



Identification of organic hydroperoxides and peroxy acids using atmospheric pressure chemical ionization–tandem mass spectrometry (APCI-MS/MS): application to secondary organic aerosol

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Abstract. Molecules with hydroperoxide functional groups are of extreme importance to both the atmospheric and biological chemistry fields. In this work, an analytical method is presented for the identification of organic hydroperoxides and peroxy acids (ROOH) by direct infusion of liquid samples into a positive-ion atmospheric pressure chemical ionization–tandem mass spectrometer ((+)-APCI-MS/MS). Under collisional dissociation conditions, a characteristic neutral loss of 51 Da (arising from loss of H₂O₂+NH₃) from ammonium adducts of the molecular ions ([M + NH₄]⁺) is observed for ROOH standards (i.e. cumene hydroperoxide, isoprene-4-hydroxy-3-hydroperoxide (ISOPOOH), *tert*-butyl hydroperoxide, 2-butanone peroxide and peracetic acid), as well as the ROOH formed from the reactions of H₂O₂ with aldehydes (i.e. acetaldehyde, hexanal, glyoxal and methylglyoxal). This new ROOH detection method was applied to methanol extracts of secondary organic aerosol (SOA) material generated from ozonolysis of α -pinene, indicating a number of ROOH molecules in the SOA material. While the full-scan mass spectrum of SOA demonstrates the presence of monomers ($m/z = 80$ – 250), dimers ($m/z = 250$ – 450) and trimers ($m/z = 450$ – 600), the neutral loss scan shows that the ROOH products all have masses less than 300 Da, indicating that ROOH molecules may not contribute significantly to the SOA oligomeric content. We anticipate this method could also be applied to biological systems with considerable value.

1 Introduction

Organic hydroperoxides and peroxy acids (ROOH) are produced by the gas-phase oxidation of volatile organic compounds (VOCs) (Jackson et al., 1999; Lee et al., 2000; Atkinson and Arey, 2003), as well as in cloud and wet aerosols (Zhao et al., 2013; Lim and Turpin, 2015). Atmospheric oxidation of VOCs leads to secondary organic aerosol (SOA), an important fraction of the atmospheric aerosol burden. Both modeling and experimental studies indicate that organic peroxides (i.e. organic peroxides (ROOR) and ROOH species) are major components of SOA (Jenkin, 2004; Bonn et al., 2004; Docherty et al., 2005). In recent years, ROOH in particular have been proposed to be involved in high-molecular-weight products leading to SOA formation (Krapf et al., 2016; Kristensen et al., 2016; Sakamoto et al., 2017). Organic peroxides are also widely used industrially as radical initiators; bleaching and disinfecting agents; and reactive intermediates in the polymer, food and pharmaceutical industries (O'dian, 2004; Moll et al., 1979; Reile et al., 2011). In biological systems, ROOH are formed from the reactions of radicals and singlet oxygen with amino acids, peptides and proteins (Gebicki and Gebicki, 1993; Wright et al., 2002; Agon et al., 2006; Morgan et al., 2008). Classified as one component of reactive oxygen species (ROS), ROOH are hazardous, irritating to skin, eyes and mucous membranes. They also cause progressive oxidative damage, cell death and even cancer (Liou and Storz, 2010).

Despite their importance in both atmospheric and biological chemistry, the identification of specific ROOH molecules in a complex mixture remains analytically challenging. There are two reasons for this: (i) unavailability of the ROOH standards because of their thermally unstable nature (Bach et al., 1996) and (ii) the lack of appropriate analytical techniques. So far, the analysis of ROOH in the condensed phase has mainly been done by means of chemical assays, such as the iodometric (Docherty et al., 2005; Banerjee and Budke, 1964), triphenylphosphine (Nakamura and Maeda, 1991), ferrous oxidation–xylenol orange (Wasylaschuk et al., 2007), and horseradish peroxidase approaches (Walker et al., 2006; Hong et al., 2008). These techniques react ROOH with reducing agents followed by analysis of the reaction products. ROOH have also been analyzed by high-performance liquid chromatography (HPLC) analysis followed by the post-column chemical derivatization method (Valverde-Canossa et al., 2005; Francois et al., 2005; Hasson et al., 2001).

The disadvantage of the assay techniques is that they measure total peroxide content (some combination of organic peroxides, organic hydroperoxides, and hydrogen peroxide) and are not able to identify specific molecules. There are limited studies on direct analysis of ROOH in the literature. Using electrospray ionization–mass spectrometry (ESI-MS), Hui et al. (2012a, b) identified ROOH formed from the oxidation of cholesteryl ester, reporting ammonium and sodium adducts of the ROOH molecular ions under positive ion mode and acetate adducts of ROOH molecular ions under negative ion mode (Hui et al., 2012a, b). Reinnig et al. (2009) identified ROOH using online ion trap mass spectrometry, proposing that neutral loss (NL) of 34 Da (loss of H₂O₂) from the protonated molecular ions is a characteristic fragmentation route for ROOH. Using this technique, the authors identified three ROOH molecules from SOA generated from reaction of α -pinene and ozone (Reinnig et al., 2009).

Recently, using high-resolution mass spectrometry, a number of studies have proposed ROOH detection arising from atmospheric oxidation of biogenic organics (Zhang et al., 2017; Riva et al., 2017). However, due to the fact that the high-resolution mass spectrometry can only provide elemental composition of the molecules, the identification of ROOH in the reaction systems remains speculative.

In the present work, a positive-ion atmospheric pressure chemical ionization–tandem mass spectrometer ((+)-APCI-MS/MS) is applied to identify specific ROOH molecules. The analytical method is developed by using ROOH commercial standards and ROOH molecules that are generated from the reactions of aldehydes with H₂O₂. The method is applied to SOA formed from ozonolysis of α -pinene, and a number of ROOH molecules are identified. The goal of this work is to provide an analytical technique that can widely be applied in not only the atmospheric chemistry field but also other settings.

