Theoretical Study on Criegee Intermediate's Role in Ozonolysis of Acrylic Acid

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S Supporting Information

ABSTRACT: Criegee intermediates have raised much attention in atmospheric chemistry because of their significance in ozonolysis mechanism. The simplest Criegee intermediate, CH_2OO, and its reactions with acrylic acid including cycloadditions and insertions as main entrance channels have been investigated at CCSD(T)/cc-pVTZ// M06-2X/6-31G(d,p) level. Temperature- and pressure-dependent kinetics were predicted by solving the time-dependent master equations based on Rice−Ramsperger−Kassel−Marcus theory using MESS program, with temperatures from 200 to 500 K and pressures from 0.001 to 1000 atm. Variational transition state theory (VTST) was used for barrierless pathways and conventional transition state theory (CTST) for pathways with distinct barriers. Results indicate that hydroperoxymethyl acrylate is the dominant product under atmospheric conditions. The combination of two reactants will reduce the volatility and makes a possible factor that induces formation of secondary organic aerosols, which suggests CH_2OO's entangled role in ever-increasing air pollution.
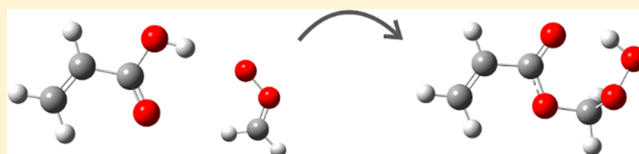
INTRODUCTION

Criegee intermediate is a carbonyl oxide zwitterion. The simplest Criegee intermediate, CH_2OO, since its first postulation[1] and first direct kinetic measurements,[2,3] has been recognized as an important intermediate species in oxidation mechanism of alkenes ozonolysis, which proceeds via formation of ozonide by ozone attacking the double bond of unsaturated alkenes, and leads to cleavage of ozonide and, at last, the production of carbonyl oxide and carbonyl compounds. It helps the formation of secondary aerosols which may reflect or absorb solar radiation and resist the climate change.[4] One of the major sources of such resistance is vegetation's production in alkenes, especially isoprene, one of the most vastly existing dienes. Ozonolysis of isoprene has been heavily investigated.[5−7] It has been reported that methyl vinyl ketone (MVK) is one of the major products from ozonolysis or oxidation of isoprene,[8−11] while the role of acrylic acid in ozonolysis of isoprene is still unnoticed.

Acrylic acid could as well contribute to the atmospheric change because as an α,β-unsaturated compounds, acrylic acid has many uses in the polymer industry as well as its derivatives like methacrylates and acrylates. The consumption of acrylic acid in China has been over 2.9 million tons in 2016.[12] It is also found as a constituent of tobacco smoke.[13] Not only anthropogenic sources from industrial production[14] but also natural beings[15] can lead to emission of acrylic acid. Rate coefficients and mechanisms of the oxygenated volatile organic compound (OVOC) with atmospherically important species would help us to determine its tropospheric lifetime and various degradation pathways. To consider its impact on the atmosphere, previous works have offered investigation on the reaction of acrylic acid with hydroxyl and chlorine atom experimentally[16] and theoretically[17] and with ozone.[18]

Therefore, the chemistry between acrylic acid and Criegee intermediates is worthy of attention and research. However, to our knowledge, theoretical and experimental investigations into interaction of acrylic acid with CH_2OO have not yet surfaced. In this work, interaction between acrylic acid and the simplest Criegee intermediate CH_2OO is focused on and studied, with a hope to illuminate the role of acrylic acid in ozonolysis of atmosphere.

Previous works[19,20] on Criegee intermediate with similar compounds like acids give applicable entrance channels, cycloaddition and insertion reactions. Cycloadditions on olefinic bond and carbonyl reveal similar minor barriers, but experimental detection[19,21] indicates a 5 orders of magnitude difference in rate coefficient, which implies that the interaction between olefinic bond and carbonyl oxide could be a kinetically controlled process. 1,2-CH-insertion, 1,2-OH-insertion, and 1,4-insertion could all be postulated while 1,3-insertion is improbable because the hydrogen in acrylic acid has been substituted. Both cycloaddition and insertion can occur in two opposite orientation. Whether it is head-first or tail-first orientation, they all go through a concerted five-membered ring and then proceed to a stable five-membered ring for cycloadditions or a chain for insertions. Such a mechanism could be as well applied to reaction of acrylic acid with CH_2OO. It is reported recently that CH_2OO, when it

reacts with acrolein, a similar species in structure, can also perform cycloadditions and insertions. And besides those, CH_2OO and acrolein can have another insertion, leading to formaldehyde and acrylic acid,[22] which was not found in our inquiry. Potential energy surface (PES) of acrylic acid and CH_2OO was investigated using *ab initio* quantum chemistry method. It is shown in following sections according to cycloaddition and insertion discussed in previous work, while exact description of structures of stable and saddle points are given in supplement material. The rate coefficients are calculated via solution of the time-dependent multiple-well master equation based on Rice−Ramsperger−Kassel−Marcus (RRKM) theory with temperature ranging over 200−500 K and pressure ranging over 0.001−1000 atm. With all of the information we can gather from this work, we hope it is a strong proof in corroborating the importance of Criegee intermediates in tropospheric ozonolysis.

