

Mimicking the atmospheric OH-radical-mediated photooxidation of isoprene: formation of cloud-condensation nuclei polyols monitored by electrospray ionization mass spectrometry

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Recently, it has been proposed (M. Claeys et al., *Science* 2004; 303: 1173) that the atmospheric OH-radical-mediated photooxidation of isoprene is a source of two major secondary organic aerosol (SOA) components, that is, 2-methylthreitol and 2-methylerythritol. These diastereoisomeric tetrols, which were characterized for the first time in the fine size fraction (<2.5 μm aerodynamic diameter) of aerosols collected in the Amazon rain forest during the wet season, were proposed to enhance the capability of the aerosols to act as cloud-condensation nuclei. In the present study, we performed the oxidation of isoprene in aqueous solution under conditions that attempted to mimic atmospheric OH-radical-induced photooxidation, and monitored and characterized on-line the reaction products via electrospray ionization mass (and tandem mass) spectrometry in the negative ion mode. The results show that the reaction of isoprene with photo- or chemically generated hydroxyl radicals indeed yields 2-methyltetrols. Other polyols were also detected, and they may therefore be considered as plausible SOA components eventually formed in normal or more extreme OH-radical-mediated photooxidation of biogenic isoprene. Copyright © 2006 John Wiley & Sons, Ltd.

Recently, detailed analysis of natural atmospheric aerosols collected in the Amazon rain forest during the wet season identified two unprecedented components of secondary organic aerosol (SOA): a diastereoisomeric mixture of 2-methylthreitol and 2-methylerythritol.^{1,2} This polar, hygroscopic and low vapor pressure isomeric pair of C₅ polyols was proposed to participate in the formation of new atmospheric particles and haze above forests and to enhance the capability of the aerosols to act as cloud-condensation nuclei. Owing to their C₅ skeleton, the 2-methyltetrols **2** were proposed to be formed by OH-radical-mediated photooxidation of isoprene via diols **1** (Scheme 1). The exact photooxidation mechanism(s) by which isoprene is converted in the atmosphere into 2-methyltetrols is (are) however still unclear at present, and gas-phase as well as mixed-phase mechanisms involving the aqueous aerosol phase have been considered. Subsequent to the field identification of 2-methyltetrols, it was shown in a laboratory study³ that isoprene could be converted in aqueous solution into 2-methyltetrols through an acid-catalyzed reaction with

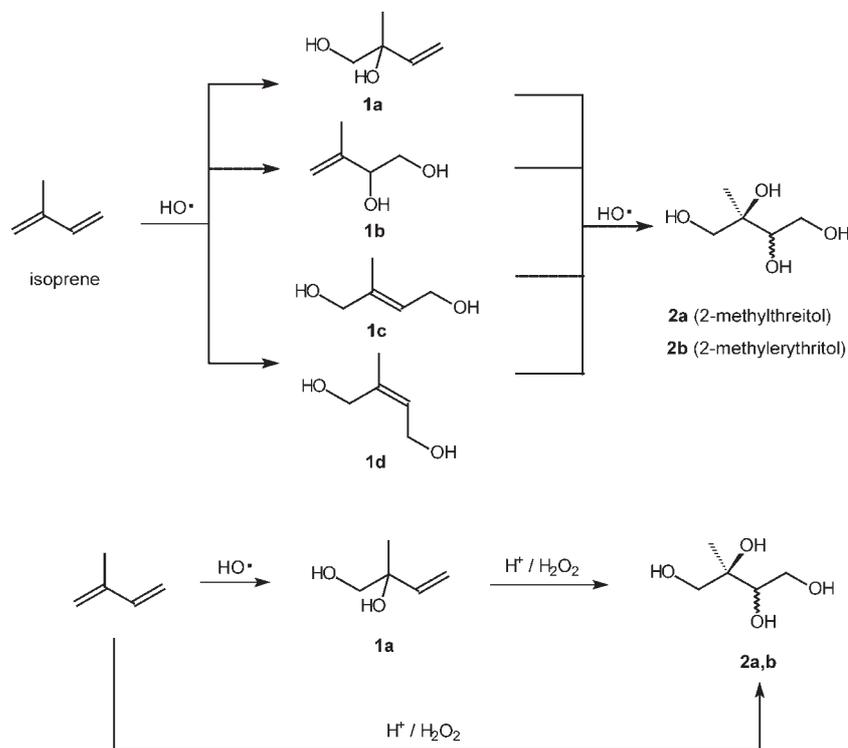
hydrogen peroxide, which is formed in the atmosphere via recombination of hydroperoxy radicals. This crucial role for isoprene is relevant considering that it is a major biogenic volatile organic compound with an annual global production estimated at about 500 teragrams and representing almost 50% of all biogenic non-methane hydrocarbons.^{4,5} More recently, the field identification of 2-methyltetrols has motivated smog chamber studies¹ in which isoprene was re-examined as a key precursor for SOA production and in which the potential use of the 2-methyltetrols **2** as molecular markers for air quality monitoring was addressed.