2 Experimental section

2.1 Chemicals and reagents

Cumene hydroperoxide (80 %), *tert*-butyl hydroperoxide (35 %), 2-butanone peroxide (35 %), peracetic acid (32 %), di-*tert*-butyl peroxide (98 %), benzoyl peroxide (≥ 98 %), di(dodecanoyl) peroxide (97 %), 2-nonenal (97 %), *meso*-erythritol (≥ 99 %), *cis*-pinonic acid (98 %), formaldehyde (37 %), acetaldehyde (> 99 %), hexanal (98 %), methyl glyoxal (40 %), glyoxal (40 %), hydrogen peroxide (H₂O₂, 30 %), α -pinene (≥ 99 %) and ammonium acetate (≥ 99.99 %) are all purchased from Sigma-Aldrich (Canada). Isoprene-4-hydrox-3-hydroperoxide (ISOPOOH) is synthesized according to the literature (Rivera-Rios et al., 2014). Methanol (MeOH, LC-MS grade) is purchased from VWR, Canada. All the chemicals and reagents are used as received.

2.2 Sample preparation and reactions of aldehydes with H₂O₂

Stock solutions for ROOH standards (i.e. cumene hydroperoxide, ISOPOOH, *tert*-butyl hydroperoxide, 2-butanone peroxide and peracetic acid), other peroxides (di-*tert*-butyl peroxide, benzoyl peroxide and di(dodecanoyl) peroxide), 2-nonenal, *meso*-erythritol and *cis*-pinonic acid are prepared by dissolution of the substances in MeOH (2.0–10 mM). One hundred microliters of stock solutions are further diluted in MeOH to a final volume of 1 mL for mass spectrometry analysis. In some cases, ammonium acetate (AA) is added (~ 5 mM) to enhance the signal for the ammonium adducts of the molecular ions in the mass spectra.

Reactions of the selected aldehydes (i.e. formaldehyde, acetaldehyde, hexanal, glyoxal and methyl glyoxal) with H₂O₂ are performed by mixing the reactants in MeOH (~ 3 mM and ~ 13 mM for aldehydes and H₂O₂, respectively) at room temperature (295 ± 3 K) for ~ 10 min. AA is added (~ 5 mM) before the samples are analyzed. Sample blanks (i.e. aldehydes + AA and H₂O₂ + AA) are prepared and analyzed in the same manner as the reaction mixtures.

2.3 Secondary organic aerosol (SOA) generation and collection

SOA is generated in a steady-state manner in a 1 m³ Teflon (FEP) chamber from gas-phase reaction of α -pinene with ozone (Aljawhary et al., 2013). α -Pinene is introduced into the chamber by passing a ~ 2 mL min⁻¹ nitrogen through a bubbler containing α -pinene that is chilled to -20 °C and mixed with 5 L min⁻¹ purified air. Ozone is generated by passing ~ 10 L min⁻¹ purified air through a mercury lamp. The final concentration of ozone is monitored to be $\sim 7.4 \times 10^{12}$ molecules cm⁻³ by a UV photometric ozone analyzer (Thermo Model 49i), and the α -pinene concentration is estimated to be $\sim 3.7 \times 10^{12}$ molecules cm⁻³.

SOA generation is confirmed by a Scanning Mobility Particle Sizer (SMPS, Model 3034) and collected on quartz fiber filters (47 mm diameter) for 72 h at a flow rate of $\sim 15 \text{ L min}^{-1}$. The filters are preheated at 500°C for 24 h to remove organic impurities before SOA collection. After SOA collection, the filter is extracted with 10 mL MeOH, and the extract is immediately analyzed by the mass spectrometer.

2.4 Atmospheric pressure chemical ionization–tandem mass spectrometer (APCI-MS/MS)

A unit resolution APCI-MS/MS instrument (Thermo TSQ Endura) is operated in positive ion mode with direct infusion of the samples into the mass spectrometer. The sample is injected at a flow rate of $10 \mu\text{L min}^{-1}$ using a syringe pump (Chemyx, Inc., USA; model: Fusion 101) to the APCI source through polyether ether ketone (PEEK) tubing. The spray voltage is set at $+2500 \text{ V}$; vaporizer temperature and ion transfer tubing temperature are set at 200°C . Sheath gas, auxiliary gas and sweep gas flows are set (arbitrary units) at 5, 2 and 0, respectively. The mass spectrometer is a triple quadrupole that is calibrated with polytyrosine. Mass spectra are obtained under either full-scan mode or selected ion monitoring (SIM) mode.

In full-scan mode, RF lens voltages are the default from the optimization in the mass calibration. The SIM scan is achieved by isolating and monitoring a range of masses with maximum mass range of 50 Da. The RF lens voltages in SIM mode can be manually varied and are optimized to maximize the intensities of the ammonium adducts of the molecular ions.

Ion fragmentation in the MS/MS is accomplished by application of electrical potentials (2–10 V) and collision gas (Argon, 0.5 mTorr) in the collision-induced dissociation (CID) cell. Mass spectra from product scans are obtained by transmitting ions of a specific m/z through the first quadrupole (precursor ions), fragmenting in the CID cell, and monitoring the resulting fragment ions (product ions) by the third quadrupole.

In the NL scan mode, the first and third quadrupoles are scanned at the same rate over mass ranges of the same width; i.e. the third quadrupole transmits ions at a fixed mass-to-charge ratio lower than the first quadrupole. In the NL scan, the CID voltage and argon pressure are set at 2–10 V and 0.5 mTorr, respectively. The limit of detection (LOD) of the analytical method is established by direct injection of the ROOH standard solution in MeOH with 2–10 mM ammonium acetate into the APCI source with the tandem mass spectrometer being operated under NL scan mode. Three ROOH standards – namely 2-butanone peroxide, *tert*-butyl hydroperoxide and cumene hydroperoxide – are analyzed. Since a neutral loss of 51 Da from the ammoniated molecular ion ($[\text{M} + \text{NH}_4]^+$) of the ROOH is characteristic for ROOH molecules, as will be seen in the next section, the calibration is performed by operating with a loss of 51 Da in

NL scan. The ROOH concentrations are selected when the $[\text{M} + \text{NH}_4]^+$ ions are well above the noise and clearly seen in the average mass spectra. The LOD is reported as 3 times the S/N where noise is estimated at mass-to-charge ratios different from the mass-to-charge ratio for $[\text{M} + \text{NH}_4]^+$.

