論文の内容の要旨

論文題目 Reactivity of Criegee intermediates in gas phase and on gas-liquid interfaces
(気相及び気液界面におけるクリーギー中間体の反応性)

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1.1 Introduction

Such a process has been postulated since the 1950s,[1] that the addition of O_3 onto a C=C bond leads to the formation of a cyclic molecule, and because of the large thermal energy released in this process, it decomposes and produces R_1R_2COO, which is known as a Criegee intermediate (CI). It has been commonly accepted that the ozonelysis of alkenes in the atmosphere is a major path for the disappearance of CIs. Not only this process is very important for the atmospheric chemistry, but also the CIs generated in situ acting as initiators of oxidation, play a significant role in the subsequent reactions.

Due to CIs' extremely low concentration, the direct observation of these intermediates has remained elusive for decades. In 2012, Welz *et al.*[2] synthesized the simplest CI, CH_2OO successfully as a result of the following synthetic route:

$CH_2I_2 + h\nu \rightarrow CH_2I + I$　(R1)

$CH_2I + O_2 \rightarrow CH_2OO + I$　(R2)

and provided a more feasible way to investigate CH_2OO kinetics in gas phase.

Nevertheless, it is just a little step in understanding the Criegee chemistry. Large quantities of unsaturated organic compounds are released from vegetation, and much more complex CIs can be formed in the ozonolysis of these compounds. As well, they can be absorbed by some oil-water mixed aerosols, and trigger a series of oxidation reactions, which may finally affect the atmospheric environment and human health.

Enami *et al.*[3] firstly reported a research on exploring the Criegee chemistry on gas-liquid interface by using a pneumatic electrospray ionization mass spectrometer. In this experiment, α-humulene was selected to react with O_3 on gas-liquid interfaces, then generate CI. Intermediately, CI reacts with water to form hydroxy-hydroperoxide (HH) as shown in Fig.1. Adducted by Cl-, HH can be detected by the mass analyzer, and the result is presented in Fig.2.

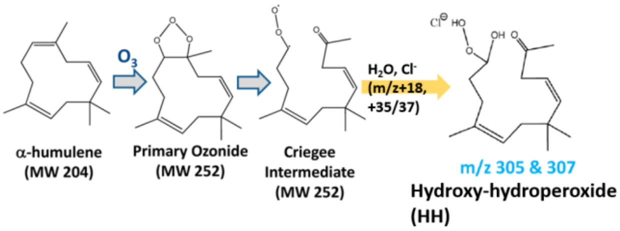


Fig.1 Reaction scheme of α-humulene reacting with O_3 on gas-liquid interfaces

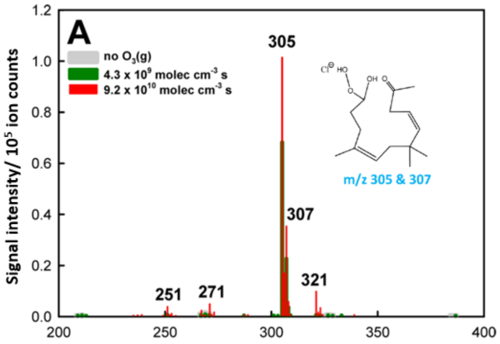


Fig.2 Negative ion mass spectra of 1 mM α-humulene + 0.2 mM NaCl in Water:Acetonitrile (1:4 = vol:vol) solution microjets (gray), or those exposed to O_3(g) (red, *E* = 3.3 x 10^{11} molecules cm^{-3} s) at 1 atm and 298 K.

2 Experiments and results

2.1 Detection of CH_2OO by using a cw QCL in gas phase

This well-established method mentioned above for the generation of CH_2OO was also applied in this study. As shown in Fig.3, a gas mixture of $CH_2I_2/O_2/N_2$ is injected throughout the reaction cell.

