

## ATMOSPHERIC CHEMISTRY Epoxying Isoprene Chemistry

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Laboratory experiments show how the gas and aerosol chemistry of isoprene may be connected.

It seems that every few months we read about another missing aspect of atmospheric chemistry: missing products, missing reactivity, missing sources, missing understanding. Thus, it is with some relief that we read in this issue the paper of Paulot et al.<sup>1</sup> The paper provides more answers than questions on a topic of considerable interest to atmospheric scientists, the formation of gas- and aerosol-phase products from the atmospheric oxidation of isoprene.

Worldwide emissions of isoprene ( $C_5H_8$ ) from vegetation have been estimated to exceed 500 teragrams per year.<sup>2</sup> Arguably, it has the most important chemistry of any single nonmethane hydrocarbon in the troposphere given these massive emissions. Having two double bonds in its structure, it is extremely reactive with hydroxyl radicals (i.e., OH), with a daytime half-life of less than two hours. The reaction is initiated by OH addition to one of its two double bonds. With nitric oxide (NO) present, as found in urban and rural areas, subsequent reactions dominate mainly through formation of carbonyl and organic nitrate compounds, which are important in ozone chemistry.<sup>3</sup> In remote or tropical environments, where NO can be less than 50 parts-per-trillion, cross reactions by intermediate peroxy radicals tend to dominate.<sup>4</sup> Much of the recent interest in isoprene has been in this low  $NO_x$  channel which the Paulot et al. paper addresses.

In the past decade, research in the atmospheric chemistry of isoprene has followed roughly two tracks. The aerosol-phase track had its starting point with the 2004 article by Claeys et al.<sup>5</sup> in which aerosol collected in the Amazon rainforest appeared to contain a substantial portion of products from the photooxidation of isoprene, based on the detection of two chemical tracers, 2-methylthreitol and 2-methylerythritol. It had been known for more than 30 years that isoprene is produced in high abundance in locations where deciduous trees are plentiful, but what has been particularly surprising is that a molecule having only five carbons could undergo atmospheric reactions to form compounds of sufficiently low volatility to condense onto submicron particles at measurable levels. Since organic aerosol of this type can influence the earth's radiation budget as well as promote cloud condensation nuclei, it became essential to establish the details of the phenomena and determine its atmospheric importance.

Among the flurry of laboratory experiments that followed, Edney et al.<sup>6</sup> showed that indeed the tracer compounds detected by Claeys et al. were generated in laboratory photooxidations of isoprene while the aerosol formation yields were considerably enhanced by heterogeneous reactions on acidic aerosol. Kroll et al.<sup>7</sup> parameterized the aerosol yield under both low and high  $NO_x$  conditions. These findings led to some success in modeling isoprene aerosol formation in the troposphere and it is now thought to be an important contributor on a global basis.<sup>8</sup>

What these studies lacked was a mechanistic rationale for their findings. Paulot et al. conducted laboratory irradiations with isoprene under  $NO_x$  conditions similar to that found in the tropics. Through the use of chemical ionization mass spectrometry (CIMS), the authors were able to measure gas-phase organic hydroperoxides similar to those probably formed in the atmosphere.



The CIMS technique, which uses  $\text{--OF}_3$  as the adduct-forming ionizing gas, represents a kind of "silver bullet" for measuring hydroperoxides of importance in the atmosphere, given the well-known resistance of these compounds to measurement by conventional analytical techniques. Moreover, the CIMS technique was shown to measure not only the hydroperoxides, but through tandem mass spectrometry, organic epoxides, as well. However, the 75% yield of epoxides is somewhat unexpected. The epoxides are the specifically proposed stable intermediates leading to isoprene aerosol formation. The authors also conducted molecular dynamics calculations which showed the energetics of reaction were consistent with their formation thus giving additional plausibility to the findings. With respect to isoprene aerosol formation, the epoxides were also attractive products because they represented reasonable precursors for oligomer formation<sup>9</sup> in isoprene aerosol and their uptake was readily accommodated by acidic aerosol.

For gas-phase chemistry, this work was extended to provide a mechanism for regeneration of hydroxyl (OH) radicals via a chain propagating mechanism of hydroperoxides. This is a second very active track of isoprene chemistry research. The conventional wisdom had been that radical-radical reactions forming organic peroxides were completely chain terminating. A chain-propagating mechanism has already been examined in field<sup>10, 11</sup> and laboratory studies and on theoretical<sup>12</sup> grounds. Laboratory studies have found direct<sup>13</sup> and indirect<sup>14</sup> evidence for OH regeneration from reactions of  $\text{HO}_2$  + peroxy radicals having an  $\alpha$ - or  $\beta$ -carbonyl group. By contrast, the theoretical study relied on isomerization reactions of the isoprene intermediates to regenerate OH. While the mechanisms and yields still have considerable uncertainty, these findings will certainly close the gap<sup>15, 16</sup> between model results and atmospheric measurements of OH levels. These findings certainly have implications to reaction chemistry much broader than isoprene.

Perhaps the most important result in the Paulot et al. work is in its practical value. At present, air quality models of secondary organic aerosol formation of importance to regulatory agencies, such as the U.S. EPA, are generally limited in their predictive power by relying on experiments that give parameterized aerosol yields from reacting precursor compounds. The work by Paulot et al. serves as an important example for providing experimentally-derived chemical mechanisms which when incorporated into deterministic models of gas-aerosol chemistry should improve their predictive capabilities. The formation of isoprene epoxides in the atmosphere together with the OH chain propagating mechanisms should provide a basis for further studies of isoprene chemistry from new and creative perspectives.

