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A VUV photoionization mass spectrometric study on the OH-initiated photooxidation of isoprene with synchrotron radiation

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Abstract

The gas-phase organic compounds resulting from OH-initiated photooxidation of isoprene have been investigated on-line by VUV photoionization mass spectrometry based on synchrotron radiation for the first time. The photoionization efficiency curves of the corresponding gaseous products as well as the chosen standards have been deduced by gating the interested peaks in the photoionization mass spectra while scanning the photon energy simultaneously, which permits the identification of the pivotal gaseous products of the photooxidation of isoprene, such as formaldehyde (10.84 eV), formic acid (11.38 eV), acetone (9.68 eV), glyoxal (9.84 eV), acetic acid (10.75 eV), methacrolein (9.91 eV), and methyl vinyl ketone (9.66 eV). Proposed reaction mechanisms leading to the formation of these key products were discussed, which were completely consistent with the previous works of different groups. The capability of synchrotron radiation photoionization mass spectrometry to directly identify the chemical composition of the gaseous products in a simulation chamber has been demonstrated, and its potential application in related studies of atmospheric oxidation of ambient volatile organic compounds is anticipated.

Key words: isoprene; photooxidation; smog chamber; VUV photoionization mass spectrometry; synchrotron radiation

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Introduction

Biogenic volatile organic compounds (BVOCs), such as isoprene and monoterpenes, are emitted into the atmosphere in substantial amounts, mainly from terrestrial vegetation. Total global biogenic organic emissions are estimated to range from 491 to 1150 Tg/year, which exceeds the estimated anthropogenic emissions by almost an order of magnitude (Guenther et al., 1995; Atkinson et al., 2000; Sharkey et al., 2008). As the largest global atmospheric emission of all non-methane VOCs (ca. 600 Tg/year) (Guenther et al., 2006), isoprene has been confirmed as one of the most important biogenic secondary organic aerosol (SOA) precursors (Claeys et al., 2004; Kroll et al., 2006; Paulot et al., 2009; Surratta et al., 2010). It is believed that the variation in chemical composition of SOA is the main factor that affects atmospheric chemistry (Pacifico et al., 2009; Carlton et al., 2009), the earth's climate (Atkinson, 2000; Wang et al., 2009), and human health (Russell et

al., 2009; Pope et al., 2009). Therefore, effective analytical methods for characterizing gas- or aerosol-phase oxidation products in real time are significant in understanding the reaction mechanism and the formation of SOA.

In the past several decades, many traditional analytical techniques have proven useful in studying the photooxidation reaction mechanism and the formation of SOA. For example, gas chromatography/mass spectrometry (GC/MS), Fourier Transform Infrared Spectroscopy (FT-IR) and gas chromatography/ion trap mass spectrometry (GC/ITMS) have been widely used in the study of the isoprene photooxidation reaction (Yu et al., 1995; Szmigielski et al., 2007; Healy et al., 2008; Nguyen et al., 2010; Liu et al., 2010). From the mid 1990s, real-time laser mass spectrometry has been remarkably developed and has offered new opportunities for studying the formation of gaseous constituents on-line (Heger et al., 1999; Wei et al., 2001). However, due to the high laser intensity required to desorb and ionize the gaseous products, the method often suffers from the massive fragmentation of molecular ionic species when organic products readily absorb multiple UV

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photons. Thus, for the characterization of chemical compositions of photooxidation products, new “soft” ionization methods are imperative to minimize fragmentation in the mass spectra (Gloaguen et al., 2006; Zahardis et al., 2011). From its beginning, synchrotron radiation (SR) has been known and characterized by its tunability over a wide range of energy (Elder et al., 1947). One benefit of the tunable VUV source of SR is that it allows the photon energy to be set very close to the ionization threshold of a molecule of interest, which will reduce the amount of fragmentation remarkably by imposing very little excess energy on the molecule during ionization. Another benefit of a tunable VUV source is the ability to obtain photoionization efficiency curves, which can be used to identify the compounds unambiguously by their ionization energies or appearance energies (Sarah et al., 2009). In 2005, a synchrotron radiation-based aerosol time-of-flight mass spectrometer was developed and used for real-time analysis of organic compounds in aerosol particles, and four high-molecular-weight, low-vapor-pressure organic compounds of importance in atmospheric aerosols were analyzed (Mysak et al., 2005). Recently, Fang et al. (2011) have also shown the advantages of the same technique by studying the organic compounds of several kinds of pure aerosol particles. As for studies on the chemical composition of complexes formed directly from the photooxidation of ambient VOCs, Huang et al. (2010) have investigated the photooxidation of the aromatic compound ethylbenzene in an environmental smog chamber off-line. It is well known that on-line analysis of the chemical composition of the reaction products is pivotal in order to learn the reaction mechanism of atmospheric VOCs and the formation of SOA. Motivated by that, we recently engaged in a project to explore the oxidation of VOCs using SR-based vacuum ultraviolet photoionization mass spectrometry combined with an environmental smog chamber system (Pan et al., 2012), which has proved that this technique can be used in the studies of particulate products. The aim of this work is to study the mechanism of the photooxidation of isoprene, instead of investigating the mechanism of SOA formation, so the gaseous reaction products are the subject we care about here.