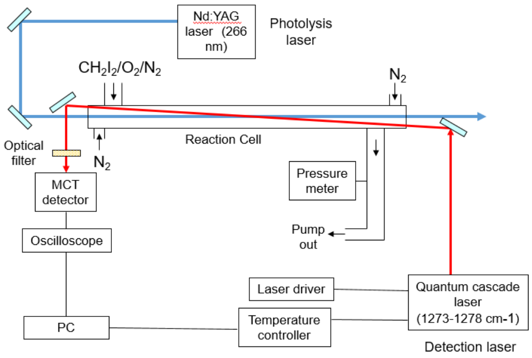


Fig.3 Scheme of experimental setup for the spectroscopic and kinetics researches of CH_2OO

The super-power beam from a Nd:YAG laser decomposes CH_2I_2 into CH_2I and I radicals, and CH_2I reacts with O_2 immediately, with CH_2OO produced. A continuous wave thermoelectrically-cooled distributed feed-back quantum cascade laser (QCL) was used as the spectroscopic light source in the detection of CH_2OO.

The highly resolved absorption was firstly recorded in this study in mid-infrared regions in Fig.4.

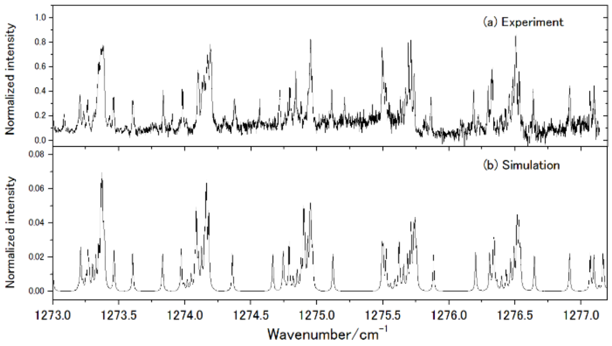


Fig.4 Comparison of the observed and simulated spectra of CH_2OO in the region 1273.0–1277.2 cm^{-1}

Some kinetics researches of CH_2OO reacting with SO_2 and NO_2 were carried out as well, because the oxidation of SO_2 finally leads to the generation of aerosol, and NOx circle contributes to the formation of smog and acid rain, as well as tropospheric ozone. In the experiment of CH_2OO+SO_2, due to the concentration of SO_2 was much higher than that of CH_2OO, the reaction of CH_2OO with SO_2 and the bimolecular self-reaction of CH_2OO are mainly responsible for the decay of CH_2OO in addition of SO_2:

$$CH_2OO+CH_2OO \rightarrow 2H_2CO+O_2 \quad \text{(R3)}$$

$$CH_2OO+SO_2 \rightarrow H_2CO+SO_3 \quad \text{(R4)}$$

The equation describing the decay of CH_2OO can be written as:

$$y = \frac{k_1'}{(\frac{k_1'}{y_{max}} - 2bk_{self})exp(k_1't - k_1't_0) - 2bk_{self}} \quad \text{(E1)}$$

where k_1' is the pseudo-first-order rate constant and $k_1' = k_1[SO_2]$. Each k_1' can be derived from decay curves of CH_2OO in addition of different concentrations of SO_2 as shown in Fig.5.

The slope of the red line in Fig. 6 is the rate coefficient k_1 for $CH_2OO + SO_2$, which was calculated to be (3.7 ± 0.3) × 10^{-11} cm^3 molecule^{-1} s^{-1}. This value is in good agreement with previous direct measurements[2, 3, 4], which demonstrates that this new method is a powerful and convenient tool to investigate CH_2OO kinetics.

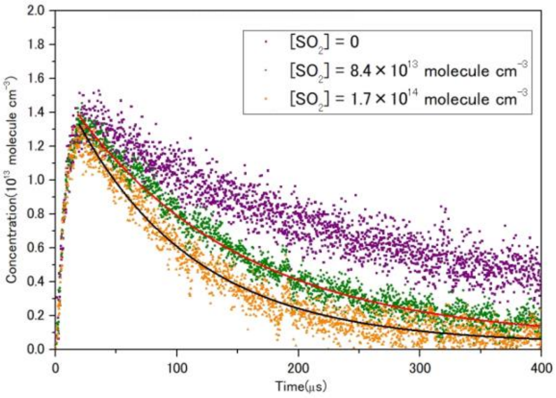


Fig.5 Time profiles of CH_2OO in addition of different concentrations of SO_2, and their fitted curves derived from E1 (red and black).