Previously, the photooxidation of isoprene in the atmosphere has been thought to result only in lighter and volatile products such as formaldehyde, methacrolein, and methyl vinyl ketone, but not in polar products that can give rise to aerosols by gas-to-particle formation processes.^{4,5} Under simulated atmospheric conditions, photooxidation of isoprene by ozone was shown to be relatively slow and to occur mainly via reaction with OH radicals.⁶ Furthermore, when the OH-radical-initiated photooxidation of isoprene was investigated in the absence of NO_x, the formation of 1,2-diol derivatives **1** was observed (Scheme 1).⁷ Note that isoprene and its 1,2-diol derivatives have been shown to serve as

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Scheme 1. Possible formation pathways of the 2-methyltetrols **2** via atmospheric photooxidation of isoprene. For more details on the gas-phase pathway involving OH radicals, see Refs. 1 and 2. For more details on the alternative pathways involving reactions in the aqueous aerosol phase, see Refs. 3 and 8.

possible precursors for the 2-methyltetrols in the recent smog chamber study by Boege *et al.*,⁸ which was performed at a high relative humidity (>45%) and used hydrogen peroxide as oxidant and acidic seed particles. The yields observed for the 1,2-diol derivatives **1** were higher than with isoprene itself, lending support to the hypothesis that 1,2-diol derivatives formed in the gas phase by OH-radical-induced reactions could be further oxidized in the aerosol liquid phase.

Molecular analysis by mass spectrometry (MS) has greatly benefited from the development of electrospray ionization (ESI).⁹ This innovative technique has enabled the ionization of a great variety of molecules of high polarity, molecular complexity or mass.^{10–13} ESI-MS(/MS) has been effectively applied to elucidate reaction mechanisms,¹³ especially of polar (basic or acidic) or ionic components in polar solutions, via detection and identification of major products and intermediates.^{13–19} To investigate further the possible role of isoprene in the formation of the SOA marker compounds, i.e. the 2-methyltetrols **2** in the liquid-phase atmospheric aerosol, we decided to use ESI-MS(/MS) with its exceptionally advantageous features to monitor on-line both the photo- and chemically initiated OH-radical-mediated oxidation of isoprene in aqueous solution.

EXPERIMENTAL

All the experiments were performed in a high-resolution hybrid double quadrupole (Qq) and orthogonal time-of-

flight (TOF) mass spectrometer (Qtof, Micromass UK). The temperature of the nebulizer was 50°C. The ESI source and the mass spectrometer were operated in the negative-ion mode. The cone and extractor potential were set to 40 and 10 V, respectively. The scan range was m/z 50–1000. The reaction between isoprene and chemically generated OH radicals was performed by mixing 5 mL of 30% H₂O₂, 1 mL of isoprene, 10 mg of AIBN, and 20 mL of distilled water. The resulting mixture was then maintained under continuous and vigorous stirring. The photooxidation of isoprene was conducted by exposing a mixture of 30% H₂O₂ (5 mL), isoprene (5 mL), and distilled water (20 mL) to a 15 W UV lamp (with a wavelength of 254 nm) under continuous and vigorous stirring. No precaution was taken to remove oxygen from the system. Upon decantation, a small portion of the aqueous phase was collected, by using a microsyringe, and introduced directly into the ESI-MS source at a flow rate of 0.01 mL/min.