■ THEORETICAL TECHNIQUES

Electronic Structure Methods. The Minnesota 06 method has been proved useful in similar study about Criegee intermediates.[20,23−25] Geometry optimization and frequency analyses for stationary points were performed at the CCSD-(T)/cc-pVTZ//M06-2X/6-31G(d,p) level using the Gaussian 09 program.[26] To ensure the validity of the 6-31G(d,p) basis set, the CBS-QB3 method was used to calculate the dominant channel, which gives very similar energies as can be seen in Figure S1. Relevant energetic minima and first-order saddle points were pinpointed and intrinsic reaction coordinate (IRC) calculation were made to confirm connection of points for some pathways. All energies were zero-point energy corrected. To achieve higher accuracy, Coupled Cluster method (CCSD(T)) with cc-pVTZ basis set was employed to better describe energy profile. Energies given by CCSD(T) method were also corrected with vibrational characteristics from M06-2X method.

Kinetic Theory. Various entrance channels of potential surface and numerous prereactive complexes in this work have characterized its complicated nature with multiple interconnected wells. The MESS program,[27] which has been effective in solving similar problems, is used for kinetic prediction of related reaction system. Temperature- and pressure-dependent rate coefficients were given by MESS program[27] via solution of time-dependent master equation based on RRKM theory. Similar method has been used to calculate rate coefficients of CH_2OO + CH_3COOH, which is 2 orders off compared to experiment values.[21] The temperature spans from 273 to 400 K and the pressure ranges from 0.001 to 100 atm. Conventional transition state theory (CTST) was utilized with rigid rotor harmonic oscillator (RRHO) assumption to characterized channels with distinct barriers. Tunneling correction is described with the asymmetric Eckart potential.[28] For direct bond dissociation channels, variational transition state theory (VTST) was employed. The minimum energy pathway (MEP) was optimized along the dissociation reaction coordinate with complete active space self-consistent field method (CASSCF) with 6-31G(d,p) basis set considering multireference character of bond dissociation. The energies of MEP were scaled by asymptotic dissociation energy of higher accuracy, procured from CCSD(T)/cc-pVTZ//M06-2X/6-31G(d,p) level. Previous works[19,20] all indicate prereactive weak van der Waals (vdW) complexes at low temperature in the beginning and finalization of reaction. Transition states of such process are

usually loose and can be described by simplified phase space theory (PST) in rate coefficient calculations where the long-range interaction potential is approximated by a simple isotropic potential $V(R) = -C_6/R^6$. R is the distance between two fragments and C_6 is estimated with $C_6 = \alpha_1\alpha_2E_1E_2/(E_1 + E_2)$ where α_i and E_i ($i = 1, 2$) are polarizability and ionization energy, respectively. C_6 is estimated in this work to be 6.28×10^5 cm^{-1} Å^6 for acrylic acid and CH_2OO. The L-J potential parameters were estimated using empirical formulas[29,30] that follow:

$$\frac{\epsilon}{k_b} = \frac{T_c}{1.2593}$$

$$\sigma = 0.809V_c^{1/3}$$

Here k_b is the Boltzmann constant and T_c and V_c are critical temperature and critical volume, respectively, which were calculated by the method of Joback and Reid.[31] ϵ/k_b and σ in this work were taken as 471.16 K, 4.80 Å for acrylic acid and 334.17 K, 3.87 Å for CH_2OO. Bath gas N_2 was parametrized as 71.40 K, 3.80 Å from previous work.[32,33] And the collision energy transfer was parametrized by a single-exponential down model utilizing a temperature-dependent form for average energy transferred, i.e., $\langle \Delta E_{down} \rangle = 200(T/300)^{0.85}$ cm^{-1}.[34]