The slope of the red line in Fig. 4 is the rate coefficient k_1 for $CH_2OO + SO_2$, which was calculated to be (3.7 ± 0.3) × 10^{-11} cm^3 molecule^{-1} s^{-1}. This value is in good agreement with previous direct measurements,[2,4,5] which demonstrates that this new method is a powerful and convenient tool in investigating CH_2OO kinetics.

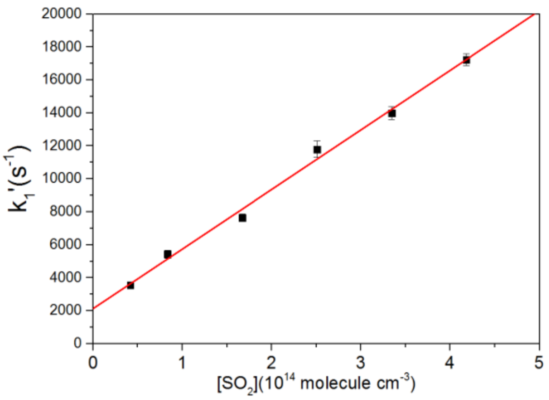


Fig.6 Plots of the pseudo-first-order rate coefficients, k_1', for the decay of CH_2OO in the presence of SO_2.

With a similar method, the rate coefficient k_2 for $CH_2OO + NO_2$ was determined to be (4.4 ± 0.2) × 10^{-12} cm^3 molecule^{-1} s^{-1}. Only two groups carried out the kinetics research of $CH_2OO + NO_2$, and they gained two different values of the rate coefficient for $CH_2OO + NO_2$, which means the result in this study could be an important reference.

2.2 Criegee intermediate reacting with benzoic acid on gas-liquid interfaces

Benzoic acid (BA) is one of the most abundant acids in the particulate matter (PM) found over polluted urban areas.[6] Previous molecular dynamics (MD) calculations, surface-tension measurements and surface-specific mass spectrometry revealed a moderate affinity of benzoate for aqueous surfaces.[7] Thus, the identification of products from the reaction of CIs with BA on the air-aqueous surface has emerged as an important issue in the atmospheric chemistry of polluted urban air.

In this work, β-caryophyllene (β-C) was selected to generate CI, and a mixture of 1mM β-C, 0.2mM NaCl, 10mM BA, and 10 mM octanoic acid(OA) was injected into a spraying chamber of an electrospray mass spectrometer flushed with N_2(g) at 1 atm, 298 K. reaction chamber. OA was added in the mixture as a reference. Microjets are exposed therein to orthogonal gas-phase O_3/O_2 beam as shown in Fig.7.

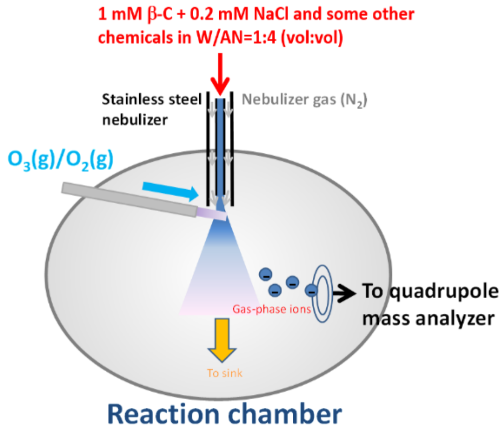


Fig.7 Schematic diagram of experimental setup for the CI research on gas-liquid interfaces[8]

The observed mass spectra correspond to species generated by heterogeneous processes in the outermost interfacial layers of the intact injected microjets, and this mechanism can be described as below in Fig. 8. The droplets (d=1 mm) of liquid solution is injected into spraying chamber, and these initial droplets are flattened by the moving N_2 gas and then stretched windward into rimmed thin-film bags. As mentioned before, Organic compounds with large propensities such as β-C have the affinity to the surfaces instead of staying in water bulks, so the thin-film on the bottom of a water bag has a relatively higher concentration of β-C. These rimmed water bags are dynamically unstable and break up into smaller secondary droplets (d ≤ 1 μm). Secondary droplets rapidly shrink via solvent evaporation by drying gas, eventually result in forming ions detected by the mass analyzer.