RESULTS AND DISCUSSION

Photo- and AIBN-initiated H₂O₂ oxidation of isoprene

Figure 1(a) displays a representative ESI(–) spectrum acquired after a reaction time of 10 min for the solution in which reactions are taking place between isoprene and hydroxyl radicals generated via the decomposition of H₂O₂ by AIBN.²⁰ Note that the ESI(–) spectrum for the H₂O₂ photooxidation of isoprene (not shown) also displayed a

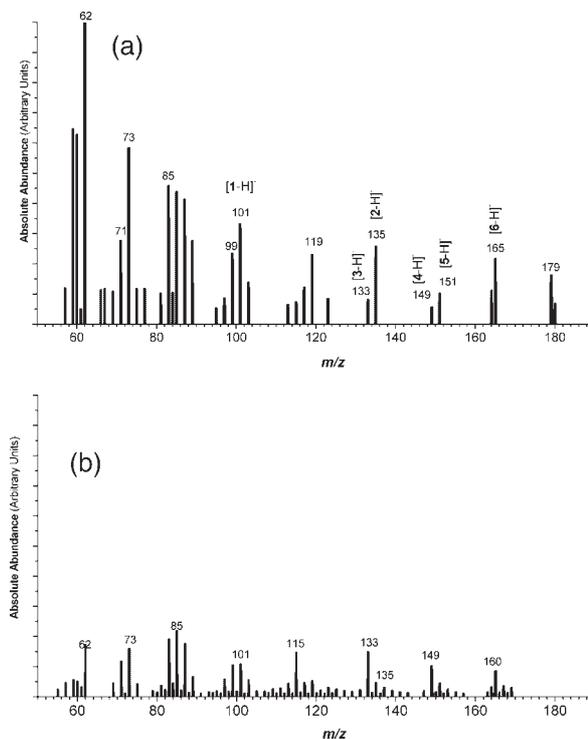


Figure 1. (a) ESI(-) spectrum for the aqueous solution in which reactions occur between isoprene and hydroxyl radicals, chemically generated via decomposition of H_2O_2 by AIBN, after a reaction time of 10 min. (b) ESI(-) spectrum for the aqueous solution in which reactions occur between isoprene and H_2O_2 in aqueous solution and in the absence of light, after a reaction time of 3 h. To allow a more consistent comparison, the absolute abundance scales in both spectra are the same.

similar set of anionic products, i.e. major ions of m/z 101, 119, 133, 135, 149, 151, and 165, but after longer reaction times.

After a reaction time of 5 to 10 min, ESI(-)-MS detects clearly an ion of m/z 135. This anion probably arises via the deprotonation of the diastereoisomeric 2-methyltetrols **2**, which is probably formed under these reaction conditions. High accuracy m/z measurement shows good agreement between the experimental (135.0595) and theoretical (135.0617) m/z values for $[\mathbf{2} - \text{H}]^-$ of chemical composition $\text{C}_5\text{H}_{11}\text{O}_4$.