In this work, the OH-initiated photooxidation of isoprene has been studied in detail based on the previous work. First, the photoionization mass spectra of gas-phase products from isoprene photooxidation were measured while the photon energy was fixed high enough to ionize almost all the products. Then, the PIE curves for the gas-phase products of interest can be obtained by scanning the photon energy. Obtaining the PIE curves permits us to identify the gas-phase products unambiguously by their ionization energy, enabling the deep understanding of the reaction mechanism for OH-initiated photooxidation of isoprene.

1 Experimental

Photooxidation of isoprene was initiated and performed using UV-irradiation of isoprene/CH₃ONO in a home-

made indoor smog chamber, which has been described previously (Hao et al., 2005; Pan et al., 2012). Prior to each run, the chamber was first evacuated to a vacuum of 10⁻¹ Pa by a mechanical pump and then continuously flushed with at least 4 chamber volumes of purified laboratory compressed air. The compressed air was processed through three consecutive packed-bed scrubbers containing, in order, activated charcoal, silica gel and a Balston DFU filter (Grade BX), to remove traces of hydrocarbon compounds, moisture and particles. Isoprene was sampled with a microliter injector and injected directly into the chamber. Methyl nitrate, which served as an OH precursor, was bled into the evacuated glass system to the desired pressure and then flushed into the smog chamber by a stream of purified air through a Teflon line. Before initiating the oxidation reaction, the whole system was completely shrouded from light with a black polyethylene tarpaulin. When the lights are turned on, hydroxyl radicals are generated by the photolysis of methyl nitrite in air at wavelengths longer than 300 nm (Atkinson et al., 1981), and then oxidation of isoprene is initiated. In this work, the initial concentration of isoprene and CH₃ONO was around 10 and 40 ppm, respectively. Since we were constrained by the mass spectrometry detection limit, the concentration of isoprene in the experiment was a little higher than the concentration of isoprene in the atmosphere. This was a qualitative study of the photooxidation mechanism of isoprene, rather than a quantitative study of the yield of SOA, so the experimental results are relevant to atmospheric chemical conditions, and are consistent with others' reports concerning the products of the photooxidation of isoprene (Tuazon and Atkinson, 1990; Ptasińska et al., 2005; Paulot et al., 2009; Nguyen et al., 2011).

The preliminary trials for this work, such as the choice of the experimental conditions and the confirmation of the photooxidation reaction, were carried out at the Laboratory of Environmental Spectroscopy, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences due to the limits on run time in the National Synchrotron Radiation Laboratory. The consumption of the isoprene precursor and the generation of the gas-phase products were detected using a home-made proton transfer reaction mass spectrometer equipped with a quadrupole mass filter with H₃O⁺ used as proton donor (Shen et al., 2009). The particle size distribution measurement of aerosols resulting from the photooxidation was monitored by a scanning mobility particle sizer (SMPS, TSI 3936, consisting of a model 3081 long column cylindrical differential mobility analyzer, and a model 3775 condensation particle counter) in this stage.

The photoionization mass spectroscopy study was performed at the Atomic and Molecular Physics Beamline, National Synchrotron Radiation in Hefei, China (Wang et al., 2006), and the photoionization mass spectrometer including the supersonic expansion molecular beam reflectron time-of-flight mass spectrometer (RTOFMS) system used here was almost the same as the setup used previously (Wang et al., 2007; Liu et al., 2009; Pan et al., 2012). In brief, the lowest-energy gratings SG1 (energy region 7.5–

22.5 eV) was employed with a resolving power of 5000 at 15.9 eV and a photon flux of 10^{12} photons/sec was selected with a grazing-incidence SGM monochromator employing a grating of 1200 grooves/mm and a slit width of 80 μm . The photon energies were calibrated using the photoionization spectrum of Ar with accuracy better than 0.002 eV.

About 40 min after the initiation of the photooxidation, the products (mixture of gaseous and particle) produced by the photooxidation were filtered first by a Balston DFU filter (retention efficiency for > 10 nm particles and droplets 99.99%), then the gas-phase products were analyzed by the VUV-PIMS on-line. FEP Teflon tubes were used to connect the main smog chamber with the VUV-PIMS to reduce the effect of absorption. During experiments, the pressures in the beam source chamber and the ionization chamber were kept in the range of 2.5×10^{-2} and 2.5×10^{-4} Pa, respectively. The PIMS of key gaseous products can be obtained at different photon energy according to the range of the ionization threshold of the products. The PIE curves were measured while the monochromator was scanned with an energy increment of 20 meV, and the accumulating time for each point was 200 sec. In order to overcome the possible higher-order harmonics contamination, a rare-gas harmonic filter was inserted into the beamline with pressure of about 5.32×10^2 Pa.

It is worth pointing out here that in order to confirm the correct measurement of the onset of ionization and the overall functional form of the PIE, two reference experiments were run, in which the PIEs of pure methacrolein and a mixture of acetone and glyoxal standard samples were measured individually.

Isoprene (99%) (CAS#78-79-5), and methacrolein (99%) (CAS#78-85-3), were obtained from Alfa Aesar, Johnson Matthey Company (USA); sodium nitrate ($> 99\%$), methanol ($> 99\%$), acetone ($> 99\%$) (CAS#67-64-1) and glyoxal (40%) (CAS#107-22-2) were purchased from the Third Reagent Manufactory (Tianjin, China). All chemicals were used without further purification.

Methyl nitrite was synthesized by dropping sulfuric acid into a methanol solution of sodium nitrate (Atkinson et al., 1981). Their reaction products were passed through a saturated sodium hydroxide trap to remove the traces of sulfuric acid at first, and then dried by passing through a calcium sulfate trap and collected at last using a liquid nitrogen condenser at 77 K. The methyl nitrite was purified using a glass vacuum system before the experiment.