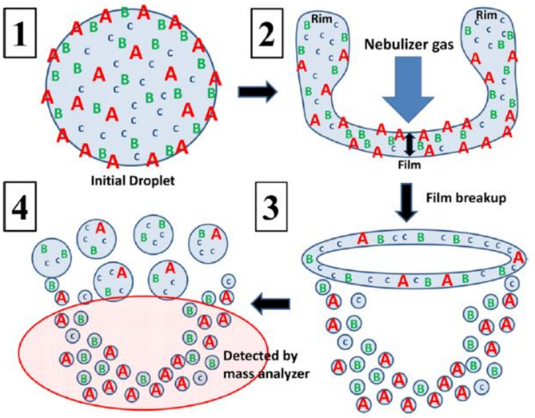


Fig.8 Schematic representation of the mechanism for detecting the molecules on surfaces[8]

Signals of each product are presented in Fig.9.

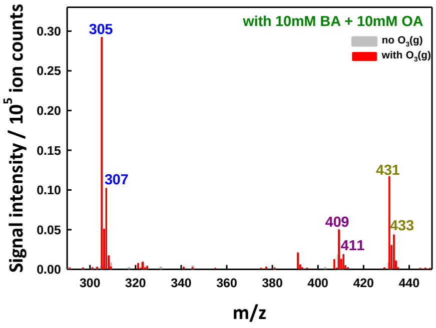


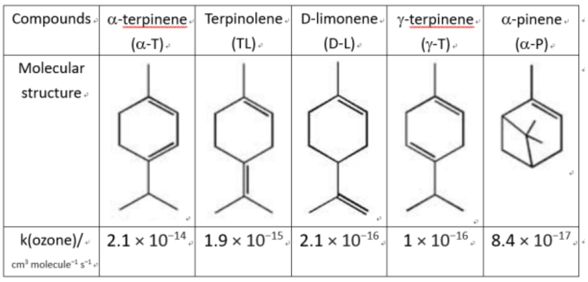
Fig.9 Negative ion mass spectra of 1 mM β-caryophyllene + 0.2 mM NaCl + 10 mM benzoic acid + 10 mM octanoic acid in W:AN (1:4 = vol:vol) solution microjets (gray), or those exposed to O_3(g) (red, E = 3.3 x 10^{11} molecules cm^{-3} s) at 1 atm and 298 K.

Such a result is beyond our expectation. The product of CI+BA (409/411=204+48+144 (BA) +35/37) is obviously less than that of CI+OA. However, both in the gas and liquid phase, BA has a better ability of dissociating H^+ than OA (in water, pKa=4.2 for BA, pKa=4.8 for OA), which means that BA should have a stronger reactivity toward CI. Nevertheless, some research[8] reported the distribution of angles of between the principal molecular axis (for BA, the axis passes through the carboxylate carbon and the neighboring carbon of the benzene ring) and the gas-liquid surface, and found that BA has a large possibility vertical to the surface(COOH in the liquid side), which hinder its valid contact with CI.

2.3 Reactivity of monoterpenes initialed Criegee intermediates on gas-liquid surfaces

In this study, several kinds of monoterpenes listed in Fig.10 are selected to explore the structure dependent

Criegee chemistry on gas-liquid interfaces, since monoterpenes released from biogenic sources are major sources of CIs (CIs) in the troposphere.