■ RESULTS AND DISCUSSION

Potential Energy Surface. The possibility of entrance channels of acrylic acid with Criegee intermediate involves cycloaddition and insertion. There are two double bonds in acrylic acid, and the asymmetry of CH_2OO indicates two different orientation of cycloaddition for each double bond, leaving four possible channels through which CH_2OO can add onto acrylic acid. 1,4-Cycloaddition can be postulated as well, but recent research[35] into reactions between CH_2OO with MVK has indicated that such adduct is not significant in products, and thus it is not included. Four types of hydrogen in acrylic acid dictate analogously eight distinctive way for CH_2OO to insert, among which there are 6 CH-insertions and 2 OH-insertions. Previous work[19] on CH_2OO with alkenes have considered CH-insertions as less important channels. Also, barriers of those insertions are also relatively high in this work. Therefore, the probability of them occurring is correspondingly inconsequential. Proceeding isomerization and decomposition after entrance steps are accounted for as well. Most of entrance channels are preceded a prereactive van der Waals complex while the rest do not, which is shown in the predictions of energies given in Figure 1, Figure 3, and Figure 4.

First four channels are cycloaddition of CH_2OO onto double bonds of acrylic acid. And the intermediates they generate then give rise to a molecular elimination to form more stable species. All four suffer minor barriers but one channel toward higher ground, which leads to 1,3-butadiene-2-ol and ozone and can be seen as the initiation of ozonolysis when tracked backward, PES of which is catalogued in Figure S5 in the Supporting Information. The attack on the C—O bond reveals a minor barrier in PES, which is different from the barrierless account of that between carbonyl oxide and formic acid.[36] P1 and P2 are isomers produced after the two five-membered rings, where CH_2OO cycloadds on olefinic bond in opposite orientations, shed formaldehyde. P3 indicates this channel is the isomerization from CH_2OO to formic acid when
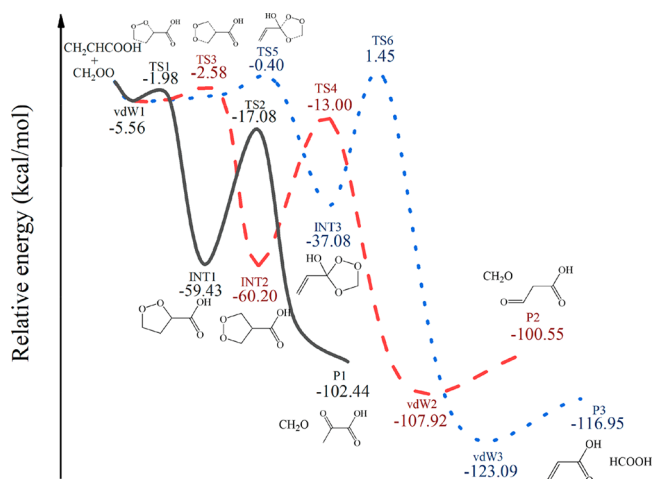
Figure 1. Prediction of energy profile of cycloadditions at the CCSD(T)/cc-pVTZ//M06-2X/6-31G(d,p) level including CH_2OO's attack on olefinic bond (black and red lines) and on carbonyl (blue dotted lines). All energies are relative to that of reactants, i.e., acrylic acid + CH_2OO.
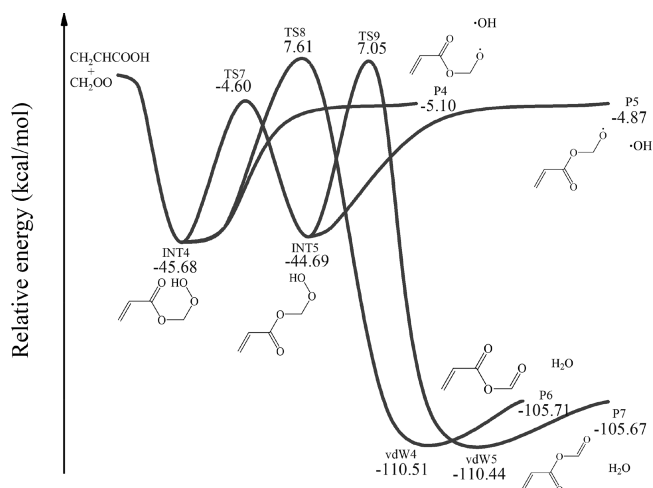

Figure 2. Details of 1,4-insertion. Direct dissociation processes have been scanned with CASSCF(2,2)/6-31G(d,p) method and corrected with energies from the CCSD(T)/cc-pVTZ//M06-2X/6-31G(d,p) level.

Figure 3. Prediction of energy profile for channels of 1,2-insertions at CCSD(T)/cc-pVTZ//M06-2X/6-31G(d,p) level. All energies are relative to that of acrylic acid + CH_2OO.

