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Cl-initiated oxidation of methacrolein under NO_x-free conditions studied by VUV photoionization mass spectrometry†

Xiaoxiao Lin,^{‡a} Rongrong Hu,^{‡a} Ziji Ma,^a Hao Yue,^a Zuoying Wen,^a Cuihong Zhang,^{a,b} Christa Fittschen,^b Weijun Zhang,^{a,*} Xiaofeng Tang^{a,*}

^a *Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, HFIPS, Chinese Academy of Sciences, Hefei, 230031 Anhui, China*

^b *University Lille, CNRS, UMR 8522, PC2A – Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France*

* Corresponding authors, E-mail: wjzhang@aiofm.ac.cn (W.Z.), tangxf@aiofm.ac.cn (X.T.)

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‡ These authors contributed equally to this work.

Abstract: The Cl-initiated oxidation of methacrolein (MACR, C₄H₆O) under NO_x-free conditions has been investigated in a fast flow tube by using a home-made vacuum ultraviolet (VUV) photoionization mass spectrometer complemented by high-level theoretical calculations. The key species such as intermediates and radicals together with products involved in the oxidation are observed online and confirmed in photoionization mass spectra. The reaction potential energy surfaces of the transient C₄H₅O and C₄H₆OCl radicals, formed from the hydrogen-abstraction reaction and the addition reaction of MACR with Cl atoms, with oxygen have been theoretically calculated to illuminate the formation of the peroxy radicals of C₄H₅OO₂ and C₄H₆OClO₂. The photoionization processes of these peroxy radicals, whose cations are not stable, and their individual self-reactions as well as bimolecular reactions with HO₂ radical are studied and discussed. In addition, kinetic experiments are also performed to get the time evolution of specific products and compared well with theoretical models, providing a detailed insight into the reaction mechanism of the Cl-initiated oxidation of MACR.

1. Introduction

Methacrolein (MACR, C₄H₆O) is a key reaction intermediate in atmospheric chemistry and plays an essential role in the atmospheric oxidation of isoprene, the most abundant non-methane volatile organic compound (VOC) in the atmosphere.^{1,2} MACR is also an important VOC in the atmosphere and its global emission can approach ~ 45 Tg yr⁻¹.³ In particular, due to its essential role involved in the oxidation of isoprene, the atmospheric fate of MACR has attracted a great deal of attention in the past decades.^{1,}

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The atmospheric fate of MACR is dominated by its reaction with the hydroxyl radical (OH), and mainly proceeds via two pathways with approximately equal rates: (i) the addition of OH to the C=C double bond of MACR to generate the OH-MACR adduct radical, and (ii) the abstraction of the aldehyde H-atom to produce the acyl radical, C₄H₅O.^{5,6} In the atmosphere, these radicals can react with O₂ and lead to the production of the hydroxyl peroxy radical and the acyl peroxy radical. In addition, these transient peroxy radicals can perform bimolecular reactions with NO_x (NO and NO₂), with themselves or other peroxy radicals (RO₂), with HO₂ or OH depending on the site and time, and contribute to air quality and regional climate.⁷⁻¹²

In recent years, researchers found that halogen radicals, particularly chlorine (Cl) atoms formed from photolysis of chlorine (Cl₂), nitrosyl chloride (ClNO), nitryl chloride (ClNO₂) and bromine chloride (BrCl), can also have important impacts on the atmospheric degradation of VOCs.¹³⁻¹⁶ Among them, Cl atoms can efficiently oxidize VOCs, and the reaction rate constants of Cl atoms with some VOCs can be ten times larger than those with OH.¹⁵⁻¹⁸ For example, the reaction rate constant of MACR with Cl atoms was measured at $3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, much larger than that of MACR with OH ($3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).^{19, 20} Therefore, considering the concentrations of OH radicals ($\sim 10^6 \text{ molecules cm}^{-3}$) and Cl atoms ($\sim 3 \times 10^5 \text{ molecules cm}^{-3}$ during daytime and up to $\sim 8 \times 10^6 \text{ molecules cm}^{-3}$ in the marine boundary layer),^{21, 22} the Cl-initiated oxidation of MACR can play a significant role in the atmosphere next to that initiated with the OH radical, at least in the marine boundary

layer, and has been the subject of experimental and theoretical studies.^{20, 23}

Similar to the case with the OH radical, the reaction of MACR with Cl atoms can proceed via two pathways too: the addition of Cl atom to the C=C bond of MACR to get the C₄H₆OCl adduct radical, and the hydrogen abstraction to produce the C₄H₅O radical.¹⁹ Previous theoretical calculations show that the Cl-addition to the external carbon of the C=C double bond is the main pathway with a predicted branching ratio of 86%, whereas the branching ratio of the aldehyde-H abstraction is 12% and that of the methyl-H abstraction is 2%.²³