3 Results and discussion

3.1 APCI mass spectra of ROOH standards

Figure 1 presents examples of the direct infusion (+)-APCI mass spectra for (a) cumene hydroperoxide (cumene HP) and (b) 4,3-ISOPOOH, with and without addition of AA. The chemical structures and molecular weights (MWs) of the ROOH analyzed are given in Fig. S1 in the Supplement. Note that we do not attempt to interpret the mass spectra of ROOH and other standards obtained under full-scan and SIM modes due to the presence of stabilizers and other impurities in the standard samples that make the mass spectra complex. Instead, we focus on the protonated and ammoniated molecular ions of the ROOH molecules.

It can be seen from Fig. 1 that, although cumene HP demonstrates the proton adduct of the molecular ion at $m/z = 153$ ($[\text{M} + \text{H}]^+$ (top panel of Fig. 1a), addition of AA results in the ammonium adduct at $m/z = 170$ ($[\text{M} + \text{NH}_4]^+$) (bottom panel of Fig. 1a). For ISOPOOH, the molecular ion is not seen in the full-scan mass spectrum (top panel of Fig. 1b), and the dehydrated molecular ion at $m/z = 101$ ($[\text{M} + \text{H} - \text{H}_2\text{O}]^+$) is clearly observed instead (top panel of Fig. 1b). This is consistent with previous studies claiming that hydroperoxy group ($-\text{OOH}$) is not a favorable protonation or deprotonation site with ESI or APCI (Reinnig et al., 2008; Rondeau et al., 2003; Nilsson et al., 2008). The addition of AA again leads to significant production of the ammonium adduct of the molecular ion at m/z 136 (bottom panel of Fig. 1b). Similar effects of AA on the APCI mass spectra are observed for other ROOH species.

In comparison, a number of other common molecules in atmospheric samples – e.g. ROOR, carbonyls, alcohols and carboxylic acids – were also analyzed. The chemical structures of the other oxygenated organics are given in Fig. S2. Similar to the ROOH samples, the ammonium adducts of the molecular ions ($[\text{M} + \text{NH}_4]^+$) are obtained for all the substances. The only difference is that in some cases, e.g. benzoyl peroxide, the ammonium adduct of the molecular ions can be clearly seen without addition of AA, via trace levels of ammonia present in the water or air.

3.2 Product spectra of $[\text{M} + \text{NH}_4]^+$ for ROOH and other organics

Figure 2 gives the CID fragment patterns (i.e. product spectra) for ammonium adducts of the molecular ions ($[\text{M} + \text{NH}_4]^+$) of (a) cumene HP and (b) ISOPOOH. Two types of fragmentation, i.e. loss of 35 and 51 Da from the respec-

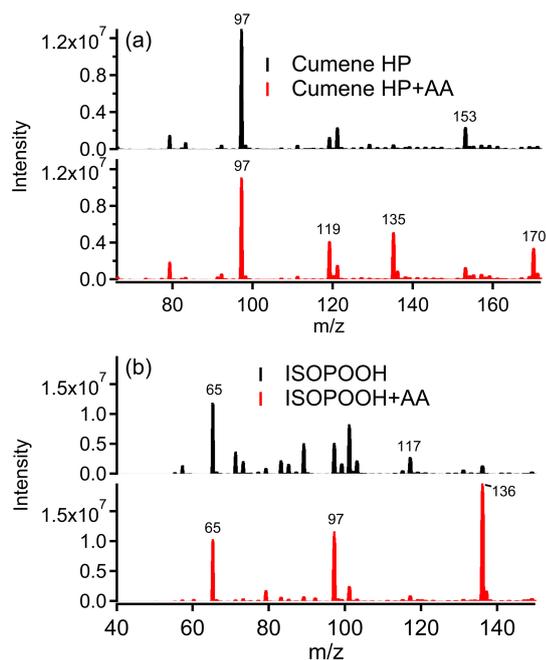


Figure 1. (+)-APCI mass spectra of ROOH with and without addition of ammonium acetate (AA) for (a) cumene HP and (b) ISOPOOH.

tive $[M + \text{NH}_4]^+$ ions, are observed in both cumene HP and ISOPOOH. The loss of 35 Da, corresponding to $[-\text{H}_2\text{O}-\text{NH}_3]$ (Fig. S3), is also observed in *meso*-erythritol and pinonic acid (Fig. S4). Neutral loss of 51 Da, corresponding to $[-\text{H}_2\text{O}_2-\text{NH}_3]$ (Fig. S3), is only observed from fragmentation of the $[M + \text{NH}_4]^+$ ions of ROOH (Figs. 2 and S4). It is known that the loss of the H_2O molecule from protonated molecular ions ($[M + \text{H}]^+$) is typical for epoxides, alcohols and carboxylic acids (Holcapek et al., 2010). But the loss of 35 Da from $[M + \text{NH}_4]^+$ is not characteristic for ROOH. Instead, the loss of 51 Da from $[M + \text{NH}_4]^+$ is only observed in ROOH standards, including peracetic acid (Fig. S5). Hence we propose that the neutral loss of 51 Da from $[M + \text{NH}_4]^+$ is characteristic for ROOH molecules. This is consistent with previous work that suggested that neutral loss of H_2O_2 from $[M + \text{H}]^+$ is also characteristic for ROOH species (Reinnig et al., 2009).