Compounds	α-terpinene (α-T)	Terpinolene (TL)	D-limonene (D-L)	γ-terpinene (γ-T)	α-pinene (α-P)
Molecular structure					
k(ozone)/ cm³ molecule⁻¹ s⁻¹	2.1×10^{-14}	1.9×10^{-15}	2.1×10^{-16}	1×10^{-16}	8.4×10^{-17}

Fig.10 Monoterpenes used in this work and their rate coefficients reacting with O_3

By employing the same setup used in the experiments described above, A mixture of [monoterpene + NaCl] in W/AN (1:4 = vol:vol) microjets is exposed to orthogonal gas-phase O_3/O_2 streams in the reaction chamber. CIs generated upon the ozonolysis of monoterpenes readily react water on gas-liquid interfaces, lead to the formation of HH. The observed relative yields of HH production are not consistent with the gas phase rate coefficients of monoterpenes reacting with O_3 as shown in Fig.11, indicating the possibility that the orientations of monoterpenes affect their reactivity toward O_3.

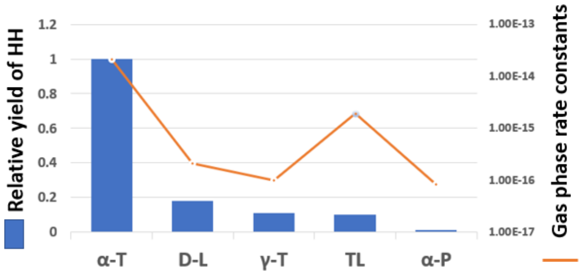


Fig.11 Relative yields of hydroxy-hydroperoxides (HH, m/z 237/239) from monoterpenes and their rate coefficients reacting with O_3

Cis-pinonic acid (CPA) is a surface-active reagent, and it has been proved to be extremely reactive toward CI on gas-liquid interfaces in previous studies. In this study, the reactivity of monoterpenes initialed CI toward CPA was investigated, and the results in Fig.12 and 13.

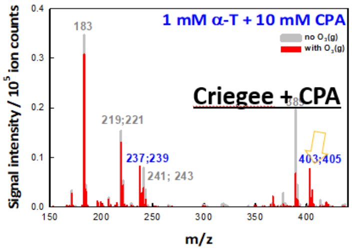


Fig.12 Negative ion mass spectrum of α-T initialed CI reacting with CPA on gas-liquid interfaces

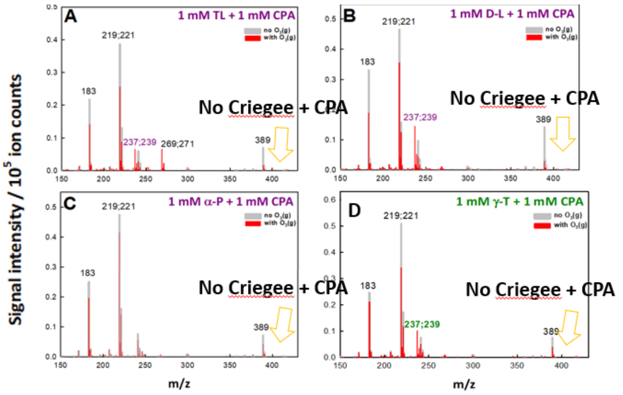


Fig.13 Negative ion mass spectrum of TL, D-L, α-P, γ-T initialed CI reacting with CPA on gas-liquid interfaces

The results show that only the product of α-T CI reacting with CPA was detected, indicating that the reactivity of CI is structure dependent.

3 Conclusion and discussions

New method in the detection of CH_2OO was established by using a cw QCL as the spectroscopic light. The rate coefficient for $CH_2OO + SO_2$ and NO_2 have been measured by using this new method. QCL demonstrated its feasibility in kinetic researches of Criegee intermediate, and our experimental setup is potentially to be enhanced in detection limit and precision

The reactivity of benzoic acid toward Criegee intermediate, and the molecular structure dependent reactivity of Criegee intermediates on gas-liquid interfaces have been investigated. Orientation and molecular structure of reactants have significant effects on Criegee chemistry on gas-liquid interfaces.

References

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