2 Results and discussion

2.1 Real-time investigation of the photooxidation of isoprene by using PTR-MS and SMPS

Figure 1 is a typical reaction profile of the OH-initiated photooxidation of isoprene. The decay of the precursor isoprene and the production of the m/z 70 component of the gaseous product were monitored in real-time using proton-transfer mass spectrometry (PTR-MS). It seems that the decay of isoprene is very fast in the initial period, and the

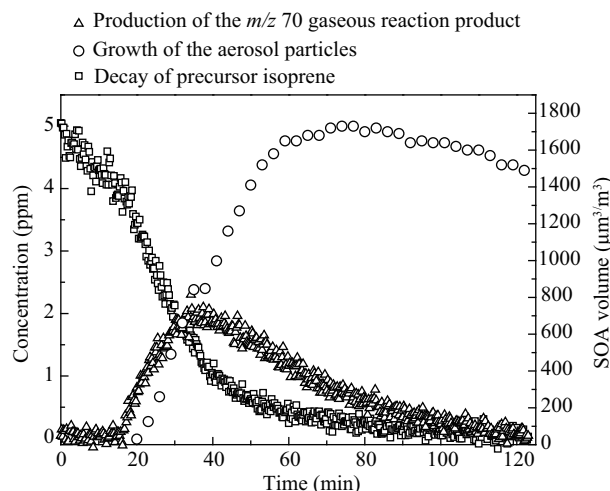


Fig. 1 Reaction profile of a typical OH-initiated isoprene photooxidation experiment.

most abundant product (m/z 70), which is attributed to the major gaseous oxidation products, methacrolein (MACR) and methylvinylketone (MVK), was detected after ca. 15 min of irradiation and observed to increase to its maximum concentration at ca. 40 min after the initiation of the photooxidation. Meanwhile, the formation and evolution of particles in the range 14–673 nm was also monitored in real-time using a scanning mobility particle sizer. It can be seen that the aerosol particles occur after most of the isoprene has been reacted and keep growing even after the isoprene has been reacted completely.

2.2 Time-of-flight mass spectra of gas-phase products

The photoionization mass spectrum of the gaseous mixture before and after the photooxidation of isoprene at photon energy of 12.0 eV is shown in Fig. 2 (partially displayed). According to the results of the PTR-MS experiment, Fig. 2b was measured ca. 40 min after the initiation of the oxidation of isoprene, when the concentration of the first-generation products reached its maximum. Compared with the “background” photoionization mass spectrum shown in Fig. 2a, it is clear that many new features corresponding to the key photooxidation products appear along with the disappearance of the precursor ion C_5H_8^+ (m/z 68) and its fragment C_5H_7^+ (m/z 67), such as m/z 30, 43, 46, 55, 58, 60, 70 (Fig. 2b).

2.3 Identification of the products by the corresponding ionization energies

It is well known that the ionization energy or appearance energy of a molecule or a radical can be determined from PIE curves, and then the molecular structures can be identified unambiguously based on the corresponding ionization energies. By recording the evolution of the mass peak of interest according to the scanning of the photo energy (at 0.02 eV energy intervals), the PIE curves of the main gaseous products in this work were obtained and the corresponding ionization energy was determined (Fig. 3). All the data have been normalized by the different photon intensities simultaneously monitored with a silicon photodiode (SXUV100, International Radiation Detector,

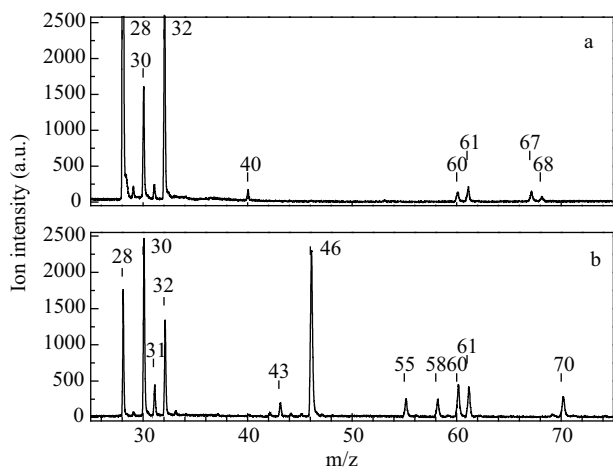


Fig. 2 Partial mass spectra of (a) air and gaseous mixture before photooxidation of isoprene and (b) gaseous products after 40 min of the initiation of photooxidation at the photon energy of 12.0 eV.

Inc.).

In Fig. 3a, b and d, it seems that the ion signals increase almost linearly with ionization energy, so the molecular ionization energies can be determined directly from the intersection of the baseline and the gradually rising line (Chiang et al., 2003); while in Fig. 3c and e, the PIE curves exhibit more complicated behavior near the thresholds, which suggests the possible presence of different chemical compositions with different ionization energies. In order to disentangle the complicated behavior and confirm the hypothesis, the PIEs of a mixture of acetone and glyoxal standard samples and of pure methacrolein were acquired individually as standards, and the comparisons of the real gaseous products with the corresponding standards are shown in Figs. 4 and 5, respectively. The tentative assignments of these key gaseous products based on their molecular weight and the photoionization energies (or electron impact ionization energies (IEs) when photoion-

ization energies data are not available) are summarized in Table 1.

