



Investigation into reactions of methyl methacrylate and ethyl acrylate with chlorine atom



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HIGHLIGHTS

- Direct adducts from acrylate esters and chlorine atom are detected.
- Mass spectra show fragments from direct adducts.
- Addition and abstraction coexist in the potential energy surfaces.
- Difference of ionized and neutral state indicates difficulty of adiabatic ionization.

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ABSTRACT

Reactions between chlorine and unsaturated esters in gas phase are examined in a slow-flow reaction tube inside the laboratory-built photoionization mass spectrometer at the energy range of 8–11 eV. 248 nm laser radiation is used to initiate the reaction. Products are distinguished, $C_5H_8O_2Cl$ for addition, and $C_5H_7O_2$, $C_5H_7O_2Cl$ and $C_5H_9O_2Cl$ for abstraction. The direct or indirect products are detected, indicating secondary reactions. And experimental ionization potentials are procured for direct adducts of methyl methacrylate to be 8.30 eV and for that of ethyl acrylate to be 9.95 eV which are well consistent with theoretical ionization potentials of likely isomers. Theoretical reaction channels are also accounted for, optimized under M06-2X/6-31 + G(d,p) level and ionization potentials of products are calculated under M06-2X/6-31 + G(d,p) level also. Differences between experimental and theoretical details are discussed.

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1. Introduction

Methyl methacrylate (MMA) and ethyl acrylate (EA) are α,β -unsaturated esters commonly used in polymer industry. Such oxygenated volatile organic compounds (OVOCs) are atmospherically important due to their extensive emission into atmosphere, which could result from massive use of these esters in polymer industry, paint industry, and other fields. Not only from anthropogenic sources, methacrylates and acrylates could also stem from biogenic sources (Silva and Neves, 1999). Emission from those sources could play an important role in atmosphere, especially when it comes to reaction with chlorine atom.

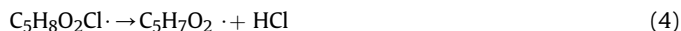
The role of chlorine atom in atmospheric environment has been more and more perceived because its abundance in coastal marine boundary where the concentration of chlorine atom is reported to be 3×10^5 molecule cm^{-3} (Chang et al., 2004). Degradation of organic halogenated compounds and oxidation of sea salt should be the most important sources of halogen in troposphere (Platt and Hönniger, 2003). Such abundance is comparable to hydroxyl, one of the most common radicals in the atmosphere. And reactivity of unsaturated esters with chlorine atom is stronger than that with hydroxyl (Blanco et al., 2009). Its reactions with alkanes, alkenes and more complicated compounds have been widely explored and examined (Pandit et al., 2017; Pilgrim and Taatjes, 1997; Preston et al., 2014; Hornung et al., 2015; Vijayakumar and Rajakumar, 2017; Chu et al., 2015; Ausmeel et al., 2017; Ballesteros et al., 2017). Addition of Cl to olefinic bond is well recognized as the major channel of reactions if such double bond exists in reactants.

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Fast reaction of Cl with unsaturated hydrocarbon is indubitably significant in understanding the atmospheric chemistry involving chlorine.

Reactions of such unsaturated esters have been researched in detail of rate coefficients (Blanco et al., 2009; Teruel et al., 2009) and theoretically (Biswas, 2015; Zhang et al., 2017), but direct detection of the products from those reactions haven't surfaced yet. Mechanism of reactions between chlorine atom and organic compounds is well established. Addition of chlorine could not only compete with the abstraction channel and in fact it was considered that the addition pathway be the dominant channel for chlorine and alkenes according to previous works (Pilgrim and Taatjes, 1997; Vijayakumar and Rajakumar 2017; Ballesteros et al., 2017). Among the competition, there exists a channel between two pathways where added chlorine could attract adjoining hydrogen after addition and form hydrogen chloride (Pilgrim and Taatjes, 1997; Preston et al., 2014; Hornung et al., 2015).