Figure 4. Prediction of energy profile of remaining 1,2-insertions at CCSD(T)/cc-pVTZ//M06-2X/6-31G(d,p) level. All energies are relative to that of acrylic acid + CH_2OO.

CH_2OO adds onto carbonyl. Considering other following steps, while it is possible for chemistry of CH_2OO with NO and SO_2,[37] the breaking of peroxyl bond and then migration of hydrogen, as is demonstrated in previous study,[20] is not feasible due to the lack of hydrogen in place. In the reaction of CH_2OO and alkenes,[19] it is believed the cycloaddition is the dominant pathway that controls kinetics. And for this study, fact that energies are all submerged under the reactants supports cycloaddition in its probability. However, although it is energetically low-lying, effect of cycloaddition is less important considering greatly lower rate coefficient of CH_2OO with alkenes.

The other eight channels are insertions into C−H or O−H bonds due to the biradical nature of Criegee intermediate. TS10−23, INT6−11 and vdW6−11 in Figure 3 and 4 are involved in the channels of C−H insertions while TS26, TS27, INT13 and vdW13 in Figure S5 are related to O−H insertion. Many are initiated through a prereactive complex involving H-
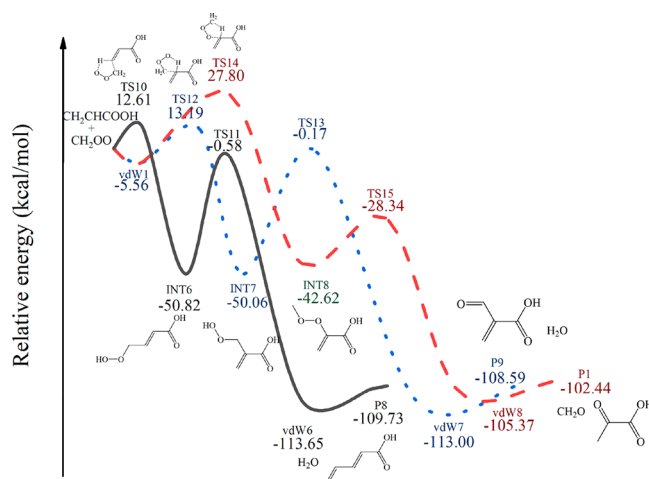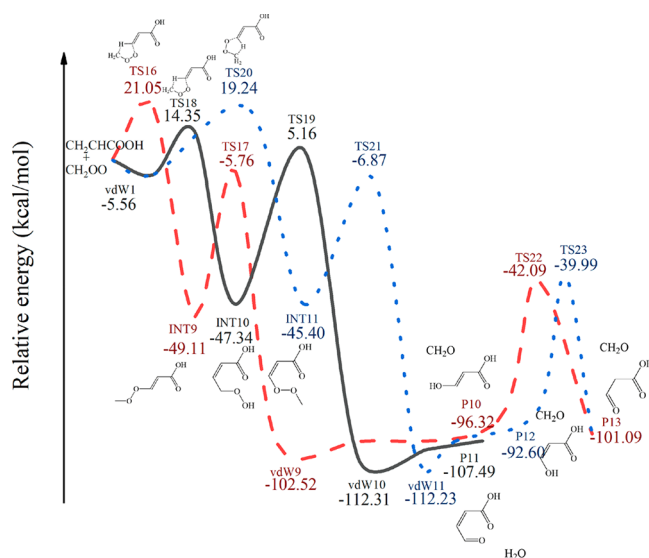
bonding like the reactions CH_2OO has with ethylene[19] and formic acid.[38] Then insertion takes form of concerted process when two radical site of CH_2OO take effect simultaneously to tear apart the C−H or O−H bond and fill in. The inserted intermediates continue to eliminate formaldehyde or water to stabilize to products. Entrance channel of 1,4-insertion reaction in the O−COH moiety, as can be seen from R to INT4, hydroperoxylmethyl acrylate (HPMA), in Figure 2 begins with a barrierless process where hydrogen of hydroxyl on acrylic acid is abstracted by the terminal oxygen of CH_2OO while at the same time a bond is established between carbon on CH_2OO and the carbonyl oxygen of acrylic acid, for which energy over separation is plotted in Figure S2 in the Supporting Information. The connection formed between carbon of CH_2OO and oxygen of acrylic acid is 1.44 Å long while bond lengths of CH_2OO are slightly elongated, C−O bond from 1.25 to 1.38 Å and O−O bond from 1.33 to 1.42 Å as shown in Figure 5. The barrierless character is similar in literature[38] except the one with trifluoroacetic acid,[39]
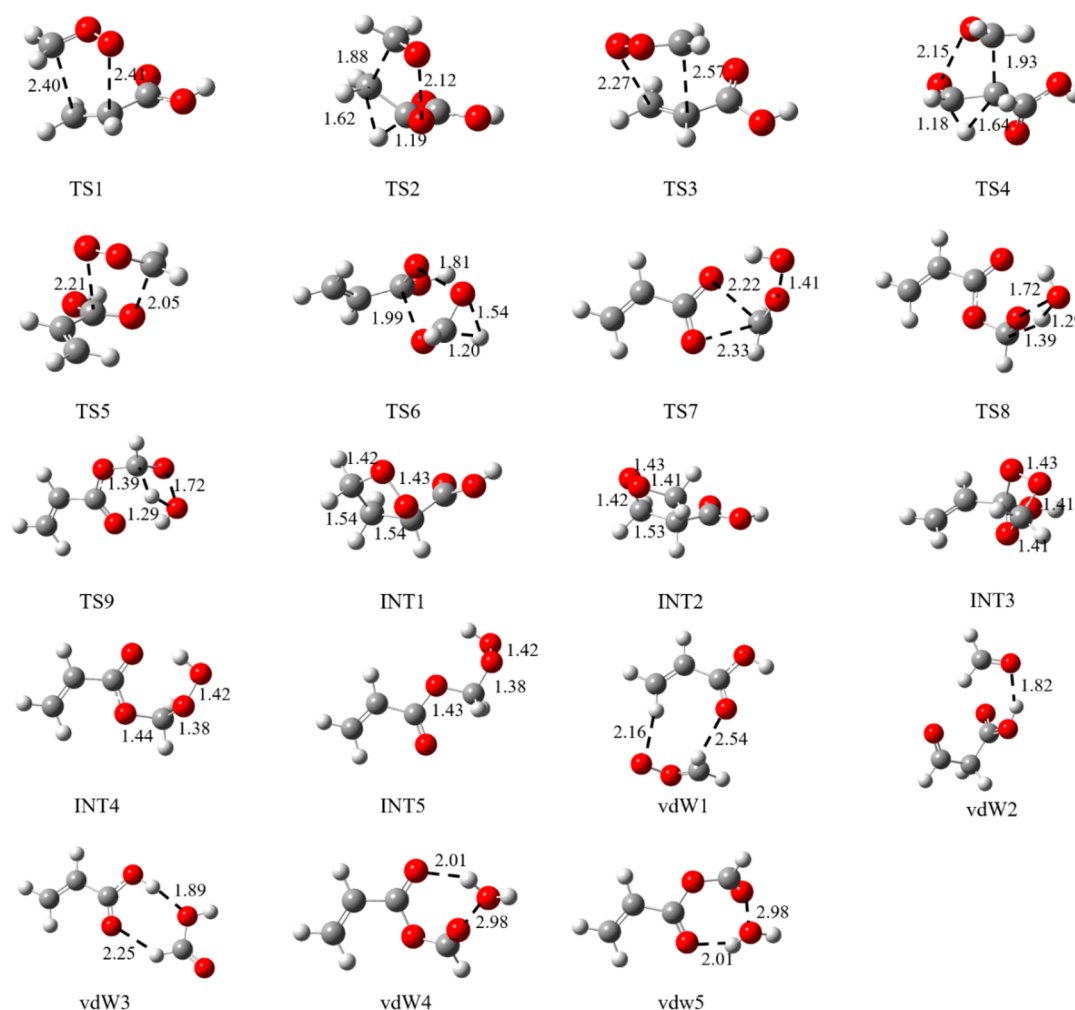
Figure 5. Geometries of stationary and saddle points. Only cycloadditions and 1,4-insertion are included for clarity. Other structures are compiled in the Supporting Information.