3.3 ROOH formation from the reactions of aldehydes and H_2O_2

Using ^1H NMR spectroscopy, it has been shown that ROOH species form from the reactions of aldehydes with H_2O_2 (Zhao et al., 2013). As shown in Fig. 3, the reaction proceeds via reversible nucleophilic addition of H_2O_2 to the carbonyl group in aldehydes, leading to α -hydroxyhydroperoxides (HHP). The addition of H_2O_2 to methylglyoxal (MGL; MW = 72) gives rise to MGL HHP (MW = 106) (Fig. 3a), whose ammonium adduct is seen at m/z 124 in Fig. 4a. The

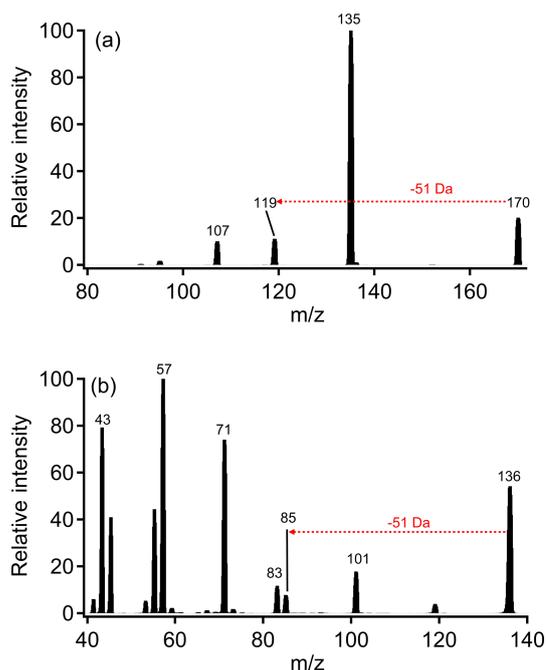


Figure 2. Product spectra of $[M + \text{NH}_4]^+$ for (a) cumene HP and (b) ISOPOOH.

mass spectrum of the reaction mixture of glyoxal and H_2O_2 suggests that, rather than a direct addition to glyoxal, H_2O_2 is instead added to the glyoxal geminal diol formed by the hydrolysis of glyoxal (Fig. 3b), producing $[M + \text{NH}_4]^+$ at m/z 128 (Fig. S6a). The $[M + \text{NH}_4]^+$ ROOH peaks are also observed in the reactions of other aldehydes with H_2O_2 (data not shown).

The fragmentation spectra of the $[M + \text{NH}_4]^+$ of the ROOH from methylglyoxal and glyoxal are given in Figs. 4b and S6b, respectively. It is clear that the neutral loss of 51 Da is again observed in the fragments of the ROOH molecules. The ROOH products from all the other aldehyde reactions with H_2O_2 also show loss of 51 Da in MS/MS mode. Overall, we conclude that the neutral loss of 51 Da from $[M + \text{NH}_4]^+$ fragmentation can be used to identify ROOH molecules.

3.4 Identification of ROOH in SOA material

Figure 5 presents mass spectra of the methanol extract of SOA generated from ozonolysis of α -pinene under dry conditions (relative humidity (RH) < 5%). There are three features of note. First, the well-characterized products from this reaction – such as nopinone aldehyde (MW = 154), terpenylic acid (MW = 172) and *cis*-pinic acid (MW = 186) (Jenkin et al., 2000; Larsen et al., 2001; Claeys et al., 2009) – are present as protonated molecular ions ($[M + \text{H}]^+$) in the full-scan mode (Fig. 5a). Second, the full-scan mass spectrum (Fig. 5a) shows the presence of monomer (m/z = 80–250), dimer (m/z = 250–450) and trimer (m/z = 450–600)

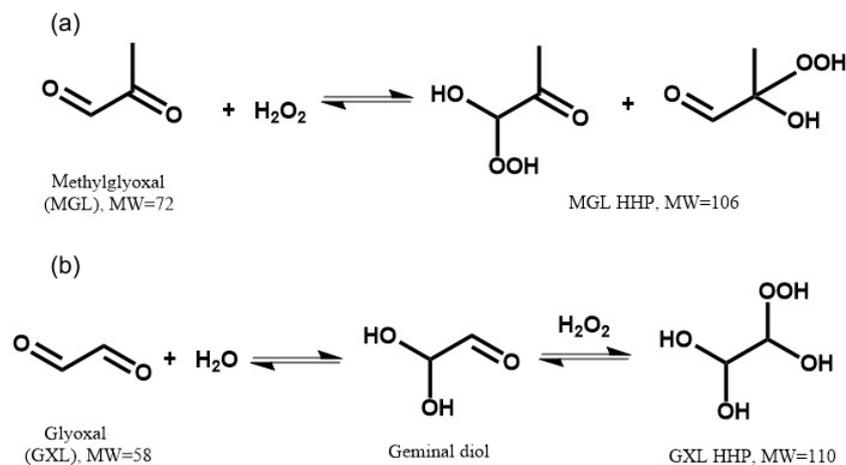


Figure 3. ROOH formation from reactions of H_2O_2 with (a) methylglyoxal and (b) glyoxal.

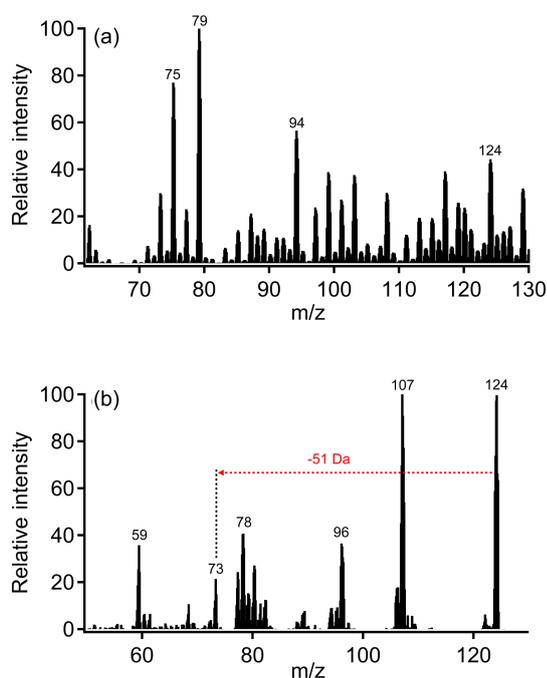


Figure 4. (a) Mass spectrum of reaction of methylglyoxal with H_2O_2 in the presence of AA; (b) product mass spectrum of m/z 124 from panel (a).

species, as has been reported in previous work (Venkatachari and Hopke, 2008). Third, and perhaps most importantly, the 51 Da neutral loss scan (Fig. 5b) indicates that all the ROOH species have masses < 300 Da (Fig. 5b).