Therefore addition pathway could end in resultant adduct or lead to another abstraction of hydrogen, namely the indirect abstraction. When propene is in question, evidence indicates that the two kinds of abstractions, both direct and indirect, could coexist (Pilgrim and Taatjes, 1997). Also, another mechanism has been reported (Chu et al., 2015) that adduct of chlorine and butene could lose one hydrogen without forming hydrogen chloride. Yet this pathway is too high in energy to cross. As for carbonyl the likelihood of chlorine reaction is very slim since the reaction of acetone or formaldehyde with chlorine atom is mainly through hydrogen abstraction (Atkinson et al., 2006). And for similar structure like lactones, HCl and CO₂ were identified as main products from reactions with chlorine atom, ascertaining the possibility of abstraction route (Ausmeel et al., 2017). Since MMA and EA, as unsaturated esters, have olefinic bond and acyloxy group, same fate may fall on them when they react with chlorine atom. Cl-addition and H-abstraction could both happen to MMA and EA. In this work, photoionization mass spectrometry has been used to identify products, and theoretical inquiry is performed to verify the plausibility of experiment. We hope that it will illuminate some shadow on the impact that polymer industry have had on environment.

2. Experimental conditions and theoretical calculations

Experiments were performed with Photoionization Mass Spectrometry (PIMS) at the Atomic and Molecular Physics Beamline, National Synchrotron Radiation Laboratory (NSRL), Hefei, China. Reactions were designed to take place in a slow-flow reaction quartz tube inside the laboratory-built photoionization mass spectrometer (Chen et al., 2016; Li et al., 2018; Wang et al., 2017; Zhao et al., 2017). The 248 nm laser radiation was used to initiate the reaction. The reaction mixture leaked through the pinhole in the middle of the quartz tube. After that it was ionized by tunable synchrotron radiation VUV photons. Cations of the species, both reactants and products, were accelerated by a pulsed electric field first and then sampled by the time-of-flight mass spectrometer. The structure is illustrated in detail elsewhere (Fockenberg et al., 1999; Osborn et al., 2008).

The Cl atom was generated by the reaction (Baklanov and

Krasnoperov, 2001) initiated by an unfocused, 20 ns pulse of 248 nm laser radiation, which was emitted from an ArF excimer laser (EX100H, Gammlaser, USA). The excimer worked in repetition with frequency of 4 Hz and energy fluence of one pulse was typically 25 mJcm⁻². The quartz tube is 1 m in length and 10 mm in inner diameter with a 0.6-mm pinhole at the center of flow tube. The calibrated mass flow controllers (1179 and 1479, MKS, USA) were used to maintain steady flow of radical precursor (oxalyl chloride, C₂Cl₂O₂, ~ 1 × 10¹⁵ moleculecm⁻³), reactants (ethyl acrylate, ~ 3 × 10¹⁴ moleculecm⁻³, and methyl methacrylate, ~ 3 × 10¹⁴ moleculecm⁻³, respectively), and He buffer gas. And roots vacuum pump were on the other end to withdraw most of gas with a feedback-regulated throttle valve before it, maintaining the gas pressure at 5 Torr. Flow rates were typically set to 4 ms⁻¹ and would suffice to deplete and replenish the gas in time for the next photolysis that laser pulse initiated. When reactants and products entered the differentially pumped ionization region, they were ionized by the tunable VUV synchrotron radiation, with its energy spanning from 8 to 11 eV. The VUV photon beam was interfered and amplified with an undulator and monochromatized by spherical gratings (made by Horiba Jobin Yvon in France). A pulse generator (DG535, SRS, USA) was used to control time sequence of the detection, simultaneously triggering the pulsed field that pushes cations and sending signal to the multiscaler (FAST Comtec P7888, Germany) for reference of T₀. The cations were detected by two zigzag stacking microchannel plates and the signals are amplified by a preamplifier (VT120C, ORTEC, USA) and then received by the multiscaler to record the time of flight since T₀.

Reaction channels and ionization potentials were calculated by Gaussian 09 suite (Frisch et al., 2016). All stationary states, namely first-order saddle points and stable states, were optimized under M06-2X/6-31 + G(d,p) level. Wave function methodology of higher accuracy, such as coupled cluster theory CCSD(T), would have been in the intention to inquire theoretical details. But for the system in question, which has 16 atoms including chlorine, it is too expensive to implement. For balance of accuracy and efficiency, density functional theory is the better option. Adiabatic ionization potentials (AIP) of relevant species are optimized under M06-2X/6-31 + G(d,p) level as well.

$$\text{AIP} = E_{\text{opt}}(\text{cation}) - E_{\text{opt}}(\text{neutral molecule}) \quad (5)$$

Vertical ionization potentials (VIP) are given by Outer Valence Green's Function (OVGF) from the energy of HOMO orbital.