For structural characterization, ESI(-)-MS/MS²¹ experiments were performed. The ion of m/z 135 was mass-selected by Q1 and subsequently submitted to collision-induced dissociation (CID) with argon in the hexapole collision cell with the product ions being analyzed by the high-resolution orthogonal TOF analyzer (Fig. 2(a)). A series of product ions formed mainly by losses of H_2 (m/z 133), H_2O (m/z 117), $\text{H}_2\text{O} + \text{H}_2$ (m/z 115), CH_3OH (m/z 103), $\text{CH}_3\text{OH} + \text{H}_2$ (m/z 101), $2 \times \text{H}_2\text{O}$ (m/z 99), $\text{H}_2\text{O} + \text{CO}$ (m/z 89), $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ (m/z 85), $3 \times \text{H}_2\text{O}$ (m/z 81), and $2 \times \text{CH}_3\text{OH}$ (m/z 71) is evident. These diverse dissociation pathways of $[\mathbf{2} - \text{H}]^-$, particularly the sequential losses of water and methanol molecules, are therefore consistent with the alleged formation and detection of compounds **2** (Scheme 2). Even more conclusive is the close similarity of the ESI(-) tandem mass spectrum of the

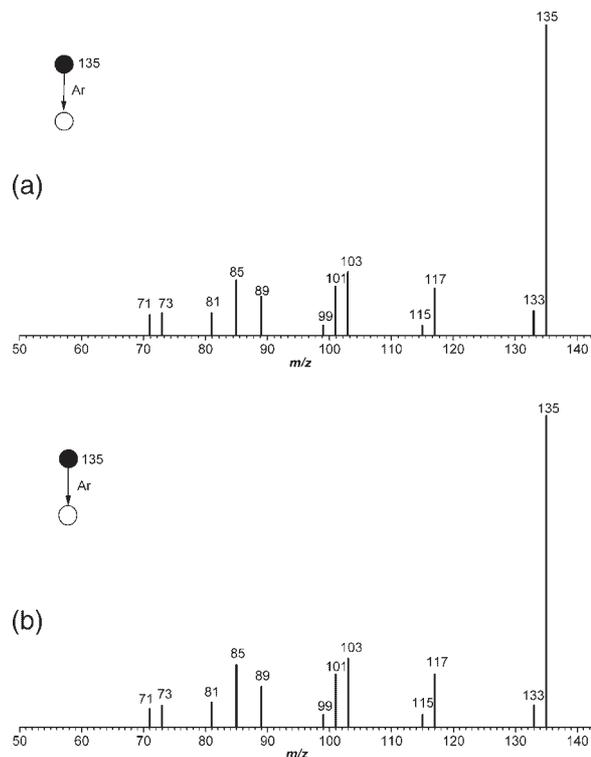
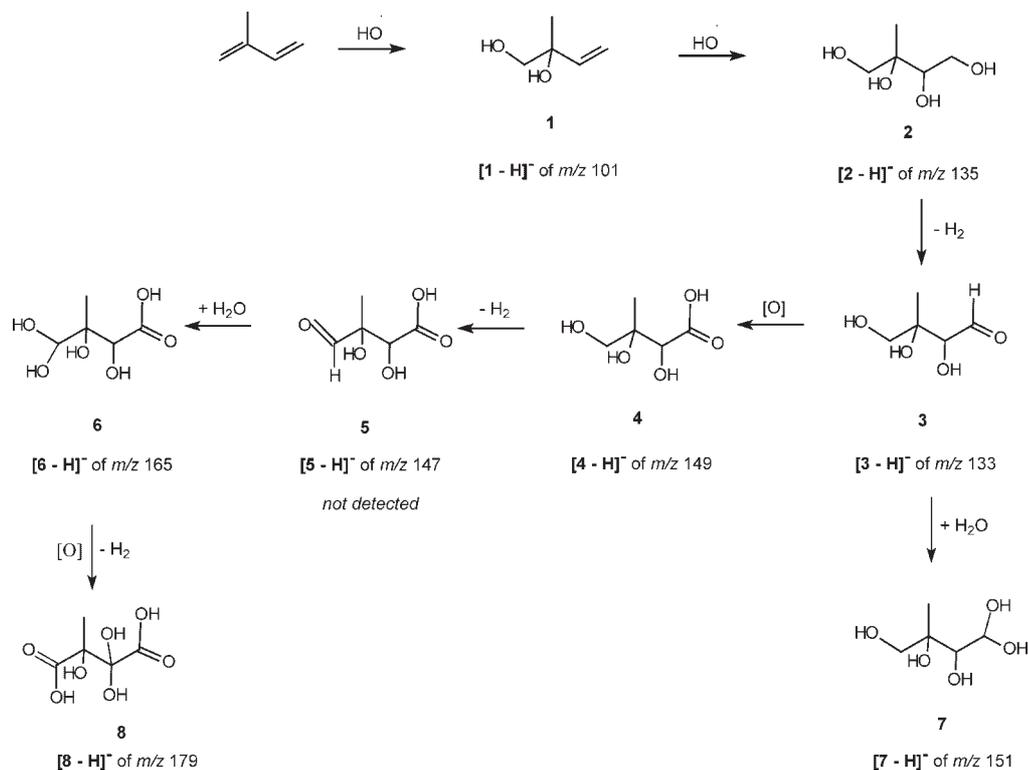


