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

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Claeys questions whether gaseous epoxydiol is formed from the oxidation of isoprene and whether it is relevant to the formation of isoprene-derived secondary organic aerosol (iSOA). We argue that the alternative mechanism she proposes for iSOA applies primarily to chamber studies with high isoprene and is not as important in the atmosphere, where isoprene concentrations are much lower.

A large fraction of isoprene is oxidized in the atmosphere under pristine conditions [where the concentration of nitric oxide (NO) is low]. The lack of adequate understanding of its gaseous photooxidation under these conditions (1) has made it difficult to determine the mechanism and atmospheric yield of isoprene-derived secondary organic aerosol (iSOA). It is actually quite challenging to mimic remote atmospheric conditions in the laboratory. In the absence of NO, the peroxy radicals (RO2) formed in the atmosphere during photooxidation of isoprene react primarily with the hydroperoxyl radical (HO2), with a minor fraction reacting with other RO2 by cross-peroxy radical reactions (2). In many previous laboratory studies, however, high isoprene concentrations were used. Under such conditions, the chemistry is typically dominated by RO2+RO2 reactions (3–6). Under these very high isoprene concentrations, the yield of gaseous epoxydiol (IEPOX) would have been much smaller than in our study, resulting in a very different iSOA composition. The mechanism presented by Claeys (7) was derived to explain iSOA formation under these conditions (6).

In our study (8), we used a soft negative ionization mass spectrometry technique to probe the photochemistry of isoprene (9, 10). This technique is much more sensitive to the suite of products generated, allowing us to use much lower isoprene concentrations to obtain lower RO2 to HO2 ratios and thus mimic remote atmospheric conditions more closely ([11, 12] and Fig. 1). Consistent with the chemistry proceeding mostly by reaction of the RO2 with HO2, negligible concentrations of diol (the precursor of trihydroxyhydroperoxide), were measured while isoprene hydroperoxide (and, subsequently, IEPOX) formed with very large yields. As noted in (8), the identification of IEPOX is challenging because it is isobaric to the isoprene hydroperoxide. Tandem mass spectrometry, isotope-labeling experiments, and theoretical methods were employed to firmly identify IEPOX as well as its formation mechanism. Given the small predicted yield of IEPOX in most previous chamber experiments, its instability in the aerosol, and its unexpected formation mechanism, it may not come as a surprise that IEPOX has eluded identification until now.

The formation of gas-phase IEPOX in high yields provides a compelling iSOA precursor. Several investigators, including Claeys, had previously hypothesized the role of such compounds in SOA formation (13, 14). Consistent with the hypothesized role of these epoxides, we reported that the rapid uptake of a four-carbon analog of IEPOX into acidic aerosol led to products characteristic of iSOA, including tetrols (8). In a recent report, Surratt et al. (15) more firmly established the role of IEPOX as an iSOA precursor. Chemical analysis of the SOA produced from IEPOX uptake showed remarkable similarity to ambient iSOA, supporting the role of IEPOX as a major atmospheric iSOA precursor. In particular, they found clear evidence of formation of 2-methyltetrol from IEPOX uptake.

We agree with Claeys (7) that much research remains to be done to fully characterize the formation of iSOA. Although the discovery that IEPOX is formed in high yield under low-NOx conditions is an important step toward a more complete understanding of iSOA, the atmospheric yield of SOA from IEPOX (and other precursors such as trihydroxyperoxide, as suggested by Claeys) is at this time largely unknown. The yield will depend on both the gas-phase oxidation chemistry of the precursors and on the rate and products of their heterogeneous uptake to aerosol.

We believe that the key to making further progress on understanding the formation of SOA in general, and iSOA in particular, is for the community to continue to improve analytical capabilities so that gas and aerosol chemical composition can be jointly characterized in laboratory studies obtained under conditions representative of the atmosphere. Because of the intrinsic nonlinearity of peroxyl radical chemistry, remote atmospheric chemistry cannot be readily inferred from the experiments referred to by Claeys (Fig. 1). Reducing the uncertainty in RO2 chemistry, a crucial step in elucidating iSOA precursors, will certainly require a better understanding of the rates and products of the peroxyl radical chemistry. This includes reactions of RO2 with HO2 (16) and RO2 (17), as well as RO2 intramolecular processes (18, 19).

Fig. 1. Schematic representation of the ratio α = RO2/(HO2 + NO) (blue = 0; red = 1.5). Conditions expected for the atmosphere are indicated by a white rectangle. The dashed (dot-dashed) arrow depicts the evolution of the volatile organic carbon (VOC) to NO ratio during a typical low (high) NOx laboratory chamber experiment. The relative rate constants of the reactions of RO2 with HO2, NO, and RO2 are, respectively, ~10−7 to 0.002 to 0.2 (17) for the isoprene system. Because of the large VOC concentrations commonly used in low NOx experiments, α is high and the chemistry is strongly affected by cross-peroxy radical reactions, resulting in the formation of trihydroxyhydroperoxide (THHP) in the case of isoprene. Conversely, in the remote atmosphere, α is much smaller and RO2+RO2 is dominated by RO2+HO2. From our isoprene experiments (α ~ 0.3 over the first isoprene e-fold decay), we showed that IEPOX is formed with high yield and could play an important role in the formation of iSOA in the remote atmosphere, whereas the yield of the isoprene diol, the precursor to trihydroxyperoxide, is minimal (8, 15).

References


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