3. Results and discussions

The mass spectrum of reacting system, methyl methacrylate with chlorine and ethyl acrylate with chlorine respectively, is acquired at the energy of 11 eV and subtracted non-photolytic counterpart from it to emphasize the effect of laser. The mass spectrum of products is shown in Fig. 1a and Fig. 1b, with the non-photolytic counterpart subtracted. At the photon energy of 11 eV, the products can be seen from the peaks of 135, 136, 137, and 138, which are assigned to C₅H₈O₂Cl, C₅H₉O₂Cl and their isotopologues. Among them, 135 and 137 are assumed to be direct adducts of esters in question and chlorine atom. And 136, 138 are designated to be secondary products of H-abstraction. In Fig. 1b the m/z = 136 is almost as high as 135, while as for MMA, m/z = 136 is much higher than 135. The intensity of those peaks is also nicely matched: The peak 137,138 is three times of peak 135,136 respectively, confirming existence of chlorine, as can be seen in Fig. 1. Kinetic isotope effect does not seem to come in the way. Moreover, peaks m/z = 76 and 78 could be observed in the mass spectrum and are nicely proportioned to 3:1, which should be fragments from fission of carbon-

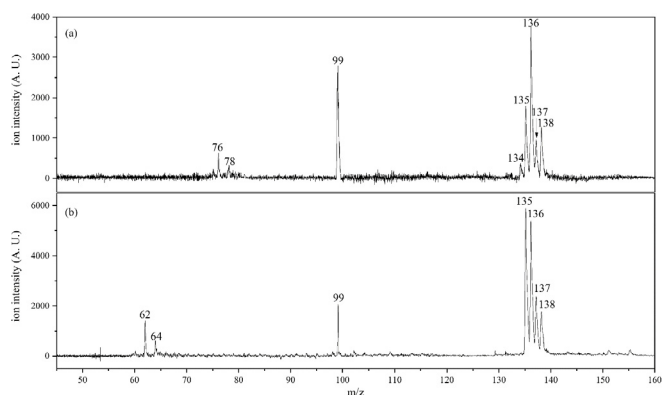


Fig. 1. Mass spectra of products and reactants. Mass spectrum is acquired under 11 eV with non-photolytic part subtracted, sampling time 100 s. (a) Mass spectrum of MMA-Cl system. (b) Mass spectrum of EA-Cl system.

carbon bond between olefinic bond and carbonyl bond. It could also be discovered similarly for ethyl acrylate, that $m/z = 62$ and 64 are found, which both indicating that chlorine atom is attached onto olefinic bond instead of carbonyl.

Besides direct adducts, $m/z = 134$ is also present for case of MMA, implying existence of substitution reactions. Its isotopic counterpart is submerged in the $m/z = 136$ and is no longer discernible. However, difference shows up for EA that $m/z = 134$ is not shown in Fig. 1b. If assumption that chlorine exists in the 134 species is valid, there will be secondary reactions where chlorine is added after hydrogen is abstracted. And $m/z = 99$ is observed to corroborate it. Although it could be attributed as the H-abstraction channel of the process, it could also be a fragment species due to photoionization at 11 eV. To eliminate that possibility, we find out that at 9.80 eV, which is lower than appearance energy of $m/z = 99$ fragment from photoionization (Sun et al., 2017), the fragment is still present.

Photoionization efficiency (PIE) is a technique that determines the threshold of species being photoionized. It is depicted in an energy-resolved plot that presents integrated area of a specific peak or peaks, which requires the tunable characteristic of synchrotron to allow us to acquire mass spectra at different energies. With it, ionization potentials or appearance potentials could be pinpointed and then interpreted to structural information we need (Figs. 2 and 3). It has been precisely pointed out (Berkowitz et al., 1994) that PIMS could only gather information about the process of lowest energy, while the ones of higher energy would be submerged.