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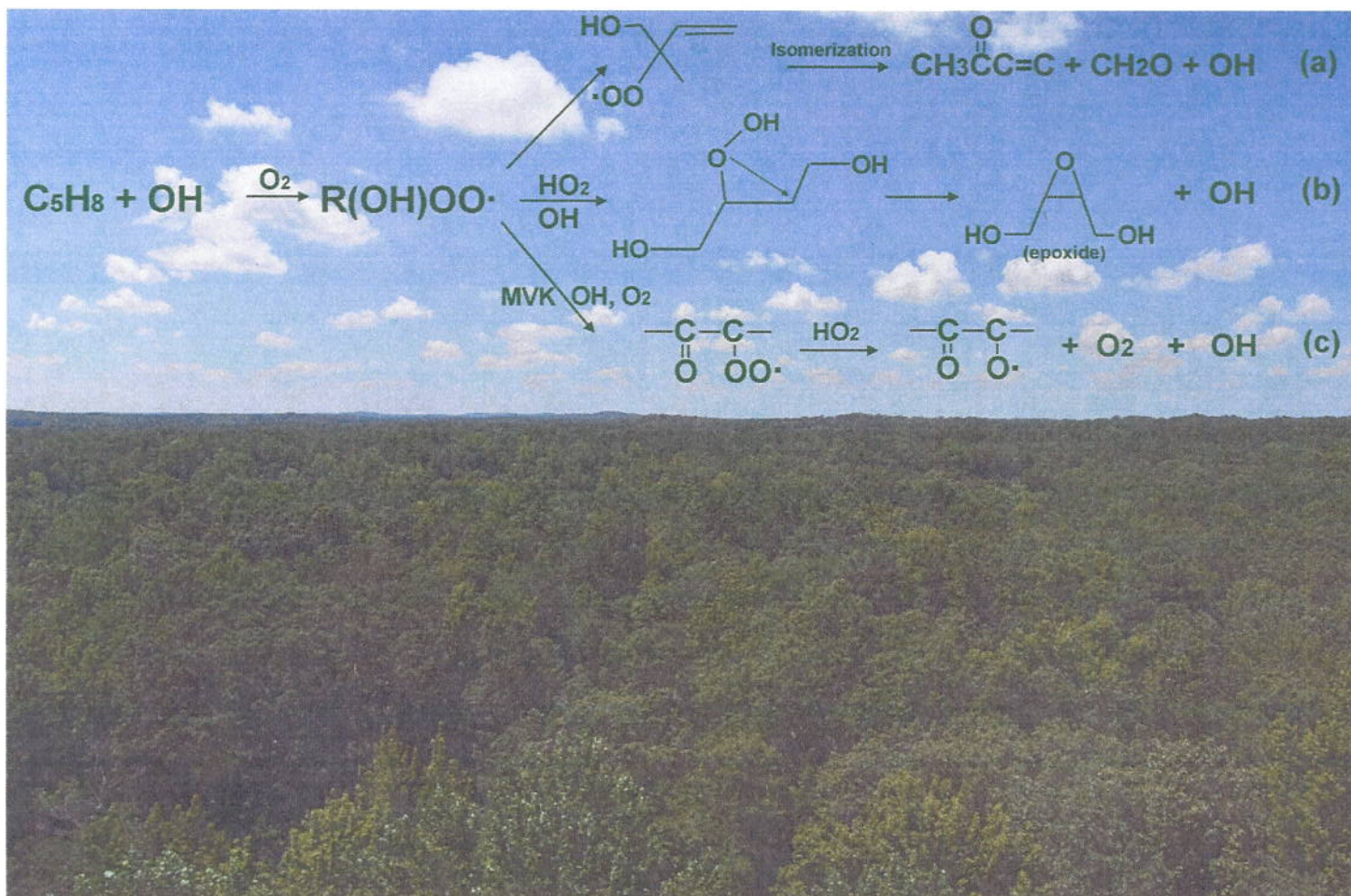
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Figure caption. As in the Amazon, isoprene emissions in Southeastern United States forests are among the highest in the world. Here a view of the forest canopy from a sampling tower at Duke Forest near Chapel Hill, North Carolina. (Overlay) Simplified depiction of possible isoprene reaction pathways for OH formation by a hydroperoxyl chain-propagating mechanism which include those from (a) a theoretical study<sup>12</sup>; (b) Paulot et al.<sup>1</sup>; (c) the reaction of HO<sub>2</sub> with a substituted  $\beta$ -carbonyl peroxy radicals from methyl vinyl ketone (MVK) similar to acetylperoxy radicals<sup>13, 14</sup> studied in the laboratory.

Photo credit: Chris Geron / Ron Bousquet

(Figure below)





As in the Amazon, isoprene emissions in Southeastern United States forests are among the highest in the world. Here a view of the forest canopy from a sampling tower at Duke Forest near Chapel Hill, North Carolina. A simplified depiction of possible isoprene reaction pathways for OH formation by a hydroperoxyl chain-propagating mechanism which include those from (a) a theoretical study<sup>12</sup>; (b) Paulot et al.<sup>1</sup>; (c) the reaction of HO<sub>2</sub> with a substituted β-carbonyl peroxy radical from methyl vinyl ketone (MVK) similar to acetylperoxy radicals<sup>13, 14</sup> studied in the laboratory.