As shown in Fig. 3a and Table 1, the IE for the gas-phase product with m/z 30 is 10.84 eV, and it can be assigned as formaldehyde due to the fact that the value of this IE is in agreement with the existing value of the IE for formaldehyde (10.88 eV). Formaldehyde is the most likely compound to be produced in our experiment, as formaldehyde had been indeed previously detected as the main product of photooxidation of isoprene in a smog chamber (Tuazon and Atkinson, 1990).

In the PIE curves of m/z 46 (Fig. 3b) and m/z 60 (Fig. 3d) products, their IEs are determined to be 11.38 and 10.75 eV, respectively. The two products are tentatively assigned as formic acid and acetic acid. According to the proposed reaction mechanism shown in Fig. 6, OH radical addition to isoprene leads to the formation of methacrolein, which can undergo further reaction with OH radical. The internal addition of OH leads to the formation of an alkyl radical, which rapidly adds to oxygen to form a peroxy radical. This peroxy radical reacts with itself to form an unstable tetroxide, which rapidly decomposes to form different reaction products through pathways to form CH_3 , HCO , CH_2OH and CH_3CO radicals. These active radicals can further react with O_2 and water vapor to form formic acid and acetic acid which has also been confirmed by Paulot et al. (2009).

As aforementioned, it seems there are maybe two onsets in the PIE curve of m/z 58 shown in Fig. 3c, which is validated further by the comparison of the PIE curve of the products formed in the chamber with that of the mixture of acetone and glyoxal standard sample shown in Fig. 4. Although the absolute ion intensities are different, the onsets of ionization and the overall functional forms of the two PIEs are almost consistent in view of the concentration differences between the pure sample and reaction product

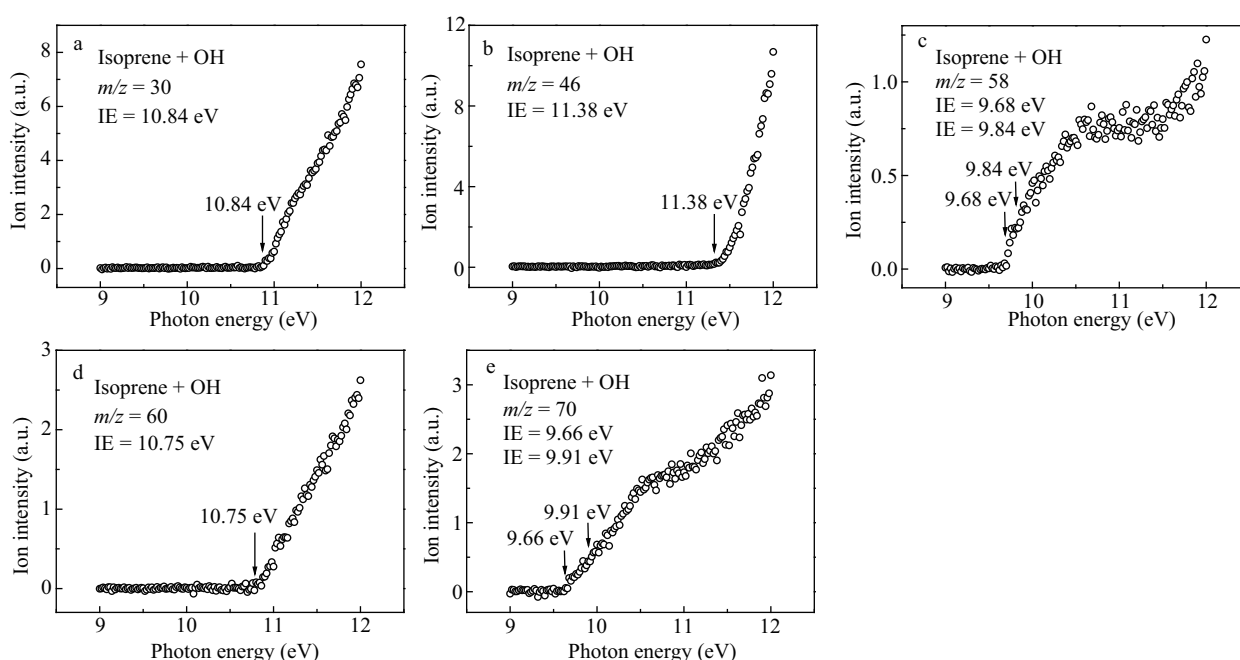


Fig. 3 PIE curves for (a) m/z 30, (b) m/z 46, (c) m/z 58, (d) m/z 60, (e) m/z 70, obtained from gating and integrating the corresponding peaks while scanning the photon energy automatically at an energy step of 0.02 eV. IE: ionization energy.

Table 1 Main gas-phase products observed by VUV-PIMS during the photooxidation of isoprene

m/z	Compound	IEs measured in this work (eV)	IEs of reference* (eV)	Reference
30	HCHO	10.84	10.88 10.86 ± 0.02	Ohno et al., 1995 Kanomata, 1961
46	HCOOH	11.38	11.314 ± 0.002	Knowles and Nicholson, 1974
58	CH ₃ COCH ₃	9.68	9.694 ± 0.006 9.69 ± 0.02	Trott et al., 1978 Wei et al., 2005
	HCO-CHO	9.84	10.21 9.48 ± 0.08	Traeger, 1985 Reed and Brand, 1958
60	CH ₃ COOH	10.75	10.63 10.66 ± 0.05	Traeger et al., 1982 Holmes and Lossing, 198
70	Methyl vinyl ketone	9.66	9.61 9.64	Tam et al., 1974 Terlouw et al., 1980
	Methacrolein	9.91	9.92	Masclat and Mouvier, 1978

* Generally, IEs are referred to the photoionization energies of the compounds. Electron impact ionization energies, however, are presented when the photoionization energies data are not available.