In this work, ionization energy of MMA is determined to be 9.70 eV and that of EA 9.95 eV, which are consistent with ionization energies determined in other works (Song et al., 2015; Sun et al., 2017). The theoretical and experimental ionization energies of products are shown in Table 1 and the theoretical calculation is

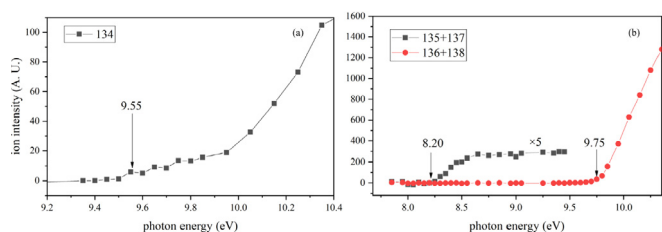


Fig. 2. Photoionization efficiency (PIE) plot of products from MMA-Cl system in question. (a) PIE plot of $m/z = 134$; (b) PIE plot of $m/z = 135, 137$, and $136, 138$. One third of intensity of $m/z = 134$ has been subtracted from $m/z = 136$.

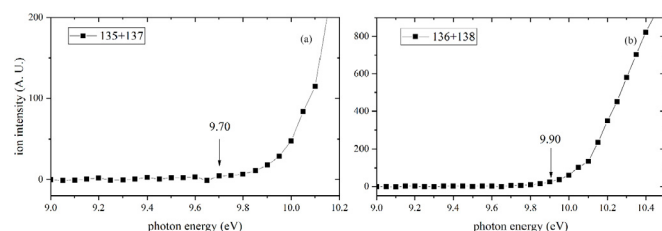


Fig. 3. PIE plot of m/z 135, 137, and 136, 138 from EA-Cl system. (a) PIE plot of $m/z = 135$ and 137; (b) PIE plot of $m/z = 136$ and 138.

performed at the level of M06-2X/6-31 + G(d,p), and all energies are zero-point corrected. VIPs are given by (OVGF) method.

The theoretical values of AIPs fit well with experimental result in the case of MMA. Ionization onsets of peak $m/z = 134$ and $136/138$ are consistent with calculated AIPs of $\text{H}_2\text{C}=\text{CH}(\text{CH}_2\text{Cl})\text{C}(\text{O})\text{OCH}_3$ and $\text{H}_3\text{C}-\text{CCl}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$, 9.72 and 9.98 eV respectively. The possible isomer of MMA-Cl adduct is determined to be $\text{H}_2\text{CCl}-\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$, whose AIP is calculated to be 8.07 eV. The turn points in the PIE plot of products from EA-Cl system are very close for $m/z = 135, 136, 137, 138$, and seem to indicate that products of both channels disappear at the similar energies. Onset energy of peak $m/z = 136/138$ matches nicely calculated AIPs of $\text{H}_3\text{C}-\text{CHClC}(\text{O})\text{OCH}_2\text{CH}_3$ and $\text{H}_2\text{CCl}-\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3$. But the AIPs of $\text{H}_3\text{C}-\text{CHClC}(\text{O})\text{OCH}_2\text{CH}_3$ and $\text{H}_2\text{CCl}-\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ are too close to distinguish the likelihood of isomers at present energy resolution of 0.05 eV. The theoretical values of AIPs, which are 7.95 eV and 8.29 eV for $\text{H}_2\text{C}=\text{CHClC}(\text{O})\text{OCH}_2\text{CH}_3$ and $\text{H}_2\text{CCl}-\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$ respectively, are not consistent with experiment very well. However, even when VIPs are under consideration, the discrepancy still exists. Another possible source of error comes from inherent underestimation of theoretical method. Conjugated radicals have been reported (Jursic, 1996) to be a very hard problem for computational chemistry. *Ab initio* methods and DFT methods tend to underestimate the ionization potential of such radicals to a degree of 1 eV (Jursic, 1996; Knoll, and Friesner, 2006). And there is a dispute (Sablier and Fujii, 2002) over whether internal thermal energy takes part in the ionization process and whether such correction should be made. Since the error for calculated ionization potentials is still quite large, it is difficult to differentiate the reason behind such discrepancy.