suggesting halogen substitution might affect the potential surface of reaction. Strong exoergicity of this step and large permanent dipole moment of both reactants dictate thermodynamically and kinetically that 1,4-insertion be the dominant pathway in all entrance channels. The MEP of 1,4-insertion clearly indicates hydrogen bond is involved during the process. Following generation of HPMA are two possible directions. The first one is direct O−O bond dissociation which gives rise to oxylmethyl acrylate (OMA) and hydroxyl, for which scan of energy over separation is shown in Figure S3 and Figure S4 in the Supporting Information. The second direction involves a transition state where hydroxyl moieties cling to adjacent hydrogen to turn into water leaving acrylic formic anhydride. HPMA formed after insertion can go through a saddle point to change its hydroperoxylmethyl moiety to another oxygen of acrylate group. The product (INT5) then continues to perform similar change, either direct O−O bond dissociation or a transition state that leads to formyl acrylate and water. The first direct O−O dissociation is the most favored pathway thermodynamically because of its lowest barrier, − 5.10 kcal/mol, giving rise to formation of hydroxyl. Considering yield of hydroxyl in ozonolysis of MVK being more than 10%,[6] it might suggest reaction between CH_2OO and acrylic acid has a role in ozonolysis of MVK. Subsequent fate of the dominant nascent product, OMA, can