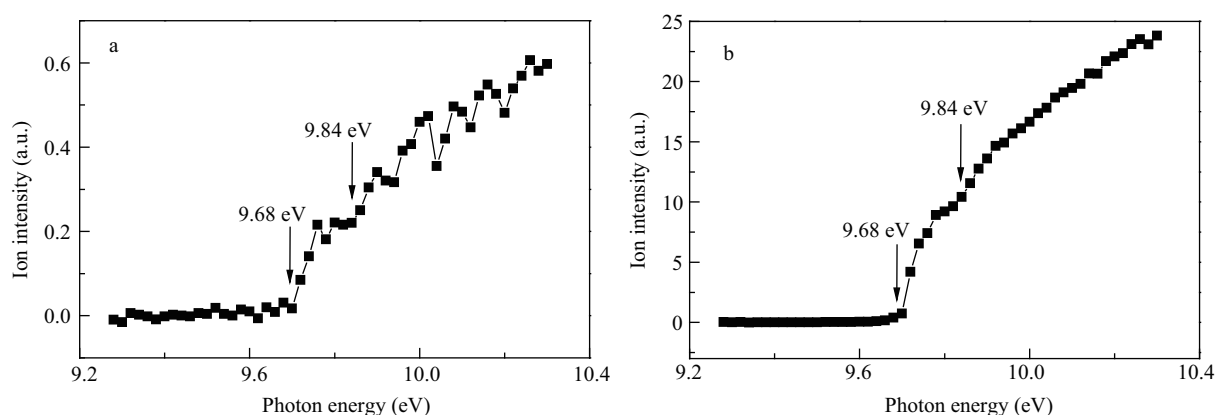


Fig. 4 PIE curves for the m/z 58 signal obtained from products of the OH-initiated photooxidation of isoprene while scanning the photon energy automatically at an energy step of 0.02 eV (a) and mixture of acetone and glyoxal while scanning the photon energy automatically at an energy step of 0.02 eV (b).

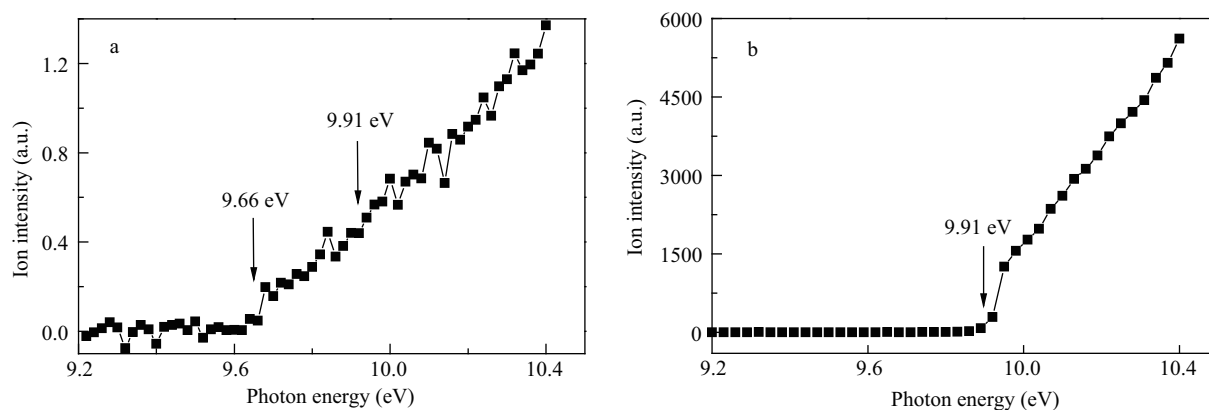


Fig. 5 PIE curves for the m/z 70 signal obtained from products of the OH-initiated photooxidation of isoprene while scanning the photon energy automatically at an energy step of 0.02 eV (a) and methacrolein while scanning the photon energy automatically at an energy step of 0.03 eV (b).

in the two separate runs. The two onsets are presumed related to the products of glyoxal (IE = 9.84 eV) and acetone (IE = 9.68 eV). Glyoxal has been investigated in the oxidation products of isoprene in many studies (Healy et al., 2008; Carlton et al., 2009; Paulot et al., 2009) and considered to be one of the second-generation products of the oxidation of isoprene, while acetone was seldom reported as a main product of the photooxidation of isoprene in a smog chamber before. Very recently, however, it was reported that acetone was also detected in the products of the photooxidation of isoprene in a smog

chamber by using PTR-TOF-MS (Nguyen et al., 2011). According to the proposed reaction mechanisms shown in Fig. 6, it is reasonable to believe that the reaction of CH₃ radicals, formed from the decomposition of tetroxide, with CH₃CO radicals may contribute to the formation of acetone. Certainly, further experimental and theoretical works are needed.