In the atmosphere, the C₄H₆OCl and C₄H₅O radicals will react with O₂ and the transient peroxy radicals, C₄H₆OClO₂ and C₄H₅OO₂, can perform various reactions.¹¹ For example, the peroxy radical C₄H₆OClO₂ reacts with itself to form the C₄H₆OClO radical, and its decomposition product, chloroacetone (C₃H₅OCl), was detected with the technique of gas chromatography flame ionization detection (GC-FID).²⁴ The stable secondary products 2,3-dichloro-2-methylpropanal (C₄H₆OCl₂) and methacryloyl chloride (C₄H₅OCl) formed from the reactions of C₄H₆OCl and C₄H₅O radicals with the remaining precursor Cl₂ were also detected in experiments with GC-FID.²⁵ But, due to the use of online probe techniques to study these reactions, the available information of the Cl-initiated oxidation of MACR is still scarce and the detailed reaction mechanism as well as the formation of the above theoretically proposed key radicals and intermediates needs to be clarified or confirmed.

In this work, the Cl-initiated oxidation reaction of MACR under NO_x-free conditions has been investigated in a fast flow tube reactor by using the online analytical method of vacuum ultraviolet (VUV) photoionization time of flight mass spectrometry complemented by high-level theoretical computations of the structures of radicals and the reaction potential energy surfaces. VUV photoionization mass spectrometry is a powerful analytical method and key species such as radicals and intermediates as well as products involved in the oxidation reactions are directly observed in the experiments.^{26, 27} The adiabatic ionization energies (AIEs) of these key species are also predicted and utilized to assign the photoionization mass spectra. In

addition, to confirm the origins of the products and then to reveal the embedded reaction mechanism, kinetic experiments have also been performed and the time behaviors of products have been obtained and compared with modeling results.

2. Methods

A fast flow tube has been used as a chemical reactor to study the Cl-initiated oxidation reaction of MACR under NO_x-free conditions and a home-made VUV photoionization orthogonal acceleration reflectron time-of-flight (TOF) mass spectrometer is employed to probe and analyze reaction intermediates, radicals and products. The configuration of the fast flow tube and the photoionization mass spectrometer has already been introduced in detail before and so only a brief description is presented here.^{28,29}

Briefly, the photoionization mass spectrometer is composed of three vacuum chambers: a source chamber, a photoionization chamber and a TOF chamber. The fast flow tube reactor is installed inside the source chamber of the mass spectrometer and is composed of a 45 cm long Pyrex main tube with a 16/12 mm outer/inner diameter and a 60 cm long coaxial movable injector with a 6/4 mm outer/inner diameter. Cl atoms were generated by microwave discharge (GMS-200W, Sairem) of 1% diluted Cl₂ gas in helium and introduced into the fast flow tube to initiate the oxidation reactions. MACR was introduced through bubbling its liquid at room temperature, and O₂ and helium bath gas were injected via the arms of the main tube or the injector. The total pressure inside the flow tube was monitored by a capacity gauge and fixed at 6 Torr by a closed-loop feedback throttle valve. The initial concentrations of MACR, O₂ and Cl₂ in the flow tube were 8×10^{12} , 1×10^{14} and 3×10^{12} molecule cm⁻³, respectively. After microwave discharge, the concentration Cl atoms was estimated at 5×10^{12} molecule cm⁻³. The inner surface of the main tube and the outer surface of the injector were coated with halocarbon wax to reduce radical loss on the walls. The reaction time was adjusted by changing the distance between the injector and the sampling skimmer.

After passing through the skimmer (1 mm diameter), the gas mixture from the fast

flow tube entered into the photoionization chamber, which was equipped with a commercial Kr discharge lamp (PKS 106, Heraeus) inside. Then the molecules and radicals absorbed the photons of the lamp with energies of $h\nu = 10.0$ and 10.6 eV, and photoionization processes were induced. A TOF mass analyzer with an orthogonal acceleration and reflectron structure was employed to analyze the masses of ions. The total ion flight length of the TOF mass spectrometer is ~ 1 m, and its mass resolving power has been measured to be $M/\Delta M \sim 2000$ (FWHM, the full width at half maximum). During the experiments the pressures of the source chamber, the photoionization chamber and the TOF chamber were 800 , 1×10^{-2} and 1×10^{-4} Pa, respectively.

High-level theoretical calculations have also been carried out to get the reaction potential energy surfaces, the structures and the ionization energies of radicals and products. Concretely, the potential energy surfaces were calculated for the reactions of C_4H_6OCl and C_4H_5O radicals with O_2 to examine the formation channels leading to the peroxy radicals and other products. The potential energy surfaces were computed at the CCSD(T)-F12a/aug-cc-pVTZ//PBE0/aug-cc-pVDZ level of theory. The structural optimizations and the vibrational frequency calculations were performed with the Gaussian 16 program package.³⁰ Then the energies of the reactants, the transition states and the products were calculated with the Molpro package.³¹ The AIEs of the products were determined from the energy difference of cations and molecules at the PBE0/aug-cc-pVDZ level of theory.

