The atmospheric chemistry of HO₂ 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 (O₃) in the presence of water vapour is a significant source of reactive hydroxyl radicals (OH) to the atmosphere:

\[
\begin{align*}
O_3 + hν (ν < 340 \text{ nm}) & \rightarrow O(^1\text{D}) + O_2 & [R1] \\
O(^1\text{D}) + H_2O & \rightarrow OH + OH & [R2]
\end{align*}
\]

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:

\[
\begin{align*}
OH + CO & \rightarrow H + CO_2 & [R3] \\
H + O_2 + M & \rightarrow HO_2 + M & [R4] \\
OH + CH_4 & \rightarrow CH_3 + H_2O & [R5] \\
CH_3 + O_2 + M & \rightarrow CH_3O_2 + M & [R6]
\end{align*}
\]

In both cases, the product is a peroxy radical, HO₂ (H-O-0•) in CO oxidation and CH₃O₂ (CH₃-O-0•) in the methane case. These radical species are short-lived and highly reactive, particularly with NO:

\[
\begin{align*}
HO_2 + NO & \rightarrow OH + NO_2 & [R7] \\
CH_3O_2 + NO & \rightarrow CH_3O + NO_2 & [R8]
\end{align*}
\]

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 HO₂ are consumed and regenerated. The net effect is the oxidation of CO to CO₂ and NO to NO₂. Coupled with the facile daytime photolysis of NO₂:

\[
\begin{align*}
NO_2 + hν (ν < 420 \text{ nm}) & \rightarrow NO + O & [R9] \\
O + O_2 + M & \rightarrow O_3 + M & [R10]
\end{align*}
\]

we see that NO and NO₂ 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 HO₂ and back to NO leads us to the concept of a radical family, in this case the HO₂ family. Members of the family interconvert among each other rapidly, generally on a shorter time scale than family members are lost or produced. NO/NO₂ also interconvert rapidly and are referred to as NOₓ. A similar story emerges when considering the net effect of [R5] through [R11]. Here, the CH₃, CH₃O₂ and CH₃O radicals cycle, along with OH and HO₂. Again, NOₓ is cycled, ozone is generated, and methane is partially oxidized to formaldehyde, CH₂O:

\[
\begin{align*}
CH_3O + O_2 & \rightarrow CH_2O + HO_2 & [R11]
\end{align*}
\]

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 10⁸ to 10⁹ molecule cm⁻³, whereas OH levels are commonly ~10⁶ molecule cm⁻³.

Peroxy radical chemistry

So far, we have considered only the simplest peroxy radicals, HO₂ and CH₃O₂. However, there can be thousands of different VOCs in the atmosphere, ranging in complexity from methane to monoterpenes (biogenic molecules with the formula C₁₀H₁₆) 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, \( \approx (7-21) \times 10^{-12} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \) (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\(_2\) (where \( R \) represents any organic fragment). The family of radicals that include \( R, RO_2, RO, OH \) and \( HO_2 \) are referred to by the general term RO\(_2\) (where \( R \) also encompasses hydrogen).

As seen above, the reactions of HO\(_2\)/RO\(_2\) 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\(_2\) and/or NO\(_x\) cycles. For example, the reaction of RO\(_2\) with NO has a second (minor) channel that generates an organic nitrate (3) and removes both HO\(_2\) and NO\(_x\) radicals:

\[
RO_2 + NO + M \rightarrow RONO_2 + M \tag{R12}
\]

Similarly, reactions among the peroxy radicals can act as a key termination step for HO\(_2\) radical cycling,

\[
\begin{align*}
\text{HO}_2 + \text{HO}_2 (+M) & \rightarrow \text{HOOH} + \text{O}_2 \tag{R13} \\
\text{CH}_3\text{O}_2 + \text{HO}_2 & \rightarrow \text{CH}_2\text{OOH} + \text{O}_2 \tag{R14}
\end{align*}
\]

In pristine regions, where peroxy radical lifetimes are longest, the importance of unimolecular reactions for some specific RO\(_2\) 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\(_x\) regions (4). The key processes involved in tropospheric chemistry, from the perspective of HO\(_2\) cycling, are summarized in Figure 1.

**Measurement methods**

Quantifying ambient peroxy radicals (and their HO\(_x\) 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\(_2\)/RO\(_2\) 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\(_2\)/RO\(_2\)/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\(_2\) or HSO\(_x\)) via a chain reaction in the inlet of the instrument, followed by detection of this product species. As an example, HO\(_2\) can be converted to multiple molecules of NO\(_2\) 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\(_x\), NO\(_x\) 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**

1. S. Ball, ‘Atmospheric chemistry at night’, (ECG Environmental Brief No 3).