be postulated by chemistry of similar compound, like oxylmethyl formate.[20] It is indicated that hydroperoxylmethyl formate, under conditions of combustion, may dissociate and return to Criegee intermediate and acids,[40] which is due to high temperature and entropy preference and is not applicable in this case. Unimolecular decomposition of oxylmethyl formate surpass energy of reactants. Analogously, unimolecular decomposition of OMA should be relatively unfavorable with barriers. Under atmospheric conditions, attack of other prevalent species such as hydroxyl is more plausible because of the large quantity and fast reaction rate of such radicals, but it is out of the scope of this work. Another roaming mechanism[20] was suggested for such species when hydroxyl abstracts adjacent hydrogen during the process of direct dissociation. Probability of it cannot be underestimated because in the MEP of direct dissociation hydroxyl keeps a close distance with the adjacent hydrogen for the very first phase of the process. However, the saddle point could not be found in the effort of optimization. The second direction generates anhydride and water and is more unfavorable than the first, even though the exoergicity is significantly larger. The other channels suffer conspicuously greater barriers and are therefore more unlikely to take place at low temperature. Interconnection of PES can be seen in Figure 1, Figure 3, and Figure 4, where P1 is produced from two different pathways,
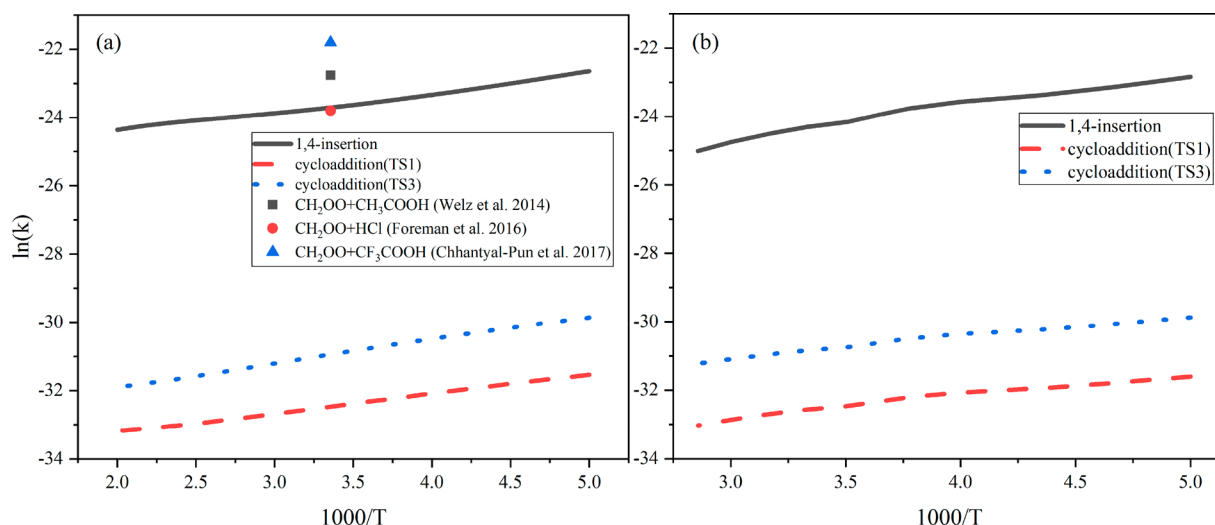
Figure 6. Rate coefficients for entrance steps of 1,4-insertion and cycloadditions (a) at 1 atm and (b) at 0.001 atm. Negative temperature dependence is consistent with the barrierless character.

and P10 and P12 are isomeric enols that can isomerize to the same ketone P13. It can be seen that most of unimolecular reactions are hard to happen after entrance channels except three cycloadditions and the 1,4-insertion. Contribution of those channels are negligible. Only the four entrance channels are considered in kinetic calculations to investigate rate of reaction between CH_2OO and acrylic acid.