3. Results and discussion

To get detailed information on the reaction system inside the fast flow tube, experiments were performed in sequence and can be divided into two parts.^{32, 33} Firstly, the experiment was performed without adding oxygen into the fast flow tube, and C_4H_6OCl and C_4H_5O radicals were formed from the Cl-addition reaction and the hydrogen abstraction reaction of MACR with Cl atoms, respectively. Then, with the addition of oxygen, the transient C_4H_6OCl and C_4H_5O radicals reacted with oxygen to

produce peroxy radicals and these peroxy radicals could perform self-reactions or react with HO₂ radicals in the flow tube under NO_x-free conditions.¹¹

3.1 The reaction of MACR with Cl

Without adding oxygen into the fast flow tube, the obtained photoionization mass spectrum is presented in Fig. 1(a). Many peaks can be observed in the mass spectrum and the major species have been assigned. The most intense peak at $m/z = 70$ is ascribed to the reactant MACR itself, whose ionization energy locates at 9.92 eV,³⁴ below the photon energy of the Kr lamp. The mass peaks at $m/z = 69$ and $m/z = 105/107$ should be assigned as C₄H₅O and C₄H₆OCl radicals, respectively, formed from the hydrogen abstraction reaction and the addition reaction of MACR with Cl atoms.^{19, 23} As far as we known, the transient C₄H₅O and C₄H₆OCl radicals are directly detected here for the first time. The ratio of the mass peaks at $m/z = 105$ and 107 corresponding to the C₄H₆O³⁵Cl and C₄H₆O³⁷Cl isotopes is measured at ~ 3 , agreeing well with the ratio of the natural abundances of the ³⁵Cl and ³⁷Cl isotopes (100:32).³⁵

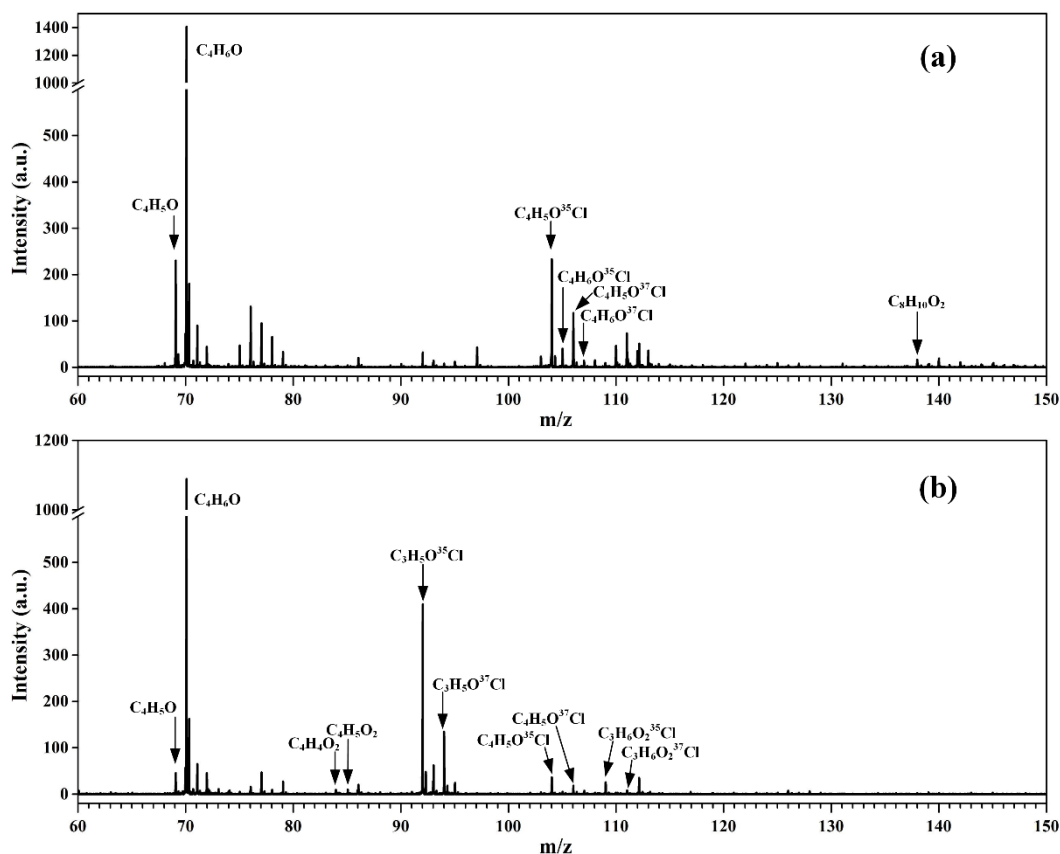


Fig. 1. Photoionization mass spectra acquired (a) without O₂ and (b) adding O₂ into the

fast flow tube.