Pathways of MMA and chlorine atom reactions are catalogued in Fig. 5. Transition states and products are optimized under M06-2X/6-31 + G(d,p) level. There are two sites for chlorine to attack the olefinic bond which produce the P1 and P2 without going through a barrier. And the energies of resultant products are 0.66 and 1.11 eV (15 kcal mol^{-1} and 26 kcal mol^{-1}) lower than reactants respectively. It was (Biswas, 2015) indicated transition states for both addition channels, but in our efforts to find them, no transition states of the addition channel could be located. To make sure the inexistence of transition states, a scanning was made from P2 to a system where chlorine is far away from MMA. As the Cl–C distance grows, the energy rises to an asymptote, which suggests TS does not exist. There is, however, a transition state between two possible adducts of chlorine and MMA that is not depicted in Fig. 5, where chlorine could jump from one carbon to the other. It was mistaken as a TS for chlorine addition channel at first, but IRC exploration has proved it is a TS for the chlorine exchange of the two olefinic carbons. As for the abstraction pathways, there are four types of hydrogen that could be abstracted, therefore four sites for chlorine to attack. P5 has the lowest energy among them. When the hydrogen of the methyl group on the methacrylate is abstracted, the left carbon has an extra unpaired electron, which will participate in the

Table 1
Ionization energies of related products. Adiabatic ionization potentials are determined under M06-2X/6-31 + G(d,p) level, vertical ionization potentials with OVGF method, pole strengths (PS) given subsequently.

Species	m/z	Exp. (eV)	Isomer	AIP (eV)	VIP (eV)	PS
MMA						
C5H7O2Cl	134	9.55	H ₂ C—CH(CH ₂ Cl)C(O)OCH ₃	9.72	10.16	0.907
			cis—ClHC—CH(CH ₃)C(O)OCH ₃	9.29	9.37	0.908
			trans—ClHC—CH(CH ₃)C(O)OCH ₃	9.41	9.42	0.908
			H ₂ C—CH(CH ₃)C(O)OCH ₂ Cl	9.85	10.06	0.909
C5H8O2Cl	135&137	8.20	H ₂ C—CCl(CH ₃)C(O)OCH ₃	7.62	8.98	0.914
			H ₂ CCl—C(CH ₃)C(O)OCH ₃	8.07	8.67	0.908
C5H9O2Cl	136&138	9.75	H ₃ C—CCl(CH ₃)C(O)OCH ₃	9.98	10.45	0.909
			H ₂ CCl—CH(CH ₃)C(O)OCH ₃	10.16	10.71	0.912
EA						
C5H8O2Cl	135&137	9.70	H ₂ C—CHClC(O)OCH ₂ CH ₃	7.95	9.16	0.916
			H ₂ CCl—CHC(O)OCH ₂ CH ₃	8.29	9.36	0.908
C5H9O2Cl	136&138	9.90	H ₃ C—CHClC(O)OCH ₂ CH ₃	10.01	10.52	0.910
			H ₂ CCl—CH ₂ C(O)OCH ₂ CH ₃	10.05	10.83	0.916

conjugation of the methacrylate group, stabilizing the whole radical. Therefore P5 is the most probable product among the abstracted radicals. And P6 is less stable because oxygen that is connecting methyl and methacrylate in the acyloxy handicaps the conjugation. They share a same intermediate (IM5) prior to the transition structures. And P3, P4 are even more labile when the carbon at the end of olefinic bond is left bare, with its hydrogen stolen. The whole processes of P3, P4 are endoergic (13 kcalmol⁻¹ and 12 kcalmol⁻¹), thus it is unlikely to happen spontaneously. But for P5, the exoergic (−11 kcalmol⁻¹) of the process is comparable with that of the addition channel. Furthermore, TS3 has a unique characteristic as an abstraction transition state, where its C—H bond is 1.13 Å and H—Cl distance is 1.92 Å. For other abstraction transition states, the C—H bond is about 1.4 Å and H—Cl distance is about 1.5 Å. All these distances indicate TS3 is at a very early stage and that it would be easier for chlorine to approach the hydrogen of methyl group of MMA (Fig. 4). It should be the most favoured pathway, as indicated by previous works (Wang and Zhang, 2015; Yang et al., 2013) as well. The P6 channel, on the other hand, is less significant in exoergic, even though barrier heights of their transition states are very close (see Fig. 6).

