Comment on “Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene”

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Paulot et al. (Reports, 7 August 2009, p. 730) reported that the photooxidation of isoprene under low-nitrogen oxides (NOx) conditions produces epoxides that can facilitate the formation of secondary organic aerosol (SOA). However, another pathway involving the formation of methyl-butenediol intermediates can also lead to isoprene-derived SOA formation. Further research is needed to clarify the fate of isoprene in the atmosphere.

Isoprene, a five-carbon diene emitted by deciduous plants, is the most abundant nonmethane hydrocarbon released into the atmosphere (~500 teragrams C/year) (1) and is thought to affect climate by acting as a source of atmospheric aerosols. 2-methyltetrols have been identified as major secondary organic aerosol (SOA) tracers of the photooxidation of isoprene under low-NOx conditions such as those encountered in the Amazon tropical rain forest during the wet season (2, 3), but it has been unclear what the immediate gas-phase precursors of the 2-methyltetrols are.

Paulot et al. (4) detected gas-phase photooxidation products of isoprene with a molecular weight of 118 and characterized them in detail using 18O-labeling (i.e., employing H218O as a precursor for the 18OH radical) and chemical ionization mass spectrometry (CIMS) techniques as second-generation photooxidation products and C5-epoxydiols (Fig. 1A). The authors presented a very elegant formation mechanism that is supported by quantum chemical calculations and that moreover regenerates the OH radical. However, a firm chemical proof is still needed to support a conclusion that the C5-epoxydiols are formed in the gas phase and act as the precursors for the 2-methyltetrols. A trapping experiment of the gas-phase products in acidified 18O-labeled water as proposed in Fig. 1A could shed light on this; detailed isotope analysis of the hydrolysyl products would provide the ultimate proof that the C5-epoxydiols formed in the gas phase are directly linked to the 2-methyltetrols generated in the particle phase.

The pathway first proposed by Claeys et al. (2) and recently modified in part by Kleindienst et al. (5), referred to as the classical pathway, remains a viable route leading to the 2-methyltetrols (Fig. 1B). This pathway involves two cycles of OH/NO2 reactions (2), disproportion of RO2 radicals after the first cycle (2, 6), and a radical terminating RO2 + HO2 → ROOH + O2 reaction after the second cycle (5). The detection of unstable SOA products from isoprene under low-NOx conditions, that is, 2-methyltetrol performat (3), hints that C5-trihydroxyhydroperoxides are potential precursors for the 2-methyltetrols. More specifically, in the gas chromatography–mass spectrometry (GC-MS) analysis with prior trimethylsilylation, the derivatives of 2-methyltetrol performat (which can be regarded as peroxymethylene acetic reaction products between formaldehyde and C5-trihydroxyhydroperoxides) are unstable in the derivatization reagent (N-methyl-N-trimethylsilyl-trifluoroacetamide:trimethylsilyl chloride; 100:1, v/v) that contains an acidic catalytic (i.e., HCl formed by hydrolysis of trimethylsilylchloride with traces of water) and are converted to trimethylsilylated 2-methyltetrols. Thus, in laboratory experiments or within the atmosphere, C5-trihydroxyhydroperoxides and derivatives thereof will, as with the C3-epoxydiols, not be stable and produce the 2-methyltetrols upon acid-catalyzed hydrolysis. In this respect, it has been shown that aliphatic hydroperoxides are unstable in acidic conditions and yield alcohols by elimination of hydrogen peroxide (7). Methylbutenediol intermediates formed through the classical pathway have been identified in low-NOx isoprene photooxidation experiments (5, 6) as well as in ambient samples (5), and have been shown to serve as precursors for the 2-methyltetrols (8). If the gas-phase formation of C3-epoxydiols were an important process in the photooxidation of isoprene under low-NOx conditions, it is hard to explain that these products escaped detection in the trimethylsilylation GC/MS analysis that was performed in a recent laboratory study on gas-phase denuder samples (5). The proposal that C3-trihydroxyhydroperoxides serve as the immediate precursors of the 2-methyltetrols can also readily be reconciled with the high organic peroxide content of isoprene SOA formed under low-NOx conditions in the presence of seed aerosol, which was estimated at one-quarter of the aerosol (3, 5).

In conclusion, we cannot rule out the possibility that the classical pathway involving gas-phase methyl-butenediol intermediates and formation of C5-trihydroxyhydroperoxides leads to the formation of 2-methyltetrols under low-NOx conditions. Detailed understanding of the underlying gas- and particle-phase reactions is still needed so that they can be incorporated into global models that are able to accurately predict SOA formation from isoprene. The secrets of the fate of isoprene in the atmosphere have been only partially unveiled, and more research is required.

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Fig. 1. (A) Formation of C5-epoxydiols and 2-methyltetrols, according to Paulot et al. (4), and proposal for an 18O-labeling experiment with H218O that allows one to directly link the formation of C5-epoxydiols in the gas phase to acid-catalyzed formation of 2-methyltetrols in the particle phase. (B) Formation of 2-methyltetrols through the classical pathway involving two cycles of OH/NO2 reactions, methyl butenediols as gas-phase intermediates, and C5-trihydroxyhydroperoxides as direct precursors. For simplicity, only one possible positional isomeric reaction product is presented for each of the reactions in both parts (A) and (B). Reactions occurring in the particle phase are highlighted in red.
needed to further unravel its complex photo-oxidation chemistry.

References

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