The transient C_4H_5O and C_4H_6OCl radicals can perform self-reactions or react with the residual Cl_2 molecules in the fast flow tube, and the corresponding products have been observed and identified in the mass spectrum too, partially with the aid of the isotopic ratio of ^{35}Cl and ^{37}Cl . For example, the peak at $m/z = 138$ in the mass spectrum of Fig. 1(a) is assigned as $C_8H_{10}O_2$, the self-reaction product of C_4H_5O radicals, and the mass peaks at $m/z = 104$ and 106 are assigned as methacryloyl chloride ($C_4H_5O^{35}Cl$ and $C_4H_5O^{37}Cl$), the product of the reaction of C_4H_5O radicals with Cl_2 .²⁵ The mass peaks at $m/z = 140$, 142 and 144 are assigned as 2,3-dichloro-2-methylpropanal ($C_4H_6OCl_2$) from the reaction of C_4H_6OCl radicals with Cl_2 .²⁵ The C_4H_6OCl radical can also perform self-reaction and the product $C_8H_{12}O_2Cl_2$ has been observed at $m/z = 210$, 212 and 214 in the mass spectrum too, as shown in Fig. S1. Some products are fragile in the photoionization and their fragment ions have also contributed to the mass spectrum, i.e., at $m/z = 76$, 78 , 111 and 113 . The detailed assignment of these peaks and their origins can be found in Table S1.

3.2 The reactions of C_4H_5O and C_4H_6OCl with O_2

After adding abundant O_2 (10^{16} molecule cm^{-3}) into the fast flow tube, the transient C_4H_5O and C_4H_6OCl radicals will mainly react with O_2 and the resulting photoionization mass spectrum is presented in Fig. 1(b). To get a detailed understanding of these processes, the potential energy surfaces (PES) of the reactions of C_4H_5O and C_4H_6OCl radicals with O_2 have been calculated at the CCSD(T)-F12a/aug-cc-pVTZ//PBE0/aug-cc-pVDZ level of theory and are presented in Figs. 2 and 3, respectively, as well as the optimized structures of the species involved in the reactions.

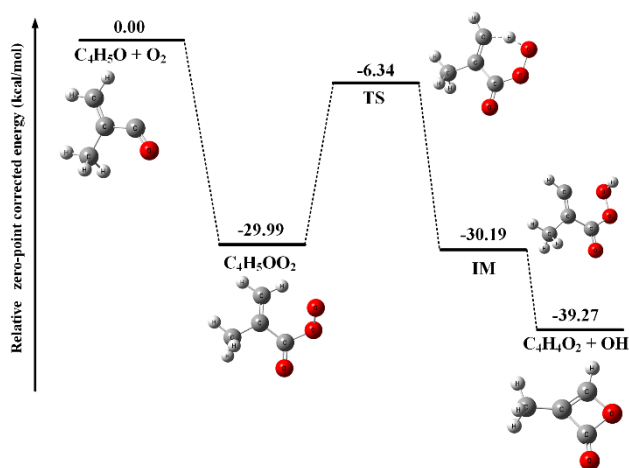


Fig. 2. Potential energy surface of the reaction of C_4H_5O with O_2 .

As shown in Fig. 2, the reaction of C_4H_5O with O_2 is an exothermic reaction and the production of the $C_4H_5OO_2$ peroxy radical is energetically favorable. In addition, the theoretical calculations show that the $C_4H_5OO_2$ peroxy radical can perform an H-transfer reaction via a transition state (TS) with a submerged barrier of $-6.34 \text{ kcal mol}^{-1}$ and then dissociate to $C_4H_4O_2$ and OH. The formation of $C_4H_4O_2$ and OH is exothermic with an energy of $-39.27 \text{ kcal mol}^{-1}$, indicating that their formation is energetically feasible. As shown in Fig. 1(b), the product $C_4H_4O_2$ has been observed and ascribes to the peak of $m/z = 84$ in the photoionization mass spectrum.

In Fig. 3, the potential energy surface of the reaction of C_4H_6OCl with O_2 shows that the formation of the $C_4H_6OClO_2$ peroxy radical is also energetically favorable. But, unlike the above case of $C_4H_5OO_2$, the unimolecular reaction of the $C_4H_6OClO_2$ peroxy radical to produce $C_4H_5ClO + HO_2$ and $C_4H_5ClO_2 + OH$ has an energy barrier with a height of $30.09 \text{ kcal mol}^{-1}$, which is too high to be overcome at room temperature. Thus the $C_4H_6OClO_2$ peroxy radical is the only product in the reaction of C_4H_6OCl with O_2 .

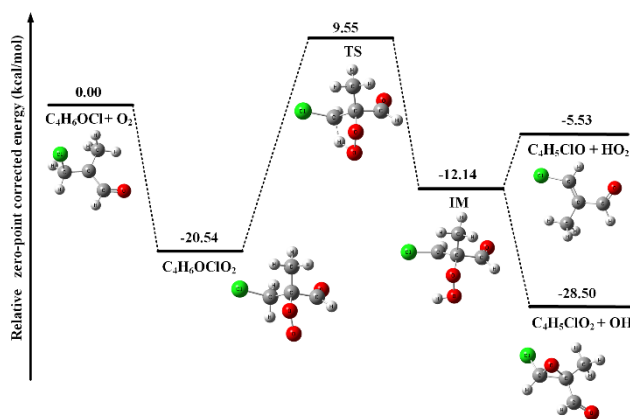


Fig. 3. Potential energy surface of the reaction of C_4H_6OCl with O_2 .