Figure 2. ESI(-) tandem mass spectra of (a) the ion of m/z 135 attributed to $[\mathbf{2} - \text{H}]^-$ from the reaction of isoprene with chemically generated (AIBN- H_2O_2) hydroxyl radicals (see Fig. 1) and (b) from a solution of authentic **2**.

ion of m/z 135 (Fig. 2(a)) with that of the authentic $[\mathbf{2} - \text{H}]^-$ from an aqueous solution of genuine **2** (Fig. 2(b)).²²

To verify whether the anionic products (as observed in the spectrum of Fig. 1(a)) could alternatively originate from the oxidation of AIBN by H_2O_2 , a blank experiment was conducted in which the reaction between both compounds in aqueous solution was continuously monitored. However, only non-coincident product ions, with lower m/z values, were detected in the corresponding ESI(-) spectrum (not shown). Another control experiment, in which reactions were performed between isoprene and H_2O_2 in aqueous solution and in the absence of light, was conducted to verify the effect of AIBN on the reaction rate and product distribution. The ESI(-)-MS spectrum for this solution (Fig. 1(b)), obtained after a reaction time of 3 h, shows the presence of a similar set of anionic products as seen in Fig. 1(a), although in much smaller abundance. This result thus confirms that hydroxyl radicals, also formed in these milder conditions, do react with isoprene to yield the corresponding oxygenated products, even in the absence of light or a strong initiator such as AIBN.

Other relevant ions in the spectrum of Fig. 1(a) are those of m/z 101, which probably correspond to the diols **1** in their deprotonated forms ($[\mathbf{1} - \text{H}]^-$), and of m/z 119, probably the water adducts of $[\mathbf{1} - \text{H}]^-$. As proposed in Schemes 1 and 2, diols **1** are intermediates in the formation of the 2-methyltetrols **2**. Again, good agreement is observed between the measured (101.0584) and calculated (101.0603) m/z values for $[\mathbf{1} - \text{H}]^-$ of chemical composition $\text{C}_5\text{H}_9\text{O}_2$.



Scheme 2. Proposed route for the formation of the oxygenated products 1–8 in the reaction of isoprene with hydroxyl radicals, generated by the AIBN decomposition of H_2O_2 .