To confirm the observation of ROOH obtained with the neutral loss scan, CID fragmentation spectra of a few intense peaks at m/z 190, 202, 206, 218 and 220 in Fig. 5b are analyzed. All the fragments of these products show loss of 51 Da. An example of the fragment pattern for m/z 206 is given in Fig. S7.

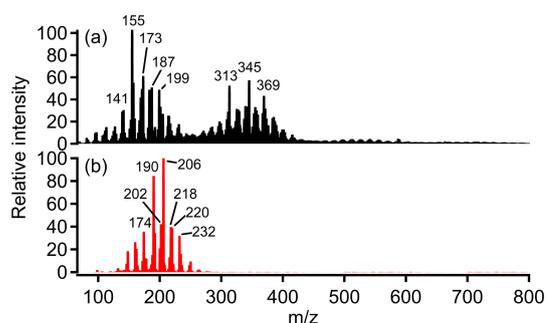
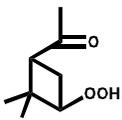
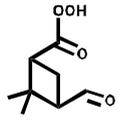
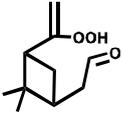
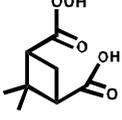
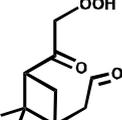
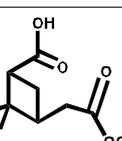
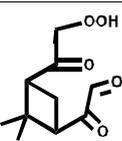


Figure 5. Mass spectra of SOA from ozone reaction with α -pinene under dry conditions ($\text{RH} < 5\%$) obtained with (a) full scan and (b) neutral loss scan of 51 Da.

The ROOH products in SOA are tentatively identified and listed in Table 1. It should be noted that the chemical structures of these products are only obtained from their molecular ions and, therefore, remain speculative.

Several mechanisms for oligomer product formation in SOA arising from VOC oxidation have been proposed: (i) self- and cross-reactions of the peroxy radicals (RO_2) (Zhang et al., 2015); (ii) reaction of ozonolysis products in the condensed-phase, such as aldol condensation, esterification, hemiacetal and peroxyhemiacetal formation (Ziemann, 2003; Tolocka et al., 2004; Kristensen et al., 2014; Docherty et al., 2005; Muller et al., 2009; Yasmeen et al., 2010; Hall and Johnston, 2012; Witkowski and Gierczak, 2014; DePalma et al., 2013; Lim and Turpin, 2015); (iii) dimer cluster formation from carboxylic acids (Hoffmann et al., 1998; Tobias and Ziemann, 2000; Claeys et al., 2009; Camredon et al., 2010; DePalma et al., 2013); (iv) reactions of Criegee intermediates (CIs) with VOCs oxidation products (Bonn et al., 2002; Lee and Kamens, 2005; Tolocka et al., 2006; Heaton et al., 2007; Witkowski and Gierczak, 2012; Kristensen et al., 2016; Wang et al., 2016); and (v) reactions of RO_2 radicals

Table 1. Possible identities of the ROOH in α -pinene SOA.

m/z ($[M + NH_4^+]^+$)	Molecular weight (MW)	Chemical structure
174	156	
190	172	
202	184	
206	188	
218	200	
220	202	
232	214	

with Cis (Sadezky et al., 2008; Zhao et al., 2015). Among them, the reactions of CIs with protic substances (water, alcohols, acids and hydroperoxides) can form ROOH. However, the nature of the ROOH products observed in SOA material suggests that these reactions do not take place to a significant extent given that ROOH do not contribute significantly to the dimer and trimer SOA signals (Fig. 5b). The similar mass patterns for the SOA and ROOH obtained under dry ($RH < 5\%$) and humid ($RH = 50\%$) conditions support this conclusion (Fig. S9). Of course, we can not rule out that the oligomeric ROOH may not be sensitive with the analytical method used. Additionally, while the ROOH formation mechanisms are proposed via gas-phase ozonolysis of α -pinene (Fig. S8), the ROOH observed in the SOA could

also potentially be arising from the decomposition of perox-hemiacetals during methanol extraction.

In the neutral loss scan mode, the LOD were measured to be 0.2, 0.3 and 20 mM for 2-butanone peroxide, cumene hydroperoxide and *tert*-butyl hydroperoxide, respectively. The LODs obtained by this method are a rough estimation and will vary dependent on a number of parameters: ionization voltage, sample injection flow, gas flow, CID gas pressure, CID voltages etc. More importantly, if a specific ROOH is to be analyzed, then multiple reaction monitoring mode would be applied and the LOD of the ROOH would be substantially reduced.

4 Conclusions

Organic hydroperoxides are molecules of crucial importance to atmospheric chemistry, arising under VOC oxidation schemes that proceed under low- NO_x conditions. Indeed, as NO_x levels continue to drop throughout many parts of the atmosphere through emission control measures, it is expected that these species will become even more prevalent. Furthermore, many of these ROOH molecules are known to constitute an important component of secondary organic aerosol material. Once in atmospheric particles, ROOH can participate in condensed-phase reactions, including nucleophilic processes and photolysis, and they are likely harmful when deposited into lung fluid.

A major complication in the study of ROOH chemistry has been the lack of detection techniques that are able to identify different ROOH species. In this work we present an off-line method for the identification of aqueous-phase ROOH molecules which involves first ionization by adduct formation with ammonium ions and then collision-induced dissociation by a unique fragmentation pathway involving the simultaneous loss of both NH_3 and H_2O_2 . Although only a fraction of the total ion fragmentation pathway involves 51 Da neutral loss, the specificity of the tandem mass spectrometry approach will yield low detection limits.