As discussed above, the $C_4H_5OO_2$ and $C_4H_6OCLO_2$ peroxy radicals are the main products of the reactions of C_4H_5O and C_4H_6OCl radicals with O_2 and their corresponding molecular ions should locate at $m/z = 101$ and $m/z = 137/139$, respectively, in the photoionization mass spectrum. However, no such mass peaks can be observed in Fig. 1(b).

Previous studies have shown that except the smallest peroxy radical, CH_3O_2 , the cations of most alkyl peroxy radicals are not stable and dissociate to the fragments of alkyl cations and oxygen following the photoionization.^{32, 33, 36} Here, to help to assign the photoionization mass spectrum and to explain the dissociative photoionization processes of the $C_4H_5OO_2$ and $C_4H_6OCLO_2$ peroxy radicals, theoretical calculations have also been performed. Fig. 4 presents the optimized structures of the $C_4H_5OO_2$ and $C_4H_6OCLO_2$ peroxy radicals and their cations in the ground electronic state. The ground electronic state of these cations is a triplet state after removing an electron from the $\sigma(C\alpha-OO)$ orbital of the $C_4H_5OO_2$ and $C_4H_6OCLO_2$ peroxy radicals. To be specific, the C–OO equilibrium bond length of the neutral $C_4H_6OCLO_2$ is calculated at 1.450 Å, whereas it is substantially elongated to 2.781 Å for the cationic ground electronic state of $C_4H_6OCLO_2^+$. Similarly, the C–OO bond length of $C_4H_5OO_2^+$ at the ground electronic state is also elongated from 1.426 to 3.263 Å during photoionization.^{27, 33}

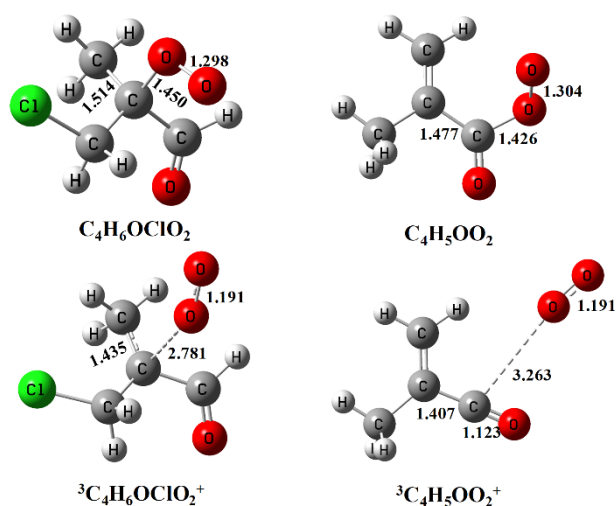


Fig. 4. The structures of the $C_4H_6OCIO_2$ and $C_4H_5OO_2$ peroxy radicals and their cations optimized at the PBE0/aug-cc-pVDZ level of theory. The bond lengths are in Å.

These apparent elongations of the C-OO bond length will reduce the stability of the peroxy radicals' cations, also making $C_4H_5OO_2^+$ and $C_4H_6OCIO_2^+$ only slightly bound and out of the Franck-Condon transition during photoionization.^{27, 33} In addition, the AIEs of the $C_4H_5OO_2$ and $C_4H_6OCIO_2$ peroxy radicals are also calculated and take the values of 7.93 and 9.23 eV, respectively, far below the present photon energy of 10.6 eV. Therefore, in the photoionization the $C_4H_5OO_2^+$ and $C_4H_6OCIO_2^+$ cations will be produced with a high internal energy and dissociate to the $C_4H_5O^+ + O_2$ and $C_4H_6OCl^+ + O_2$ fragments, respectively. The adiabatic appearance energies (AEs) of the fragments ions $C_4H_5O^+$ ($m/z=69$) and $C_4H_6OCl^+$ ($m/z=105/107$) in the dissociation of $C_4H_5OO_2^+$ and $C_4H_6OCIO_2^+$ are also calculated and locate at 8.00 and 9.08 eV, respectively. Thus, the mass peak at $m/z = 69$ ($C_4H_5O^+$) in Fig 1(b) is attributed to $C_4H_5OO_2$, and the mass peaks at $m/z = 105/107$ ($C_4H_6OCl^+$) is ascribed to the $C_4H_6OCIO_2$ peroxy radical.