The PIE curve recorded for the ion with m/z 70 is shown in Fig. 3e and Fig. 5a, and the reference PIE curve for pure methacrolein is also shown in Fig. 5b. Generally it is believed there are two candidates, methyl vinyl ketone

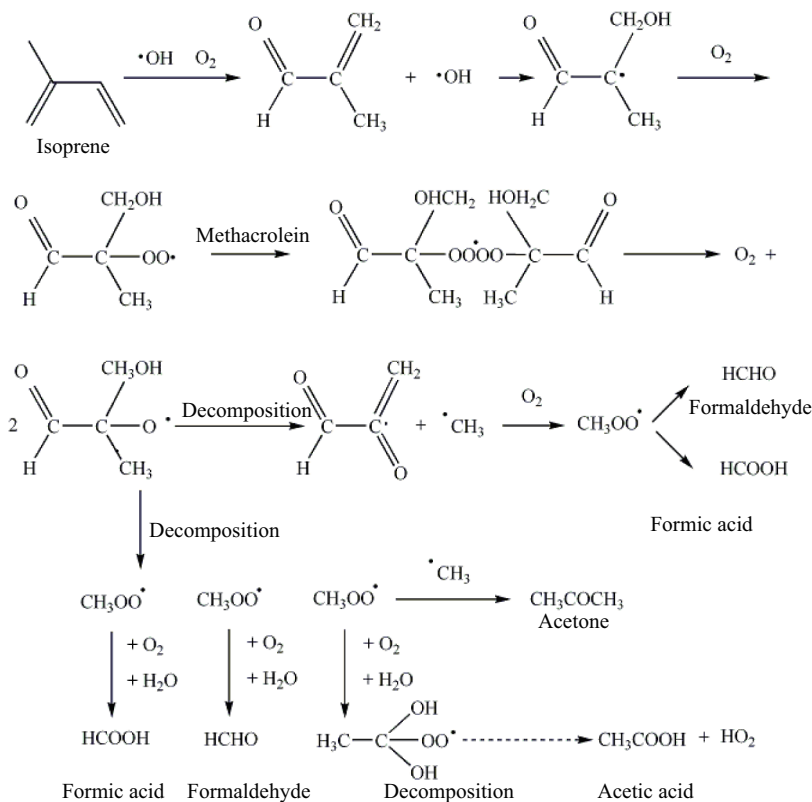


Fig. 6 Proposed reaction mechanisms leading to the formation of products of photooxidation of isoprene.

(MVK; IE = 9.61 eV; Tam et al., 1974) and methacrolein (MACR; IE = 9.92 eV; Masclat and Mouvier, 1978), for the ion with m/z 70. The two species have been determined by many works to be the key first-generation oxidation products of isoprene, and the sum yield of these two products is as high as 50%–70% (Tuazon and Atkinson, 1990; Sprengnether et al., 2002; Ptasińska et al., 2005). The onset corresponding to methyl vinyl ketone (IE = 9.66 eV) is very noticeable as shown in Fig. 3e and Fig. 5a, however, the onset corresponding to methacrolein (IE = 9.91 eV) is not so clear compared with that shown in Fig. 5b. Experiments have been conducted using two isoprene first-generation gas-phase oxidation products as the VOC precursor, and it was shown that although SOA formation was observed from MACR oxidation, there was no aerosol growth observed from MVK oxidation (Kroll et al., 2006). Thus it is reasonable to believe that as an unstable gas-phase intermediate, MACR is more readily involved in further reactions leading to the formation of SOA compared to MVK in the reaction system inside the smog chamber, and then it is hard to detect at low level in the gaseous products.

3 Conclusions

An in-depth VUV photoionization mass spectrometry (PIMS) study on the photooxidation of isoprene with synchrotron radiation is presented based on our previous work. The predominant photooxidation products in the gas phase, such as formaldehyde, formic acid, acetone, glyoxal, acetic acid, methacrolein, and methyl vinyl ketone,

were determined according to the corresponding ionization energies deduced from photoionization efficiency curves. Moreover, the isomeric products of acetone and glyoxal, methacrolein and methyl vinyl ketone, were detected and distinguished by on-line VUV-PIMS based on synchrotron radiation for the first time. The proposed reaction mechanisms are discussed and shown to have reasonable consistency with the previous work of the different groups, which indicates the potential application of the technique in related studies of the atmospheric oxidation of ambient volatile organic compounds.

Acknowledgments

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References

- Atkinson R, 2000. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*, 34(12-14): 2063–2101.
- Atkinson R, Carter W P L, Winer A M, Pitts J N, 1981. An experimental protocol for the determination of OH radical rate constants with organics using methyl nitrite photolysis as an OH radical source. *Journal of the Air Pollution Control Association*, 31(10): 1090–1092.
- Carlton A G, Wiedinmyer C, Kroll J H, 2009. A review of