Reaction Kinetics. The rate coefficients are calculated with geometries optimized at CCSD(T)/cc-pVTZ//M06-2X/6-31G(d,p) level by the MESS program[27] which is designed to solve the afore-mentioned interconnected PES. It can be seen from Figure 6 that HPMA is surely the dominant product on account of rate coefficients which is 4.71×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 300 K and 1 atm, larger than any other entrance channel in magnitude, which is in good agreement with similar reactions.[21,39,41] The largest discrepancy in Figure 6 is still within one magnitude of difference and that probably because of larger permanent dipole moment of trifluoroacetic acid. The reaction rate rises with pressure as can be seen from Figure 7 when the pressure is lower than the atmosphere, and it converges toward an asymptote when the pressure grows larger. It is clear that entrances of cycloaddition giving rate coefficient around 7.76×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K and 1 atm are much slower than 1,4-insertion, but higher than kinetics of CH_2OO with alkenes that gives rate coefficient of around 10^{-15} cm^3 $molecule^{-1}$ s^{-1}.[19] Attack on carbonyl bond turns out to be very slow, rate coefficient lower than 10^{-20} cm^3 $molecule^{-1}$ s^{-1}, thus not included in Figure 6. It seems most of the flux is channeled to 1,4-insertion because of the barrierless nature. Other channels are too slow to be considered. Therefore, pathways of cycloaddition take up to no more than 4% of the overall reaction rate.

With that of CH_2OO with saturated organic acids being near 10^{-10} cm^3 $molecule^{-1}$ s^{-1},[20] the significant discrepancy may be due to high dipole moments of CH_2OO and $-COOH$, and H-bonding between hydrogen and terminal oxygen of CH_2OO. What's more, experimental detection shows higher rate coefficient than collision theory predicts for reaction of CH_2OO with trifluoroacetic acid. Experiment reaching theoretical limit probably indicates as well strong dipole moments of both reactant control the reaction kinetically. In Figure 6 and Figure 7, the rate coefficients show slight negative
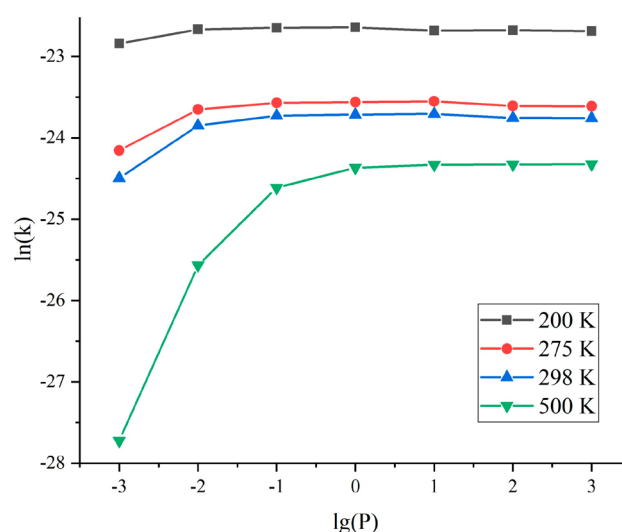

Figure 7. Rate coefficients for entrance steps of 1,4-insertion over different pressures. Positive pressure dependence is most significant when 500 K. The dependence is no longer perceivable after pressure gets higher than 1 atm.

temperature dependence and nearly no pressure dependence with pressure above atmosphere, which is consistent with minor negative temperature dependence and no significant pressure dependence given at 294 K for trifluoroacetic acid.[39] Limited or no temperature dependence for CH_2OO with organic acids[20] roughly matches the result as well. The negative dependence goes significant when pressure is getting lower. But it is at odd with positive temperature dependence for CH_2OO with alkenes,[19] which indicates limited contribution from reaction on olefinic bond of acrylic acid. The negative dependence is probably because the submerged wells of Van de Waals complexes before cycloaddition or barrierless nature of 1,4-insertion.

Direct dissociation should be the most probable pathway for following steps, however the rate coefficient could not be fast enough to deplete HPMA generated at 300 K. External scavenger must be considered in decomposition of HPMA since unimolecular reaction of HPMA cannot suffice to

consume the production of HPMA at normal temperature. At higher temperature, however, positive temperature dependency of dissociation of O−O bond will make it significant and cannot be neglected.

