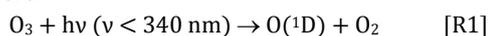


# The atmospheric chemistry of HO<sub>2</sub> and organic peroxy radicals

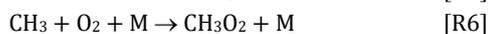
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The lower part of the Earth's atmosphere (the troposphere, up to about 9 to 18 km) serves as a sunlight-driven reactor that removes emitted species from the atmosphere, but that can generate potentially harmful by-products such as ozone and particulate matter. This *ECG Environmental Brief* outlines the key chemical processes involved in this reactor system, with a focus on the role played by peroxy radicals.

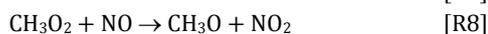
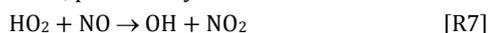
ECG Environmental Brief No 3 (1) provided a nice introduction to the daytime chemistry of the troposphere. There, it was shown that sunlight-driven photolysis of ozone (O<sub>3</sub>) in the presence of water vapour is a significant source of reactive hydroxyl radicals (OH) to the atmosphere:



These OH radicals are responsible for initiating the atmospheric removal of most trace gases, such as volatile organic compounds (VOCs), such as CO and methane:

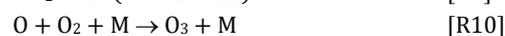
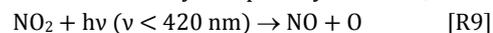


In both cases, the product is a peroxy radical, HO<sub>2</sub> (H-O-O•) in CO oxidation and CH<sub>3</sub>O<sub>2</sub> (CH<sub>3</sub>-O-O•) in the methane case. These radical species are short-lived and highly reactive, particularly with NO:



Peroxy radical lifetimes are controlled by their proximity to NO emission sources, ranging from milliseconds in urban locations to minutes in pristine forests.

Consider now the combined effect of reactions [R3], [R4] and [R7]. We see that radical cycling is occurring, in which OH, H, and HO<sub>2</sub> are consumed and regenerated. The net effect is the oxidation of CO to CO<sub>2</sub> and NO to NO<sub>2</sub>. Coupled with the facile daytime photolysis of NO<sub>2</sub>,



we see that NO and NO<sub>2</sub> also cycle between each other, generating ozone in the process. This reaction of a peroxy species with NO is the only method for generating tropospheric ozone, which is harmful to human and vegetative health and is an important greenhouse gas.

The cycling of radicals from OH, to H, to HO<sub>2</sub> and back to OH leads us to the concept of a radical family, in this case the HO<sub>x</sub> family. Members of the family interconvert among each other rapidly, generally on a shorter time scale than family members are lost or produced. NO/NO<sub>2</sub> also interconvert rapidly and are referred to as NO<sub>x</sub>. A similar story emerges when considering the net effect of [R5] through [R11]. Here, the CH<sub>3</sub>, CH<sub>3</sub>O<sub>2</sub>, and CH<sub>3</sub>O radicals cycle, along with OH and HO<sub>2</sub>. Again, NO<sub>x</sub> is cycled, ozone is generated, and methane is partially oxidized to formaldehyde, CH<sub>2</sub>O:



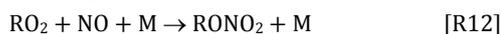
The lifetime of the peroxy radical species exceeds that of the other species in the family, and their ambient concentrations are thus larger; typical daytime peroxy radical concentrations are 10<sup>8</sup> to 10<sup>9</sup> molecule cm<sup>-3</sup>, whereas OH levels are commonly ≈10<sup>6</sup> molecule cm<sup>-3</sup>.

## Peroxy radical chemistry

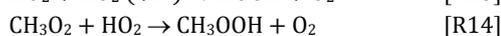
So far, we have considered only the simplest peroxy radicals, HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>. However, there can be thousands of different VOCs in the atmosphere, ranging in complexity from methane to monoterpenes (biogenic molecules with the formula C<sub>10</sub>H<sub>16</sub>) to diesel fuel components. There is a concomitant complexity in the range of peroxy radicals that can be generated. Thankfully, many reactions involving peroxy species are

similar across the whole range of species. For example, all known reactions of peroxy radicals with NO have rate coefficients that vary over a fairly narrow range,  $\approx (7\text{--}21) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (2). Thus, knowledge of the detailed identities of organic peroxy radicals present is often less important than knowing the total peroxy radical concentration, and it becomes convenient to label the entire collection of atmospheric organic peroxy radicals as RO<sub>2</sub> (where R represents any organic fragment). The family of radicals that include R, RO<sub>2</sub>, RO, OH and HO<sub>2</sub> are referred to by the general term RO<sub>x</sub> (where R also encompasses hydrogen).