- secondary organic aerosol (SOA) formation from isoprene. *Atmospheric Chemistry and Physics*, 9(14): 4987–5005.
- Chiang S Y, Bahou M, Sankaran K, Lee Y P, Lu H F, Su M D, 2003. Dissociative photoionization of CH_2Cl_2 and enthalpy of formation of CHCl^+ : Experiments and calculations. *Journal of Chemical Physics*, 118(1): 62–69.
- Claeys M, Graham B, Vas G, Wang W, Vermeylen R, Pashynska V et al., 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science*, 303(5661): 1173–1176.
- Elder F R, Gurewitsch A M, Langmuir R V, Pollock H C, 1947. Radiation from electrons in a synchrotron. *Physical Review*, 71(11): 829–830.
- Fang W Z, Gong L, Shan X B, Liu F Y, Wang Z Y, Sheng L S, 2011. A VUV photoionization organic aerosol mass spectrometric study with synchrotron radiation. *Journal of Electron Spectroscopy and Related Phenomna*, 184(3-6): 129–133.
- Gloaguen E, Mysak E R, Leone S R, Ahmed M, Wilson K R, 2006. Investigating the chemical composition of mixed organic-inorganic particles by “soft” vacuum ultraviolet photoionization: the reaction of ozone with anthracene on sodium chloride particles. *International Journal of Mass Spectrometry*, 258(1-3): 74–85.
- Guenther A, Hewitt C N, Erickson D, Fall R, Geron C, Graedel T et al., 1995. A global model of natural organic compound emissions. *Journal of Geophysical Research*, 100(D5): 8873–8892.
- Guenther A, Karl T, Harley P, Wiedinmyer C, Palmer P I, Geron C, 2006. Estimates of global terrestrial isoprene emissions using MEGAN (model of emissions of gases and aerosols from nature). *Atmospheric Chemistry and Physics*, 6(11): 3181–3210.
- Hao L Q, Wang Z Y, Huang M Q, Pei S X, Yang Y, Zhang W J, 2005. Size distribution of the secondary organic aerosol particles from the photooxidation of toluene. *Journal of Environmental Sciences*, 17(16): 912–916.
- Healy R M, Wenger J C, Metzger A, Duplissy J, Kalberer M, Dommen J, 2008. Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1, 3, 5-trimethylbenzene. *Atmospheric Chemistry and Physics*, 8(12): 3215–3230.
- Heger H, Boesl U, Zimmermann R, Dorfner R, Kettrup A, 1999. On-line resonance-enhanced multiphoton ionization time-of-flight laser mass spectrometry for combined multi-component-pattern analysis and target-compound monitoring: non-chlorinated aromatics and chlorobenzene in flue gases of combustion processes. *European Journal of Mass Spectrometry*, 5(1): 51–57.
- Holmes J L, Lossing F P, 1980. Gas-phase heats of formation of keto and enol ions of carbonyl compounds. *Journal of the American Chemical Society*, 102(5): 1591–1595.
- Huang M Q, Zhang W J, Hao L Q, Wang Z Y, Fang L, Kong R H et al., 2010. Experimental study of photooxidation products of ethylbenzene. *Journal of Environmental Sciences*, 22(10): 1570–1575.
- Kanomata I, 1961. Mass-spectrometric study on ionization and dissociation of diethyl ether by electron impact. *Bulletin of the Chemical Society of Japan*, 34(12): 1864–1871.
- Knowles D J, Nicholson A J C, 1974. Ionization energies of formic and acetic acid monomers. *Journal of Chemical Physics*, 60(3): 1180–1181.
- Kroll J H, Ng N L, Murphy S M, Flagan R C, Seinfeld J H, 2006. Secondary organic aerosol formation from isoprene photooxidation. *Environmental Science & Technology*, 40(6): 1869–1877.
- Liu X Y, Zhang W J, Huang M Q, Wang Z Y, 2010. FTIR spectra of isoprene and its photooxidation products. *Journal of Infrared and Millimeter Waves*, 29(2): 114–116.
- Liu X Y, Zhang W J, Wang Z Y, Huang M Q, Yang X B, Tao L et al., 2009. Dissociative photoionization of isoprene: experiments and calculations. *Journal of Mass Spectrometry*, 44(3): 404–409.
- Masclat P, Mouvier G, 1978. Study of conjugated ethylenic aldehydes and ketones using photo-electric spectrometry. *Journal of Electron Spectroscopy and Related Phenomena*, 14(2): 77–97.
- Mysak E R, Wilson K R, Jimenez-Cruz M, Ahmed M, Baer T, 2005. Synchrotron radiation based aerosol time-of-flight mass spectrometry for organic constituents. *Analytical Chemistry*, 77(18): 5953–5960.
- Nguyen T B, Batemana A P, Bones D L, Nizkorodov S A, Laskin J, Laskin A, 2010. High-resolution mass spectrometry analysis of secondary organic aerosol generated by ozonolysis of isoprene. *Atmospheric Environment*, 44(8): 1032–1042.
- Nguyen T B, Roach P J, Laskin J, Laskin A, Nizkorodov S A, 2011. Effect of humidity on the composition of isoprene photooxidation secondary organic aerosol. *Atmospheric Chemistry and Physics*, 708(11): 6931–6944.
- Ohno K, Okamura K, Yamakado H, Hoshino S, Takami T, Yamauchi M, 1995. Penning ionization of HCHO, CH_2CH_2 , and CH_2CHCHO by collision with He(23S) metastable atoms. *Journal of Physical Chemistry*, 99(39): 14247–14253.
- Pacifico F, Harrison S P, Jones C D, Sitch S, 2009. Isoprene emissions and climate. *Atmospheric Environment*, 43(39): 6121–6135.
- Pan G, Hu C H, Wang Z Y, Cheng Y, Zheng X H, Gu X J et al., 2012. Direct detection of isoprene photooxidation products by using synchrotron radiation photoionization mass spectrometry. *Rapid Communications in Mass Spectrometry*, 26(2): 189–194.
- Paulot F, Crounse J D, Kjaergaard H G, Kroll J H, Seinfeld J H, Wennberg P O, 2009. Isoprene photooxidation: new insights into the production of acids and organic nitrates. *Atmospheric Chemistry and Physics*, 9(4): 1479–1501.
- Paulot F, Crounse J D, Kjaergaard H G, Kürten A, Clair J M S, Seinfeld J H et al., 2009. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science*, 325(5941): 730–733.
- Pope C A III, Ezzati M, Dockery D W, 2009. Fine-particulate air pollution and life expectancy in the United States. *New England Journal of Medicine*, 360(4): 376–386.
- Ptasińska S, Denifl S, Scheier P, Märk T D, 2005. Electron impact ionization of glycolaldehyde. *International Journal of Mass Spectrometry*, 243(2): 171–176.
- Reed R I, Brand J C D, 1958. Electron impact studies. Part 4.-glyoxal, methylglyoxal, and diacetyl. *Journal of the Chemical Society, Faraday Transactions*, 54(424): 478–482.
- Russell A E, Brunekreef B, 2009. A focus on particulate matter and health. *Environmental Science & Technology*, 43(13): 4620–4625.
- Sarah J, Campuzana-Jost H P, Simpson E A, Burak I, Blades M W, Hepburn J W et al., 2009. A study of oleic acid and 2,4-DHB acid aerosols using an IR-VUV-ITMS: insights into the strengths and weaknesses of the technique. *Physical Chemistry Chemical Physics*, 11(36): 7963–7975.