P5 channel is considered as thermodynamically more favoured pathway. And the experimental details support the presumption in that m/z = 136,138 peaks are significantly higher in Fig. 1a. Therefore, it is more probable for the system to go through TS3 or directly towards chlorine adducts.

Pathways for the cases of MMA and EA unveil close similarity but distinctions still can be found. Discrepancy of Fig. 7 and Fig. 5 is discernible not only by scrupling over numbers. There are five types

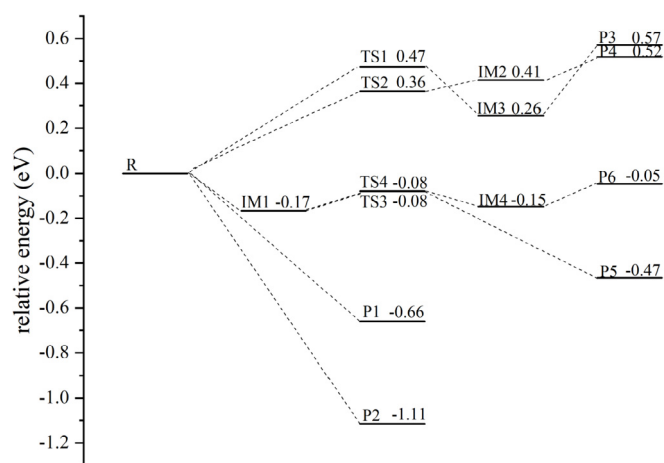


Fig. 5. The pathways of MMA-chlorine system, optimized under M06-2X/6-31 + G(d,p) level.

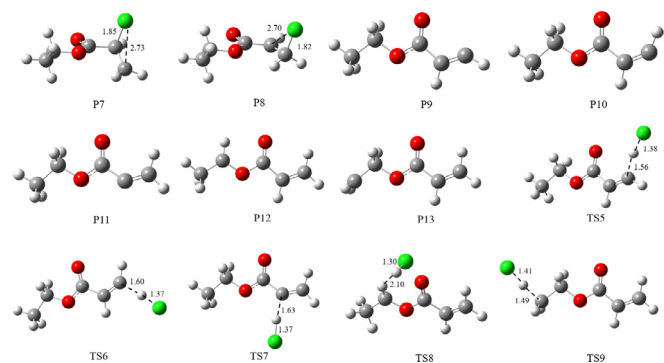


Fig. 6. Geometries of related species in EA-chlorine system, optimized under M06-2X/6-31 + G(d,p) level.

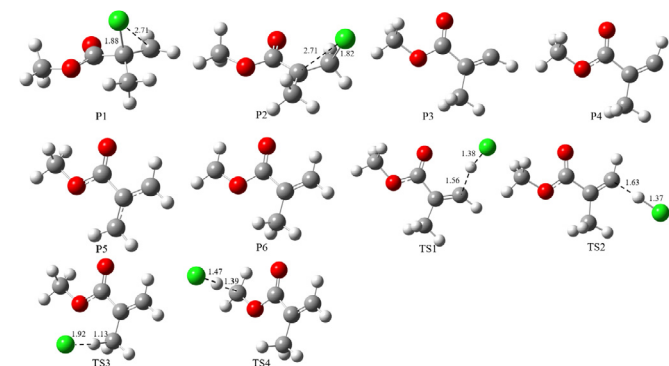


Fig. 4. Geometries of related species in MMA-chlorine system, optimized under M06-2X/6-31 + G(d,p) level. Length unit in this figure is angstrom.

of hydrogen instead of four in EA, therefore five pathways could be constructed, most of which are endoergic. P3, P4, and P5 are at least 11 kcalmol⁻¹ more unstable than reactants. And P7 requires energy of about 2.3 kcalmol⁻¹ to be produced (Fig. 6). Only channel 6 is exoergic, giving some probability of abstraction. All above surely cannot compete with addition channels, which release 15 and 23 kcalmol⁻¹ to generate P1 and P2 respectively. But thermodynamical plausibility cannot cover the potential obstacles in dynamics. The existence of methyl group could make the chemistry of those