As seen above, the reactions of HO<sub>2</sub>/RO<sub>2</sub> with NO are part of a radical cycling mechanism that consumes primary pollutants (VOCs) and generates ozone. Were this the only chemistry to happen, radicals would propagate forever. However, other reactions do occur, some that propagate radicals and continue ozone production chemistry, others that terminate HO<sub>x</sub> and/or NO<sub>x</sub> cycles. For example, the reaction of RO<sub>2</sub> with NO has a second (minor) channel that generates an organic nitrate (3) and removes both HO<sub>x</sub> and NO<sub>x</sub> radicals:



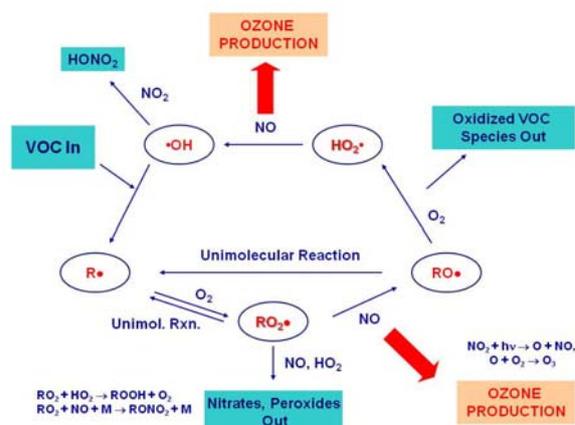
Similarly, reactions among the peroxy radicals can act as a key termination step for HO<sub>x</sub> radical cycling,



In pristine regions, where peroxy radical lifetimes are longest, the importance of unimolecular reactions for some specific RO<sub>2</sub> is increasingly being recognized. One such reaction involves isomerization of a hydroxy-peroxy radical derived from isoprene, a process that increases OH concentrations in low-NO<sub>x</sub> regions (4). The key processes involved in tropospheric chemistry, from the perspective of HO<sub>x</sub> cycling, are summarized in **Figure 1**.

## Measurement methods

Quantifying ambient peroxy radicals (and their HO<sub>x</sub> family member, OH) is challenging because of their low abundances, short lifetimes and spatial and temporal non-uniformity. Techniques available for measurement of ambient HO<sub>2</sub>/RO<sub>2</sub> largely fall into two groups (5). The first involves OH detection by laser-induced fluorescence. Here, OH is either determined directly by quantifying the fluorescence observed after laser-induced excitation to its first electronic excited state. Alternatively, the sum of HO<sub>2</sub>/RO<sub>2</sub>/OH can be detected after chemical conversion to OH *via* addition of NO to the instrument inlet ([R8], [R11], and [R7]). In the second technique, each peroxy radical is converted to more than one product species (NO<sub>2</sub> or HSO<sub>4</sub><sup>-</sup>) *via* a chain reaction in the inlet of the instrument, followed by detection of



**Figure 1.** Key processes involved in cycling of the HO<sub>x</sub>/RO<sub>x</sub> family in the troposphere.

this product species. As an example, HO<sub>2</sub> can be converted to multiple molecules of NO<sub>2</sub> by adding NO and CO to inlet air, initiating a chain reaction involving [R3] and [R7].

## Outlook

Understanding tropospheric ozone production, the Earth's self-cleansing capacity, and related problems in atmospheric chemistry requires quantitative understanding of chemistry involving HO<sub>x</sub>, NO<sub>x</sub> and VOCs. This understanding comes from a combination of ambient measurements of critical components of the system, laboratory investigations of relevant chemistry, atmospheric modelling, and theoretical studies. Progress emerges from the feedbacks between these endeavours. For example, attempts to resolve disagreements between models and measurements may include checks of instrument calibration and interferences or updates to the model based on targeted laboratory studies. Similarly, discovery of a relevant peroxy radical reaction in a theoretical study may drive laboratory studies to quantify the process, followed by its inclusion in an atmospheric model to assess its importance.

## References

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