- Sharkey T D, Wiberley A E, Donohue A R, 2008. Isoprene emission from plants: Why and how? *Annals of Botany*, 101(1): 5–18.
- Shen C Y, Li J Q, Han H Y, Wang H M, Jiang H H, Chu Y N, 2009. Triacetone triperoxide detection using low reduced-field proton transfer reaction mass spectrometer. *International Journal of Mass Spectrometry*, 285(1-2): 100–103.
- Sprengnether M, Demerjian K L, Donahue N M, Anderson J G, 2002. Product analysis of the OH oxidation of isoprene and 1,3-butadiene in the presence of NO. *Journal of Geophysical Research*, 107(D15): 4268–4275.
- Surratt J D, Chan A W H, Eddingsaasa N C, Chan M, Loza C L, Kwan A J et al., 2010. Atmospheric chemistry special feature: reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proceedings of the National Academy of Sciences*, 107(15): 6640–6645.
- Szmigielski R, Surratt J D, Vermeylen R, Szmigielska K, Kroll J H, Ng N L et al., 2007. Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using gas chromatography/ion trap mass spectrometry. *Journal of Mass Spectrometry*, 42(1): 101–116.
- Tam W C, Yee D, Brion C E, 1974. Photoelectron-spectra of some aldehydes and ketones. *Journal of Electron Spectroscopy and Related Phenomena*, 4(1): 77–80.
- Terlouw J K, Heerma W, Holmes J L, Burgers P C, 1980. Structure and formation of gaseous $[C_4H_6O]^+$ ions: 1-The enolic ions $[CH_2=C(OH)-CH=CH_2]^+$ and $[CH_2=CH-CH=CH(OH)]^+$ and their relationship with their keto counterparts. *Organic Mass Spectrometry*, 15(11): 582–586.
- Traeger J C, 1985. Heat of formation for the formyl cation by photoionization mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes*, 66(3): 271–282.
- Traeger J C, McLoughlin R G, Nicholson A J C, 1982. Heat of formation for acetyl cation in the gas phase. *Journal of the American Chemical Society*, 104(20): 5318–5322.
- Trott W M, Blais N C, Walters E A, 1978. Molecular beam photoionization study of acetone and acetone-d6. *Journal of Chemical Physics*, 69(7): 3150–3158.
- Tuazon E C, Atkinson R, 1990. A product study of the gas phase reaction of isoprene with the OH radical in the presence of NOx. *International Journal of Chemical Kinetics*, 22(12): 1221–1236.
- Wang K, Dickinson R E, Liang S, 2009. Clear sky visibility has decreased over land globally from 1973 to 2007. *Science*, 323(5920): 1468–1470.
- Wang S S, Kong R H, Shan X B, Zhang Y W, Sheng L S, Wang Z Y et al., 2006. Performance of the atomic and molecular physics beamline at the National Synchrotron Radiation Laboratory. *Journal of Synchrotron Radiation*, 13(Pt 6): 415–420.
- Wang Z Y, Hao L Q, Zhou S K, Yang B, Huang C Q, Wang S S et al., 2007. VUV dissociative photoionization of CHF_2Cl . *Journal of Molecular Structure*, 826(2-3): 192–197.
- Wei J, Zhang B, Zheng H Y, Zhang L D, Kong X H, Xia Z H et al., 2001. Rapid analysis of trace pollutants using laser mass spectrometry. *Science China*, 44(7): 940–946.
- Wei L X, Yang B, Yang R, Huang C Q, Wang J, Shan X B et al., 2005. A vacuum ultraviolet photoionization mass spectrometric study of acetone. *Journal of Physical Chemistry A*, 109(19): 4231–4241.
- Yu J Z, Jeffries H E, Lacheur R M L, 1995. Identifying air borne carbonyl compounds in isoprene atmospheric photooxidation products by their PFBHA oximes using gas chromatography/ion trap mass spectrometry. *Environmental Science & Technology*, 29(8): 1923–1932.
- Zahardis J, Geddes S, Petrucci G A, 2011. Improved understanding of atmospheric organic aerosols via innovations in soft ionization aerosol mass spectrometry. *Analytical Chemistry*, 83(7): 2409–2415.

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