3.3 The reactions of $C_4H_5OO_2$ and $C_4H_6OCIO_2$ under NOx free conditions

Under NOx free conditions in the fast flow tube, the $C_4H_5OO_2$ and $C_4H_6OCIO_2$ peroxy radicals can perform self-reaction or react with HO_2 radicals.¹¹ Normally, the self-reaction of peroxy radicals (RO_2) has two channels, (i) $2RO_2 \rightarrow 2RO + O_2$ and (ii)

$2\text{RO}_2 \rightarrow \text{R-HO} + \text{ROH} + \text{O}_2$.³⁷ But, based on the specific structures of $\text{C}_4\text{H}_5\text{OO}_2$ and $\text{C}_4\text{H}_6\text{OCIO}_2$, as shown in Fig. 4, there are no H atoms on the tertiary α -oxyl carbon to be abstracted and thus the self-reactions of $\text{C}_4\text{H}_5\text{OO}_2$ and $\text{C}_4\text{H}_6\text{OCIO}_2$ do not proceed via channel (ii).³⁸

Normally the reaction of the alkoxy radical RO with O_2 is one of the major sources to produce HO_2 radicals. But, the reaction of $\text{C}_4\text{H}_5\text{OO}$ with O_2 will not produce HO_2 , as still there is no H atoms on the tertiary α -oxyl carbon to be abstracted. A previous study shows that the reaction of $\text{C}_4\text{H}_6\text{OCIO}$ with O_2 can generate HO_2 , via more than one elementary reaction step,³⁹ and presently this reaction should be the main source of HO_2 in the fast flow tube. Note that the AIE of HO_2 locates at 11.359 eV, above the present photon energy, and thus presently no HO_2 radicals are observed in the mass spectra.⁴⁰

Previous study predicts that the reaction of the $\text{C}_4\text{H}_5\text{OO}_2$ peroxy radical with HO_2 has three channels, (R1a) $\text{C}_4\text{H}_5\text{OO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_5\text{OO}_2\text{H} + \text{O}_2$, (R1b) $\text{C}_4\text{H}_5\text{OO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_5\text{OOH} + \text{O}_3$, and (R1c) $\text{C}_4\text{H}_5\text{OO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_5\text{OO} + \text{OH} + \text{O}_2$.³⁹ The reaction of $\text{C}_4\text{H}_6\text{OCIO}_2$ with HO_2 has two channels, (R2a) $\text{C}_4\text{H}_6\text{OCIO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_6\text{OCIOOH} + \text{O}_2$, (R2b) $\text{C}_4\text{H}_6\text{OCIO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_6\text{OCIO} + \text{OH} + \text{O}_2$, and the branching ratio was predicted at $Y_{\text{R2a}} = 0.2 \pm 0.2$ and $Y_{\text{R2b}} = 0.8 \pm 0.2$.³⁹

The alkoxy radical $\text{C}_4\text{H}_6\text{OCIO}$ formed from the self-reaction of $\text{C}_4\text{H}_6\text{OCIO}_2$ or its bimolecular reaction with HO_2 can decompose to the stable product of chloroacetone ($\text{C}_3\text{H}_5\text{O}^{35}\text{Cl}$ and $\text{C}_3\text{H}_5\text{O}^{37}\text{Cl}$) with a fast rate of $\sim 10^7 \text{ s}^{-1}$ and has been completely consumed in the fast flow tube within the reaction time of $\sim 1 \text{ ms}$ under the present experimental conditions.³⁹ Therefore, the signal of $\text{C}_4\text{H}_6\text{OCIO}$ ($m/z = 121$) is not observed in the photoionization mass spectrum of Fig. 1(b), and its decomposition product of chloroacetone ($\text{C}_3\text{H}_5\text{OCl}$) contributes to the mass peaks of $m/z = 92$ and 94 with a ratio of 3:1.

The reaction of $\text{C}_4\text{H}_6\text{OCIO}_2$ with HO_2 can produce the hydroperoxide $\text{C}_4\text{H}_6\text{OCIOOH}$ ($m/z = 138$). The AIE of $\text{C}_4\text{H}_6\text{OCIOOH}$ is calculated at 9.30 eV at the

PBE0/aug-cc-pVDZ level of theory, and the appearance energy of its fragment ion $C_3H_5ClO_2H^+$ is predicted at 9.97 eV. Thus in the photoionization the hydroperoxide cation $C_4H_6OCIOOH^+$ is produced with a high internal energy and dissociates into the fragment ion of $C_3H_5ClOOH^+$, plus the neutral fragment of CHO, contributing to the peaks of $m/z = 109$ and 111 in the photoionization mass spectrum of Fig. 1(b).

The peroxy radical of $C_4H_5OO_2$ performs self-reaction and reacts with HO_2 to generate the radical C_4H_5OO , contributing to the mass peak of $m/z = 85$ in Fig. 1(b). The reaction of $C_4H_5OO_2$ with HO_2 can also produce C_4H_5OOH ($m/z = 86$) and $C_4H_5OO_2H$ ($m/z = 102$). The AIEs of C_4H_5OOH and $C_4H_5OO_2H$ are calculated at 9.58 and 9.44 eV, respectively, at the PBE0/aug-cc-pVDZ level of theory. In the photoionization, the cations of $C_4H_5OOH^+$ and $C_4H_5OO_2H^+$ are produced with a high internal energy and might dissociate into the $C_4H_5O^+$ ($m/z = 69$), OH and HO_2 fragments.