We illustrate the utility of this analytical method by demonstrating that a set of ROOH molecules is present in α -pinene ozonolysis SOA, all arising from known oxidation mechanisms. Perhaps most interestingly, ROOH species were not observed to be present in the oligomeric fraction of α -pinene ozonolysis SOA, indicating that reactions such as Criegee radicals reacting with protic substances are not a source of such dimeric and trimeric molecules (Lim and Turpin, 2015). In this manner, we believe that this new analytical approach could be used widely to decipher the prevalence of ROOH molecules in different forms of SOA. Given the specificity of the method, it could also be used to monitor the kinetics of condensed-phase reactions of individual ROOH molecules.

Although this work focused on the use of this new analytical method to analyze for atmospheric ROOH molecules,

it could equally well be applied to the detection of ROOH molecules in other systems, especially biological ones.

Data availability. Data are available upon request from Jonathan P. D. Abbatt (jabbatt@chem.utoronto.ca).

The Supplement related to this article is available online at <https://doi.org/10.5194/amt-11-3081-2018-supplement>.

Competing interests. The authors declare that they have no conflict of interest.

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References

- Agon, V. V., Bubb, W. A., Wright, A., Hawkins, C. L., and Davies, M. J.: Sensitizer-mediated photooxidation of histidine residues: evidence for the formation of reactive side-chain peroxides, *Free Radical Bio. Med.*, 46, 698–710, 2006.
- Aljawhary, D., Lee, A. K. Y., and Abbatt, J. P. D.: High-resolution chemical ionization mass spectrometry (ToF-CIMS): application to study SOA composition and processing, *Atmos. Meas. Tech.*, 6, 3211–3224, <https://doi.org/10.5194/amt-6-3211-2013>, 2013.
- Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103, 4605–4638, 2003.
- Bach, R. D., Ayala, P. Y., and Schlegel, H. B.: A reassessment of the bond dissociation energies of peroxides. An *ab Initio* study, *J. Am. Chem. Soc.*, 118, 12857–12765, 1996.
- Banerjee, D. K. and Budke, C. C.: Spectrophotometric determination of traces of peroxides in organic solvents, *Anal. Chem.*, 36, 792–796, 1964.
- Bonn, B., Schuster, G., and Moortgat, G. K.: Influence of water vapor on the process of new particle formation during monoterpene ozonolysis, *J. Phys. Chem. A*, 106, 2869–2881, 2002.
- Bonn, B., von Kuhlmann, R., and Lawrence, M. G.: High contribution of biogenic hydroperoxides to secondary organic aerosol formation, *Geophys. Res. Lett.*, 31, L10108, <https://doi.org/10.1029/2003GL019172>, 2004.
- Camredon, M., Hamilton, J. F., Alam, M. S., Wyche, K. P., Carr, T., White, I. R., Monks, P. S., Rickard, A. R., and Bloss, W. J.: Distribution of gaseous and particulate organic composition during dark α -pinene ozonolysis, *Atmos. Chem. Phys.*, 10, 2893–2917, <https://doi.org/10.5194/acp-10-2893-2010>, 2010.
- Claeys, M., Iinuma, Y., Szmigielski, R., Surratt, J. D., Blockhuys, F., Van Alsenoy, C., Böge, O., Sierau, B., Gomez-Gonzalez, Y., Vermeylen, R., Van Der Veken, P., Shahgholi, M., Chan, A. W. H., Herrmann, H., Seinfeld, J. H., and Maenhaut, W.: Terpenylic acid and related compounds from the oxidation of α -pinene: Implications for new particle formation and growth above forests, *Environ. Sci. Technol.*, 43, 6976–6982, 2009.
- DePalma, J. W., Horan, A. J., Hall, W. A., and Johnston, M. V.: Thermodynamics of oligomer formation: implications for secondary organic aerosol formation and reactivity, *Phys. Chem. Chem. Phys.*, 15, 6935–6944, 2013.
- Docherty, K. S., Wu, W., Lim, Y. B., and Ziemann, P. J.: Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O₃, *Environ. Sci. Technol.*, 39, 4049–4059, 2005.
- Francois, S., Sowka, I., Monod, A., Temime-Roussel, B., Laugier, J. M., and Wortham, H.: Development of an online analyzer of atmospheric H₂O₂ and several organic hydroperoxides for field campaigns, *Atmos. Res.*, 74, 525–545, 2005.
- Gebicki, S. and Gebicki, J. M.: Formation of peroxides in amino acids and proteins exposed to oxygen free radicals, *Biochem. J.*, 289, 743–749, 1993.
- Hall, W. A. and Johnston, M. V.: Oligomer formation pathways in secondary organic aerosol from MS and MS/MS measurements with high mass accuracy and resolving power, *J. Am. Soc. Mass Spectr.*, 23, 1097–1108, 2012.
- Hasson, A. S., Ho, A. W., Kuwata, K. T., and Paulson, S. E.: Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes. 2. Asymmetric and biogenic alkenes, *J. Geophys. Res.*, 106, 34143–34153, 2001.
- Heaton, K. J., Dreyfus, M. A., Wang, S., and Johnston, M. V.: Oligomer in the early stage of biogenic secondary organic aerosol formation and growth, *Environ. Sci. Technol.*, 41, 6129–6136, 2007.
- Hoffmann, T., Bandur, R., Marggraf, U., and Linscheid, M.: Molecular composition of organic aerosols formed in the α -pinene/O₃ reaction: implication for new particle formation processes, *J. Geophys. Res.*, 103, 25569–25578, 1998.
- Holcapek, M., Jirasko, R., and Lisa, M.: Basic rules for the interpretation of atmospheric pressure ionization mass spectra of small molecules, *J. Chromatogr. A*, 1217, 3908–3921, 2010.
- Hong, S. B., Kim, G. S., Kang, C. H., and Lee, J. H.: Measurement of ambient hydroperoxides using an automated HPLC system and various factors which affect variations of their concentrations in Korea, *Environ. Monit. Assess.*, 147, 23–34, 2008.
- Hui, S.-P., Sakurai, T., Ohkawa, F., Furumaki, H., Jin, S., Fuda, H., Takeda, S., Kurosawa, T., and Chiba, H.: Detection and characterization of cholesteryl ester hydroperoxides in oxidized LDL and oxidized HDL by use of an Orbitrap mass spectrometer, *Anal. Bioanal. Chem.*, 404, 101–112, 2012a.
- Hui, S.-P., Taguchi, Y., Takeda, S., Ohkawa, F., Sakurai, T., Yamaki, S., Jin, S., and Fuda, H.: Quantitative determination of phosphatidylcholine hydroperoxides during copper oxidation of LDL and HDL by liquid chromatography/mass spectrometry, *Anal. Bioanal. Chem.*, 403, 1831–1840, 2012b.
- Jackson, A. V. and Hewitt, C. N.: Atmospheric hydrogen peroxide and organic hydroperoxides: A review, *Environ. Sci. Technol.*, 29, 175–228, 1999.

