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Free Radicals in the Atmosphere

The atmosphere contains a wide variety of chemically active species, among which free radicals are particularly important.

Free radicals are atoms or molecules that possess an unpaired electron in their outer shell. This unpaired electron makes them extremely reactive, allowing them to participate in many atmospheric chemical reactions.

Although free radicals have very short lifetimes, they play a crucial role in:

- _Oxidation of pollutants
- _Formation of ground-level (tropospheric) ozone
- _Aerosol chemistry
- _Natural atmospheric self-cleaning processes

Key Free Radicals in the Atmosphere

A. Hydroxyl Radical (OH)

Definition: Often referred to as the "atmosphere's detergent" due to its role in oxidizing pollutants.

Formation:

1. $O_3 + h\nu \text{ (UV)} \rightarrow O_2 + O(^1D)$
2. $O(^1D) + H_2O \rightarrow 2 OH$

Importance:

Oxidation of CO \rightarrow CO₂

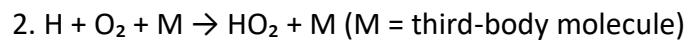
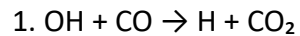
Oxidation of CH₄ and other volatile organic compounds (VOCs)

Initiates chain reactions leading to tropospheric ozone formation

Properties: Extremely short-lived (seconds to minutes) but highly reactive

B. Hydroperoxyl Radical (HO₂)

Formation:



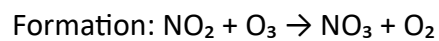
Role:

Converts NO → NO₂ in the tropospheric ozone cycle

Participates in smog and secondary ozone formation

Properties: Less reactive than OH but sufficiently stable to react with NO

C. Nitrate Radical (NO₃)



Role:

Important in nighttime chemistry of nitrogen oxides

Oxidizes organic compounds during the night; decomposes rapidly during daylight

Properties: Predominantly nocturnal radical

Other Important Radicals:

Cl and Br radicals: Involved in stratospheric ozone depletion

RO₂ (Peroxy radicals): Derived from VOCs; contribute to ozone and aerosol formation

Mechanism of Free Radical Action in the Atmosphere

Free radicals often act as catalysts in oxidation chain reactions. For example:

1. $\text{OH} + \text{CO} \rightarrow \text{HO}_2$
2. $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \rightarrow$ Contributes to ground-level ozone formation

These chain reactions regulate air purification and maintain the balance of ozone in the troposphere.

Environmental Importance of Free Radicals

1. Air Purification: Transform gaseous pollutants into less harmful compounds
2. Tropospheric Ozone Formation: Key component of smog, affecting human health
3. Aerosol Chemistry: Contribute to the formation of acidic particles such as H₂SO₄ and HNO₃
4. Atmospheric Chemical Balance: Changes in pollutant levels alter free radical concentrations, impacting ozone and air quality

Techniques for Studying Free Radicals

Laser Spectroscopy: High-precision measurement of OH and HO₂ radicals

Chemical Tracers: Detection of NO₃ and Cl radicals

Atmospheric Chemistry Models: Simulation of radical behavior and chemical reactions on local and global scales

Summary

Free radicals, despite their short lifetimes, are fundamental to atmospheric chemistry. They:

Oxidize pollutants

Contribute to tropospheric ozone formation

Drive aerosol chemical reactions

Understanding their behavior is essential for predicting air quality, smog formation, and climate-related atmospheric processes.