ATMOSPHERIC IMPLICATION

The large reaction rate and the mechanism behind it suggest an important role of CH_2OO and larger Criegee intermediates in the degradation of carboxylic acid in the atmosphere, acrylic acid for instance. The primary product of CH_2OO and acrylic acid, HPMA, could play an important role in secondary organic aerosol as nucleation core because volatility of products tends to be very low when molecule size gets larger.[42] Since the reaction with water dimer is the dominant removal pathway of CH_2OO,[43] the possibility of degradation through other pathways is associated with water concentration in the atmosphere. Because of the strong dependence of relative humidity, the yield of a product like HPMA would be competitive in a dry winter of high latitude of a northern area.[21,44] Rate coefficients of 3.88×10^{-11} cm^3 molecule^{-1} s^{-1} of CH_2OO with SO_2,[45] and 4.4×10^{-12} cm^3 molecule^{-1} s^{-1} of CH_2OO with NO_2,[46] respectively, are comparable with that of CH_2OO with acrylic acid. The concentration of SO_2 is around 20 μg m^{-3},[47] and the concentration of NO_2 in air is around 50 μg m^{-3},[47,48] while the concentration of acrylic acid was reported to be 2.9 μg m^{-3},[49] putting acrylic acid in a similar place as NO_2 in reacting with CH_2OO. Comparing pseudo first order rate constants indicates that the reaction of CH_2OO with acrylic acid is of a similar magnitude as that with NO_2 but smaller than that with SO_2. Moreover, severe pollution will imbue the air with pollutants like SO_2, NO_2, and organic acids of similar concentration.[50] Reaction between CH_2OO and acrylic acid could be a major sink of concentration of CH_2OO in some regions, with a large emission of carboxylic acid.[51] Besides, not only for acrylic acid, fast reaction with CH_2OO should be characteristic of carboxylic acid because of the existence of the carboxylic moiety. From organic acid concentration[50] and other common species in the atmosphere along with rate coefficients,[52] it can be seen that, to CH_2OO, acrylic acid, and more generally carboxylic acids, are potent scavengers. However, the unimolecular reaction and the reactions with water and water dimer of stabilized Criegee intermediates are strong competitors. Pseudo first order rate constants of CH_2OO are 0.3, 260, and 280 respectively.[53] Even though the self-reaction of CH_2OO is relatively slow, reaction with acrylic acid cannot still challenge that with water and water dimer.[43]

As to perspective of acrylic acid, reaction with OH is still competitive $(1.75 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}[17]$)$ while rate coefficients of acrylic acid with other species are still absent to our knowledge. Even though concentration of acrylic acid are usually low, it is reported[54,55] that biomass burning event like bonfire, fireworks or forest fire could lead to high concentration of aerosol of acrylic acid. And formation of HPMA could again intensify formation of secondary organic aerosol (SOA). Therefore, interaction between CH_2OO and acrylic acid could pose strong impact at some specific time. For acrylic acid's rate constant with chlorine 3.99×10^{-10} cm^3 molecule^{-1} s^{-1}[16] the reaction rate is competitive. But for that with ozone 0.73×10^{-18} cm^3 molecule^{-1} s^{-1},[18] it is much slower. Considering ozonolysis of acrylic acid strongly affected by presence of formic acid,[18] the bottleneck of ozonolysis of acrylic acid is not at reaction with CH_2OO.

CONCLUSION

The importance of Criegee intermediate in ozonolysis has led much interest, including ours focus on the simplest CI CH_2OO's reaction with acrylic acid. When the PES is explored at CCSD(T)/cc-pVTZ//M062X/6-31G(d,p) level, entrance channels of cycloaddition and insertion have been unveiled to show the overall picture of potential that CH_2OO and acrylic acid are faced with. Among them, 1,4-insertion is the dominant pathway under atmospheric conditions, where the dipole−dipole capture mechanism is the initiative force of reaction. The nascent product of 1,4-insertion, HPMA, takes up most of the production with the overall rate coefficient being 4.71×10^{-11} cm^3 molecule^{-1} s^{-1}. Negative temperature dependence is found in kinetic calculations and is consistent with the barrierless nature of 1,4-insertion. For pressure that is lower than atmosphere, the rate coefficient has a positive pressure dependence while for larger pressure, pressure dependence is close to none and rate coefficient grows to an asymptote when pressure grows over the limit. Under atmospheric conditions, the rate coefficient of reaction between acrylic acid and CH_2OO is still competitive compared with other common species and pollutants such as OH, SO_2, and NO_2 in air. Low volatility of products may facilitate formation of SOA, especially when the nucleating agent is the critical factor. It holds true not only for acrylic acid but also for other organic acids which possess a carboxylic group. It is noteworthy that human activities including industrial production, bonfires, and fireworks have a strong correlation with emission of acid and formation of related SOA,[13−15,51,55] showing CH_2OO's weaved involvement in atmospheric chemistry. More information is still needed to validate the mechanism experimentally and atmospherically and to raise attention toward the possibly overlooked formation source of SOA.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b11671.

Scan curves of dissociation in the barrierless processes, the potential surface of possible channels where MVK reacts with ozone to produce acrylic acid and CH_2OO, and geometry details of structures under consideration (PDF)

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