- Jenkin, M. E.: Modelling the formation and composition of secondary organic aerosol from α - and β -pinene ozonolysis using MCM v3, *Atmos. Chem. Phys.*, 4, 1741–1757, <https://doi.org/10.5194/acp-4-1741-2004>, 2004.
- Jenkin, M. E., Shallcross, D. E., and Harvey, J. N.: Development and application of a possible mechanism for the generation of cis-pinic acid from the ozonolysis of α - and β -pinene, *Atmos. Environ.*, 34, 2837–2850, 2000.
- Krapf, M., Haddad, I. E., Bruns, E. A., Molteni, U., Daellenbach, K. R., Prevot, A. S. H., Baltensperger, U., and Dommen, J.: Labile peroxides in secondary organic aerosol, *Chemistry*, 1, 603–616, 2016.
- Kristensen, K., Cui, T., Zhang, H., Gold, A., Glasius, M., and Surratt, J. D.: Dimers in α -pinene secondary organic aerosol: effect of hydroxyl radical, ozone, relative humidity and aerosol acidity, *Atmos. Chem. Phys.*, 14, 4201–4218, <https://doi.org/10.5194/acp-14-4201-2014>, 2014.
- Kristensen, K., Watne, Å. K., Hammes, J., Lutz, A., Petäjä, T., Halqu Coast, M., Bilde, M., and Glasius, M.: High-molecular weight dimer esters are major products in aerosols from α -pinene ozonolysis and the boreal forest, *Environ. Sci. Tech. Lett.*, 3, 280–285, 2016.
- Larsen, B. R., Di Bella, D., Glasius, M., Winterhalter, R., Jensen, N. S., and Hjorth, J.: Gas-phase OH oxidation of monoterpenes: gaseous and particulate products, *J. Atmos. Chem.*, 38, 231–276, 2001.
- Lee, M., Heikes, B. G., and O'Sullivan, D. W.: Hydrogen peroxide and organic hydroperoxide in the troposphere: A review, *Atmos. Environ.*, 34, 3475–3494, 2000.
- Lee, S. and Kamens, R. M.: Particle nucleation from the reaction of α -pinene and O₃, *Atmos. Environ.*, 39, 6822–6832, 2005.
- Lim, Y. B. and Turpin, B. J.: Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the aqueous phase and implications for aqueous OH, *Atmos. Chem. Phys.*, 15, 12867–12877, <https://doi.org/10.5194/acp-15-12867-2015>, 2015.
- Liou, G.-Y. and Storz, P.: Reactive oxygen species in cancer, *Free Radical Res.*, 44, 479–496, <https://doi.org/10.3109/10715761003667554>, 2010.
- Moll, C., Biermann, U., and Grosch, W.: Occurrence and formation of bitter-tasting trihydroxy fatty acids in soybeans, *J. Agr. Food Chem.*, 27, 239–243, 1979.
- Morgan, P. M., Pattison, D. I., Hawkins, C. L., and Davies, M. J.: Separation, detection, and quantification of hydroperoxides formed at side-chain and backbone sites on amino acids, peptides, and proteins, *Free Radical Bio. Med.*, 45, 1279–1289, 2008.
- Muller, L., Reinnig, M. C., Hayen, H., and Hoffmann, T.: Characterization of oligomeric compounds in secondary organic aerosol using liquid chromatography coupled to electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, *Rapid Commun. Mass Sp.*, 23, 971–979, 2009.
- Nakamura, T. and Maeda, H.: A simple assay for lipid hydroperoxides based on triphenylphosphine oxidation and high-performance liquid chromatography, *Lipids*, 26, 765–768, 1991.
- Nilsson, J., Carlberg, J., Abrahamsson, P., Hulthe, G., Persson, B. A., and Karlberg, A. T.: Evaluation of ionization techniques for mass spectrometric detection of contact allergenic hydroperoxides formed by autoxidation of fragrance terpenes, *Rapid Commun. Mass Sp.*, 22, 3593–3598, 2008.
- Odian, G.: Principles of Polymerization, 4th ed., Wiley-Interscience, New York, USA, 2004.
- Reile, I., Paju, A., Müürisepp, A.-M., Pehk, T., and Lopp, M.: Oxidation of cyclopentane-1,2-dione: a study with ¹⁸O labeled reagents, *Tetrahedron*, 67, 5942–5948, 2011.
- Reinnig, M. C., Mueller, L., Warnke, J., and Hoffmann, T.: Characterization of selected organic compound classes in secondary organic aerosol from biogenic VOCs by HPLC/MSn, *Anal. Bioanal. Chem.*, 391, 171–182, 2008.
- Reinnig, M. C., Warnke, J., and Hoffmann, T.: Identification of organic hydroperoxides and hydroperoxy acids in secondary organic aerosol formed during the ozonolysis of different monoterpenes and sesquiterpenes by on-line analysis using atmospheric pressure chemical ionization ion trap mass spectrometry, *Rapid Commun. Mass Sp.*, 23, 1735–1741, 2009.
- Riva, M., Budisulistiorini, S. H., Zhang, Z., Gold, A., Thornton, J. A., Turpin, B. J., and Surratt, J. D.: Multiphase reactivity of gaseous hydroperoxide oligomers produced from isoprene ozonolysis in the presence of acidified aerosols, *Atmos. Environ.*, 152, 314–322, 2017.
- Rivera-Rios, J. C., Nguyen, T. B., Crouse, J. D., Jud, W., St. Clair, J. M., Mikoviny, T., Gilman, J. B., Lerner, B. M., Kaiser, J. B., de Gouw, J., Wisthaler, A., Hansel, A., Wennberg, P. O., Seinfeld, J. H., and Keutsch, F. N.: Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation: Observational bias in diagnosing pristine versus anthropogenically controlled atmospheric chemistry, *Geophys. Res. Lett.*, 41, 8645–8651, 2014.
- Rondeau, D., Vogel, R., and Tabet, J. C.: Unusual atmospheric pressure chemical ionization conditions for detection of organic peroxides, *J. Mass Spectrom.*, 38, 931–940, 2003.
- Sadezky, A., Winterhalter, R., Kanawati, B., Römpf, A., Spengler, B., Mellouki, A., Le Bras, G., Chaimbault, P., and Moortgat, G. K.: Oligomer formation during gas-phase ozonolysis of small alkenes and enol ethers: new evidence for the central role of the Criegee Intermediate as oligomer chain unit, *Atmos. Chem. Phys.*, 8, 2667–2699, <https://doi.org/10.5194/acp-8-2667-2008>, 2008.
- Sakamoto, Y., Yajima, R., Inomata, S., and Hirokawa, J.: Water vapour effects on secondary organic aerosol formation in isoprene ozonolysis, *Phys. Chem. Chem. Phys.*, 19, 3165–3175, 2017.
- Tobias, H. J. and Ziemann, P. J.: Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids, *Environ. Sci. Technol.*, 34, 2105–2115, 2000.
- Tolocka, M. P., Jang, M., Ginter, J. M., Cox, F. J., Kamens, R. M., and Johnston, M. V.: Formation of oligomers in secondary organic aerosol, *Environ. Sci. Technol.*, 38, 1428–1434, 2004.
- Tolocka, M. P., Heaton, K. J., Dreyfus, M. A., Wang, S. Y., Zordan, C. A., Saul, T. D., and Johnston, M. V.: Chemistry of particle inception and growth during α -pinene ozonolysis, *Environ. Sci. Technol.*, 40, 1843–1848, 2006.
- Valverde-Canossa, J., Wieprecht, W., Acker, K., and Moortgat, G. K.: H₂O₂ and organic peroxide measurements in an orographic cloud: The FEBUKO experiment, *Atmos. Environ.*, 39, 4279–4290, 2005.

