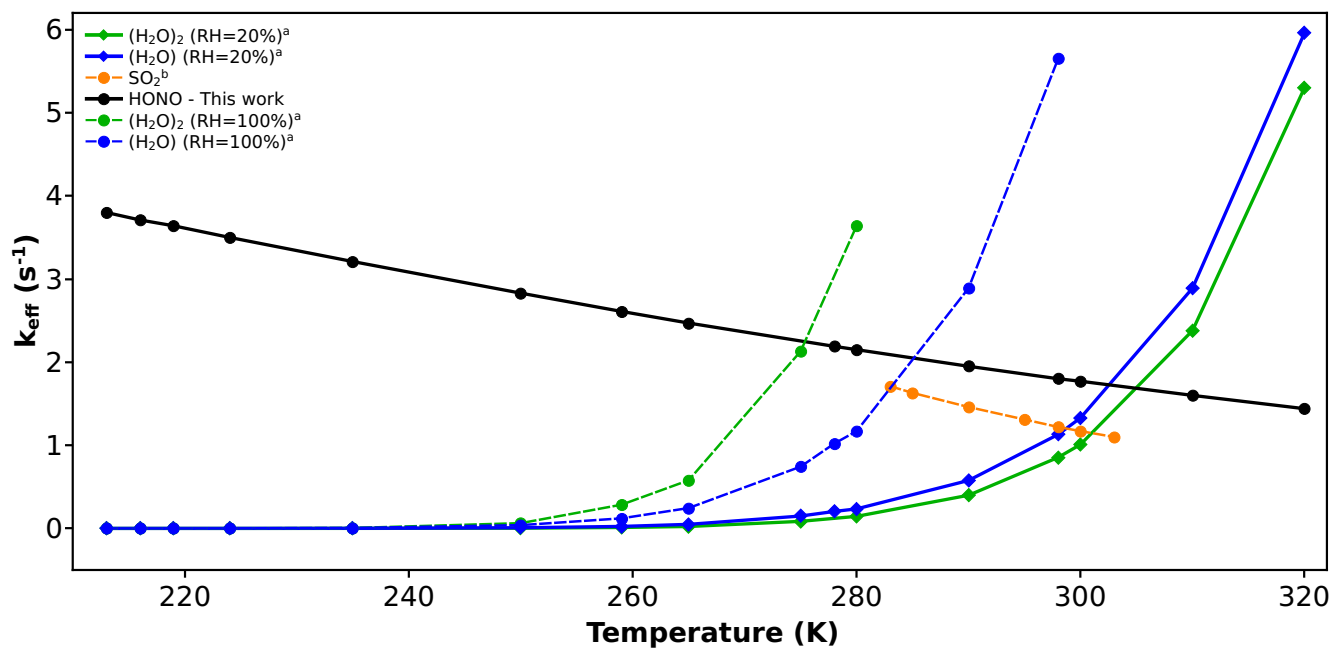


Figure 4. Effective rate constant comparison (k_{eff} , in sec^{-1}) of $(\text{CH}_3)_2\text{COO} + \text{HONO}$ with the k_{eff} of previously known sinks of $(\text{CH}_3)_2\text{COO}$.

a. Values are taken from reference (Vereecken et al., 2017)

b. Values are taken from reference (Smith et al., 2016)

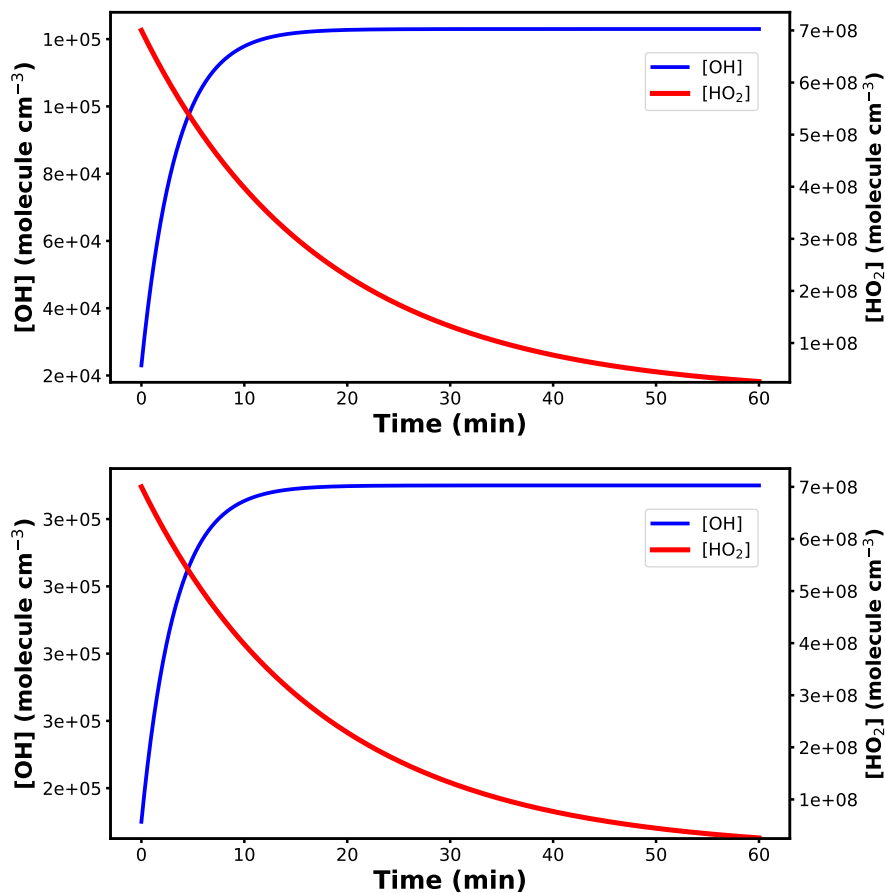


Figure 5. Top panel: Concentration profiles of $\text{HO}_2^\bullet$ and $\text{OH}^\bullet$ using $\text{CH}_2\text{OO} + \text{HONO}$ reaction into the model. Bottom panel: Concentration profiles of $\text{HO}_2^\bullet$ and $\text{OH}^\bullet$ using $(\text{CH}_3)_2\text{COO} + \text{HONO}$ reaction into the model.