3.4 Reaction mechanism

Kinetic experiments have also been performed for the Cl-initiated oxidation reaction of MACR by changing the distance between the injector and the sampling skimmer, to get information the reaction mechanism inside the fast flow tube and to confirm the above species' assignments.^{28,29} The time evolution of ion signals has been measured and some of them, i.e. $m/z = 84$, 85 and 92 corresponding to $C_4H_4O_2$, C_4H_5OO and C_3H_5OCl , are presented in Fig. 5. In addition, theoretical results have also been calculated based on the oxidation reactions listed in Table 1 and can be compared well with the experimental results in Fig. 5.^{41,42}

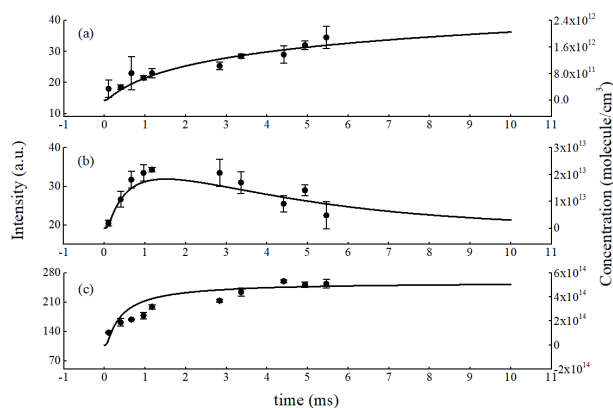


Fig. 5. The experimental (dots) and theoretical (lines) time behavior of products in the Cl-initiated oxidation of MACR. (a) $m/z = 84$, (b) $m/z = 85$ and (c) $m/z = 92$.

We can see that the ion signal of $m/z = 84$ increases with time within the experimentally covered time region, which is consistent with the theoretically modeled time behavior of $C_4H_4O_2$ in Fig. 5(a). The signal intensity at $m/z=85$ firstly increases and then decreases with time, which is a typical radical behavior of C_4H_5OO , as shown in Fig. 5(b). The signal of $m/z = 92$ firstly increases and then stabilizes, which is in agreement with the expected time behavior of chloroacetone. The detailed reaction mechanism of the Cl-initiated oxidation of MACR under NO_x free conditions has been summarized in Fig. 6. Note that Fig. 6 only presents the two dominant entrance channels for the reaction of MACR with Cl atoms, the terminal addition of the C=C double bond and the aldehyde-H abstraction with their branching ratios of about 86% and 12%, respectively.³⁹ The branching ratio of the minor methyl-H abstraction channel is predicted at 2%, not shown in Fig. 6, and this isomeric production channel is difficult to be separated only with the fixed-photon-energy photoionization mass spectrometry.

Table 1. Reaction mechanism used to model experiments in this work.

	Reaction	Rate coefficient / $cm^3 molecule^{-1} s^{-1}$ or s^{-1}	Reference
1	$C_4H_6O + Cl \rightarrow C_4H_6OCl$	1.98×10^{-10}	23
2	$C_4H_6O + Cl \rightarrow C_4H_5O + HCl$	2.76×10^{-11}	23
3	$C_4H_6OCl + O_2 \rightarrow C_4H_6OClO_2$	2.87×10^{-12}	43
4	$C_4H_5O + O_2 \rightarrow C_4H_5OO_2$	2.0×10^{-12}	44
5	$C_4H_5OO_2 \rightarrow C_4H_4O_2 + OH$	12.9	45

6	$2\text{C}_4\text{H}_6\text{OCIO}_2 \rightarrow 2\text{C}_4\text{H}_6\text{OCIO} + \text{O}_2$	2.4×10^{-12}	39
7	$2\text{C}_4\text{H}_5\text{OO}_2 \rightarrow 2\text{C}_4\text{H}_5\text{OO} + \text{O}_2$	1.0×10^{-11}	39
8(a)	$\text{C}_4\text{H}_6\text{OCIO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_6\text{OCIO}_2\text{H} + \text{O}_2$	2.0×10^{-12}	39
8(b)	$\text{C}_4\text{H}_6\text{OCIO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_6\text{OCIO} + \text{OH} + \text{O}_2$	8.0×10^{-12}	39
9(a)	$\text{C}_4\text{H}_5\text{OO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_5\text{OO}_2\text{H} + \text{O}_2$	7.7×10^{-12}	39
9(b)	$\text{C}_4\text{H}_5\text{OO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_5\text{OOH} + \text{O}_3$	5.5×10^{-12}	39
9(c)	$\text{C}_4\text{H}_5\text{OO}_2 + \text{HO}_2 \rightarrow \text{C}_4\text{H}_5\text{OO} + \text{OH} + \text{O}_2$	8.8×10^{-12}	39
10	$\text{C}_4\text{H}_6\text{OCIO} (+\text{O}_2) \rightarrow \text{C}_3\text{H}_5\text{OCl} + \text{HO}_2 + \text{CO}$	1×10^7 ^a	39
11	$\text{C}_4\text{H}_5\text{OO} \rightarrow \text{C}_3\text{H}_5 + \text{CO}_2$	7×10^2	46
12	$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.7×10^{-12}	47
13	$\text{HO}_2 \rightarrow \text{diffusion}$	3	41

^aThe reaction consists of more than one elementary reaction step, seen the detail in Ref. 39.