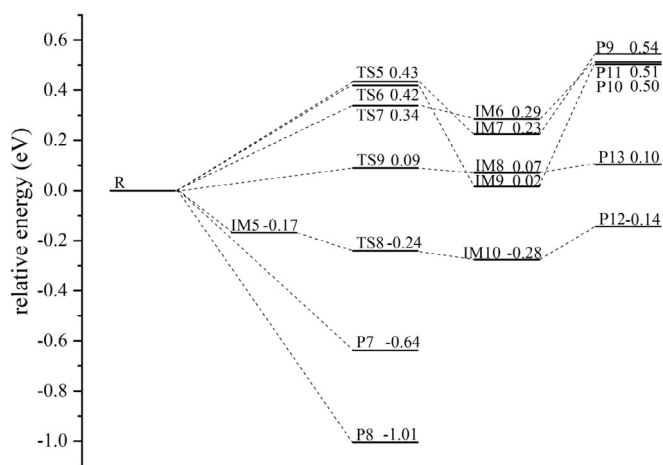


Fig. 7. Pathways of EA reacting with chlorine atom, optimized under M06-2X/6-31 + G(d,p) level.

two with chlorine change.

The potential energy surface (PES) surely has given important information about interaction between those esters and chlorine atom. For addition channel, it can be seen that the reaction goes through no barrier. It is reported, however, that barriers exist before chlorine is added to the double bond for reactions of MMA and chlorine (Biswas, 2015). But the TS that leads to addition is never found on M06-2X/6-31 + G(d,p) level and the scan where chlorine is getting away from carbon, also fails to locate a summit, only to find an asymptote. Addition of chlorine to EA shows no sign of barriers as well, whether in literature (Zhang et al., 2017) or in this work. It is also suggested (Biswas, 2015) that chlorine could attack carbonyl bond, but the products, CH_3CCH_3 ($m/z = 41$) and $\text{CH}_3\text{OC(O)Cl}$ ($m/z = 94$ or 96), are not found. Barriers do exist, on the other hand, in the process of abstraction. Direct abstractions of hydrogen are located theoretically (Biswas, 2015; Zhang et al., 2017), and the product $m/z = 99$ is also observed experimentally. As for indirect abstraction, the adducts of esters and chlorine could again eliminate a hydrogen chloride to form the abstracted products. But its transition states cannot be discovered in this work and also not reported in literature (Biswas, 2015; Zhang et al., 2017). Besides H-abstraction, the methyl group of MMA could also be abstracted by chlorine (Biswas, 2015). Unfortunately, products are not found in mass spectra. It is indicated (Zhang et al., 2017) that further reactions could take place after the addition or abstraction. A second chlorine might join with products to form dichloro esters. It was not shown in the spectrum, however, that $m/z = 170$ could be detected by our apparatus.

Since addition is considered as dominant channel for alkenes and chlorine, presumably when MMA react with chlorine it will be mostly Cl-addition. But there is a methyl group in MMA beside the olefinic bond, steric effect could intervene and obstacle Cl-addition. Furthermore, it was given rate coefficients as 2.82×10^{-10} and $2.53 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reactions of MMA and EA with chlorine respectively (Blanco et al., 2009; Teruel et al., 2009). And another set of rate coefficients for those of MMA and EA has been given as 2.30×10^{-10} and $1.82 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as well (Porrero et al., 2010).

Those experimental rate coefficients indicate that contribution of methyl group to the reactions is more help than hindrance. Rate coefficients for reactions with chlorine of methyl isobutyrate, the one with no olefinic bond but similar in structure as MMA, is found to be $3.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ifang et al., 2015). With rate coefficients said earlier, it could be assumed that addition channel

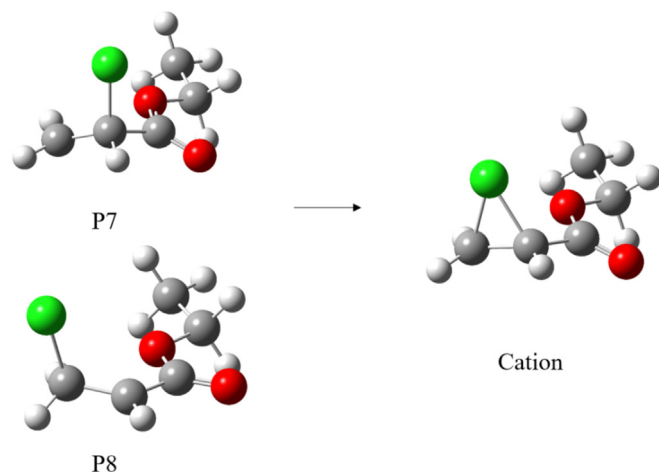


Fig. 8. Geometries of P1 and P2 in case of EA, and their ionized state.