Likewise, the ESI(–)-MS detection of the anions of m/z 133, 149, 165, 151, and 179 (Fig. 1(a)) suggests the formation of other polyoxygenated products such as 3, 4, 6, 7, and 8, respectively, as proposed in Scheme 2. As expected, for longer reaction times, the abundance of the ions of m/z 133, 149, 151, 165, and 179 continuously increases whereas that of the ions of m/z 101 and 135 simultaneously decreases (spectra not shown). This variation in ion abundances is likely related to the consumption of precursors 1 and 2 and formation of the polyoxygenated products 3–8 via further oxidation of 2. In Scheme 2 we suggest that one of the CH_2OH groups of 2 is oxidized to form aldehyde 3, which can be easily converted into carboxylic acid 4. Subsequent oxidation of the CH_2OH moiety of 4 is suggested to produce 5, whose deprotonated form of m/z 147 was unfortunately not detected in the spectrum of Fig. 1(a). The hydrates 6 and 7, which are possibly stable species in aqueous solution, are proposed to be formed via the common nucleophilic addition of water at the reactive carbon of the aldehyde carbonyl of 5 and 3, respectively.²³ Note also that the structures for 3–8 are chemically reasonable based on classical OH-radical-mediated oxidation reactions,²⁴ but other possible isomeric structures (and other likely pathways leading to them) can also be proposed. The ESI(–) tandem mass spectra of deprotonated 3–8 (not shown) also show dissociations characteristic of polyhydroxylated carboxylic acids. The presumed $[6 - H]^-$ ion of m/z 165 dissociates by the losses of a methyl radical (CH_3 , m/z 150), $CH_3 + H$ (m/z 149), $CH_3 + CO$ (m/z 122), and $CH_3 + CO_2$ (m/z 106). The ESI(–) tandem mass spectrum of $[7 - H]^-$ of m/z 151 shows the ion to dissociate mainly by losses of CH_3 (m/z 136) and $CH_3 + CO$ (m/z 108). Similarly, the ESI(–)-MS/MS spectrum of $[8 - H]^-$ of m/z 179 shows

fragments of m/z 164 (loss of CH_3) and 120 (loss of $CH_3 + CO_2$). Additionally, $[4 - H]^-$ of m/z 149 dissociates by the losses of H_2O (m/z 131), $CH_3OH + H_2$ (m/z 115), $CO + H_2O$ (m/z 103), and CH_3CO_2H (m/z 89), whereas $[3 - H]^-$ of m/z 133 dissociates by the losses of H_2O (m/z 115), $CO + H_2$ (m/z 103), and $CH_3OH + H_2$ (m/z 99). Furthermore, the experimental high accuracy m/z values of these ions show again good agreement with that calculated for the proposed polyols (only formulae based on carbon, hydrogen and oxygen were considered): $[3 - H]^-$ (found: 133.0455; calculated: 133.0501 for $C_5H_9O_4$), $[4 - H]^-$ (found: 149.0511; calculated: 149.0450 for $C_5H_9O_5$), $[6 - H]^-$ (found: 165.0325; calculated: 165.0309 for $C_5H_9O_6$), $[7 - H]^-$ (found: 151.0643; calculated: 151.0607 for $C_5H_{11}O_5$), and $[8 - H]^-$ (found: 179.0177; calculated: 179.0191 for $C_5H_7O_7$).

CONCLUSIONS

In conclusion, the OH-radical-mediated oxidation of isoprene by H_2O_2 in solution initiated either photochemically or by AIBN seems to mimic adequately the liquid-phase aerosol atmospheric oxidation of isoprene, as revealed by ESI(–)-MS(/MS) monitoring. The *in situ* detection and structural characterization of 2-methyltetrols 2, which were recently identified by Claeys *et al.*² in atmospheric aerosols of the Amazon forest and proposed to enhance the capability of aerosols to act as cloud-condensation nuclei, shows that isoprene is indeed, via reactions with OH radicals, a liable candidate for the precursor of the 2-methyltetrols, especially in such liquid-phase atmospheric aerosols. Other polyoxygenated compounds assigned as 1 (the diol precursors of 2), 3, 4, 6, 7, and 8 have also been intercepted and structurally characterized by ESI(–)-MS(/MS) monitoring. Products 3–8

are probably formed by further oxidation of **1** and **2**, and they may therefore be also considered as plausible SOA components eventually formed in normal or more extreme OH-radical-mediated photooxidation of biogenic isoprene. The present approach may also be useful in similar studies aimed at characterizing first-generation products of OH-radical-mediated oxidation of other atmosphere-relevant chemicals. A possible target is methacrolein, which is not inert in the atmosphere and may be further oxidized by dark photochemistry in the aqueous aerosol phase.³

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