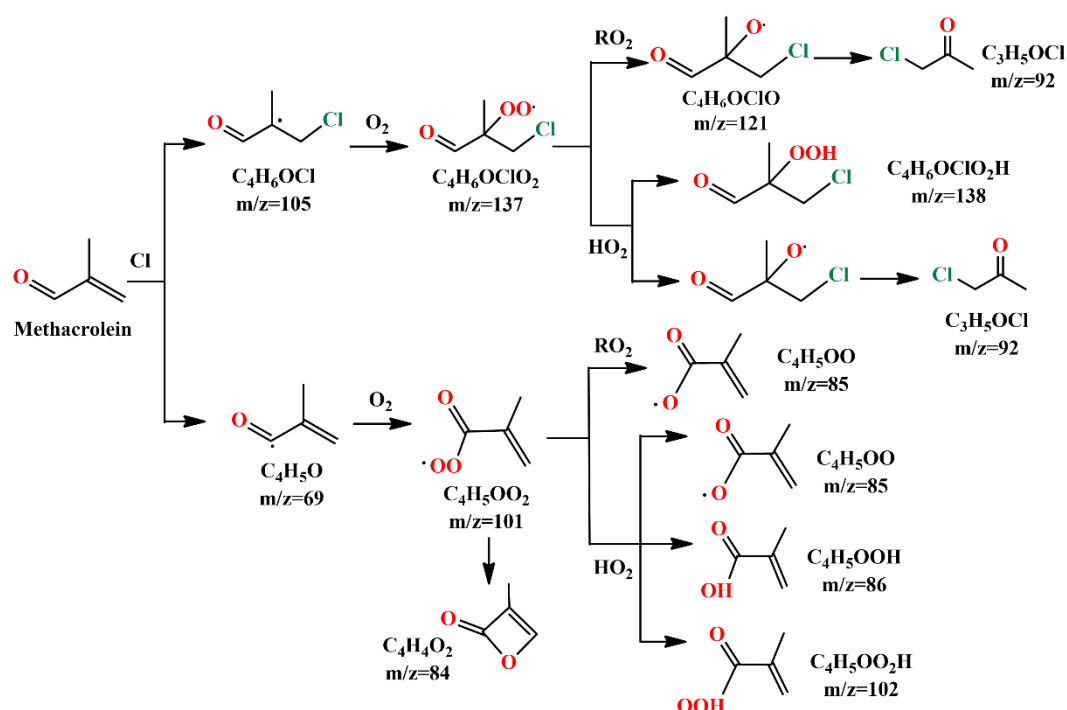


Fig. 6. Reaction mechanisms of Cl-initiated oxidation of MACR under NO_x free conditions.

4. Conclusions

In summary, we present here a combined experimental and theoretical study on the Cl-initiated oxidation of MACR under NO_x-free conditions. A microwave discharge fast flow tube was used to investigate the oxidation reaction of MACR. The reaction products and the key intermediates as well as radicals have been observed online by using a home-made VUV photoionization mass spectrometer. It is shown that the reaction of MACR with Cl atoms can proceed via two pathways, the addition of Cl

atom to the C=C double bond of MACR to produce the C₄H₆OCl adduct radical and the abstraction of the aldehyde hydrogen atom to produce the C₄H₅O radical. These radicals can react with oxygen to produce their corresponding peroxy radicals, whose photoionization processes have also been discussed and utilized to assign the photoionization mass spectra. Under NO_x-free conditions, these peroxy radicals will perform self-reaction and react with HO₂ radical. In particular, the transient C₄H₅O and C₄H₆OCl radicals, as well as the peroxy radicals C₄H₅OO₂ and C₄H₆OClO₂, are experimentally detected here for the first time, directly confirming the above reaction mechanisms. The resulting specific products are clearly identified in the photoionization mass spectra too, with the aid of theoretical calculations. In addition, the time evolutions of products have been measured in the kinetic experiments and compared well with theoretically modeled results. The present work provides a detailed insight into the reaction mechanisms of the Cl-initiated oxidation of MACR and will be very helpful to understand the atmospheric fate of MACR.

CRediT author contributions

Xiaoxiao Lin: Conceptualization, Formal analysis, Investigation, Writing – original draft. Rongrong Hu: Investigation, Writing – original draft. Ziji Ma: Investigation. Hao Yue: Investigation. Zuoying Wen: Investigation. Cuihong Zhang: Investigation. Christa Fittschen: Writing – review & editing. Weijun Zhang: Investigation. Xiaofeng Tang: Conceptualization, Methodology, Investigation, Funding acquisition, Project administration, Writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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