consists of up to around 80% of the reactions. But note that existence of olefinic bond facilitates abstraction of allyl hydrogen, thus more probably the abstraction will take place and this should be the upper limit of percentage of addition channel. For ethyl propionate, the compound with similar structure as EA but without olefinic bond, the rate coefficient with chlorine was reported to be $3.11 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Andersen et al., 2012). Compared with that of EA, $2.53 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Teruel et al., 2009), it tells the percentage of Cl-addition should be about 80% (ignoring contribution of two more hydrogen of ethyl propionate to total rate coefficient), which is consistent with the claim (Vijayakumar and Rajakumar 2017) that addition channel should dominate the reactionary process of chlorine and alkenes. All above considerations are under the assumption that reaction behavior does not change from atmospheric pressure to relatively lower pressure under which this work was performed. A close value of rate coefficient on reaction between acrylic acid and chlorine atom at lower pressure (Aranda et al., 2003) implies such assumption is valid.

Because the geometries of neutral and ionized molecule are noticeably different, the ionization processes of products from addition are debatable. For EA, geometries of $\text{H}_2\text{C}=\text{CHClC(O)OCH}_2\text{CH}_3$ (P7) and $\text{H}_2\text{CCl}-\text{CHC(O)OCH}_2\text{CH}_3$ (P8) and their ionized counterparts are shown in Fig. 8. Even though their optimized geometries differ inherently, their ionized states share the same geometry however. The resultant chloronium cation is so different with P7 and P8 that it seems new bond has been established in Fig. 9a and b. It has been mentioned (Berkowitz et al., 1994) that if

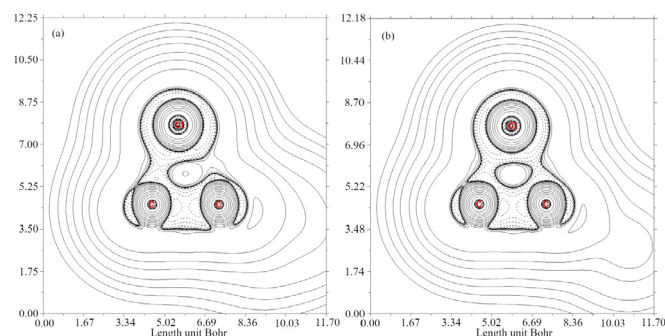


Fig. 9. Laplacian contour in the CCl plane of two chloronium cations. (a) MMA-Cl chloronium cation. (b) EA-Cl chloronium cation.

geometries of two states are too different, it would be difficult to measure adiabatic ionization energies. Such drastic change in geometry may forbid the channel of (0,0) transition, making the adiabatic ionization improbable.

4. Conclusion

At last, the approach of laser flash photolysis with TOF mass spectrometry is proved useful in study of the reactions of the chlorine atom with MMA and EA utilizing a tunable synchrotron VUV radiation at the energy range of 9–11 eV. At photon energy of 11 eV, signals of chlorine adducts, $C_5H_8O_2Cl$ have been detected directly and distinguished while abstraction channel is observed through secondary product detection including $C_5H_9O_2Cl$. Fragments of adducts are discovered as well, which corroborates that chlorine adds on olefinic bonds. $C_5H_7O_2Cl$ is only observed for MMA reacting system. Also ionization potentials of products have been determined to be 8.30 eV for MMA-Cl adduct and 9.70 eV for EA-Cl adduct, among which ionization energy of EA-Cl adduct is not consistent with its AIP but with VIP calculated with OVG method. Channels of reactions of MMA and EA with chlorine have been constructed and details of the interaction have been discussed under M06-2X/6-31 + G(d,p) indicating abstraction channel is easier for MMA with chlorine. It is consistent with experiment that for MMA H-abstraction channel is more prevalent than that for EA.

Conflict of interest

The authors declare no competing financial interest in this article.

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