- Venkatachari, P. and Hopke, P. K.: Characterization of products formed in the reaction of ozone with α -pinene: Case for organic peroxides, *J. Environ. Monitor.*, 10, 966–974, 2008.
- Walker, S. J., Evans, M. J., Jackson, A. V., Steinbacher, M., Zellweger, C., and McQuaid, J. B.: Processes controlling the concentration of hydroperoxides at Jungfrauoch Observatory, Switzerland, *Atmos. Chem. Phys.*, 6, 5525–5536, <https://doi.org/10.5194/acp-6-5525-2006>, 2006.
- Wang, M., Yao, L., Zheng, J., Wang, X., Chen, J., Yang, X., Worsnop, D. R., Donahue, N. M., and Wang, L.: Reactions of atmospheric particulate stabilized Criegee intermediates lead to high-molecular-weight aerosol components, *Environ. Sci. Technol.*, 50, 5702–5710, 2016.
- Wasylaschuk, W. R., Harmon, P. A., Wagner, G., Harman, A. B., Templeton, A. C., Xu, H., and Reed, R. A.: Evaluation of hydroperoxides in common pharmaceutical excipients, *J. Pharm. Sci.*, 96, 106–116, 2007.
- Witkowski, B. and Gierczak, T.: Early stage composition of SOA produced by α -pinene/ozone reaction: α -Acyloxyhydroperoxy aldehydes and acidic dimers, *Atmos. Environ.*, 95, 59–70, 2014.
- Wright, A., Bubb, W. A., Haekins, C. L., and Davis, M. J.: Singlet oxygen-mediated protein oxidation: Evidence for the formation of reactive side chain peroxides on tyrosine residues, *Photochem. Photobiol.*, 76, 35–46, 2002.
- Yasmeen, F., Vermeylen, R., Szmigielski, R., Iinuma, Y., Böge, O., Herrmann, H., Maenhaut, W., and Claeys, M.: Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of α - and β -pinene, *Atmos. Chem. Phys.*, 10, 9383–9392, <https://doi.org/10.5194/acp-10-9383-2010>, 2010.
- Zhang, X., McVay, R. C., Huang, D. D., Dalleska, N. K., Aumont, B., Flagan, R. C., and Seinfeld, J. H.: Formation and evolution of molecular products in α -pinene secondary organic aerosol, *P. Natl. Acad. Sci. USA*, 112, 14168–14173, 2015.
- Zhang, X., Lambe, A. T., Upshur, M. A., Brooks, W. A., Be, A. G., Thomson, R. J., and Geiger, F. M.: Highly oxygenated multifunctional compounds in α -pinene secondary organic aerosol, *Environ. Sci. Technol.*, 51, 5932–5940, 2017.
- Zhao, R., Lee, A. K. Y., Soong, R., Simpson, A. J., and Abbatt, J. P. D.: Formation of aqueous-phase α -hydroxyhydroperoxides (α -HHP): potential atmospheric impacts, *Atmos. Chem. Phys.*, 13, 5857–5872, <https://doi.org/10.5194/acp-13-5857-2013>, 2013.
- Zhao, Y., Wingen, L. M., Perraud, V., Greaves, J., and Finlayson-Pitts, B. J.: Role of the reaction of stabilized Criegee intermediates with peroxy radicals in particle formation and growth in air, *Phys. Chem. Chem. Phys.*, 17, 12500–12514, 2015.
- Ziemann, P. J.: Formation of alkoxyhydroperoxy aldehydes and cyclic peroxyhemiacetals from reactions of cyclic alkenes with O_3 in the presence of alcohols, *J. Phys. Chem. A*, 107, 2048–2060, 2003.