

Interconnection of Reactive Oxygen Species Chemistry across the Interfaces of Atmospheric, Environmental, and Biological Processes

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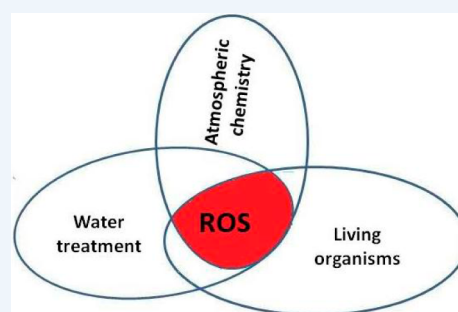
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CONSPECTUS: Oxidation reactions are ubiquitous and play key roles in the chemistry of the atmosphere, in water treatment processes, and in aerobic organisms. Ozone (O_3), hydrogen peroxide (H_2O_2), hydrogen polyoxides (H_2O_x , $x > 2$), associated hydroxyl and hydroperoxyl radicals ($HO_x = OH$ and HO_2), and superoxide and ozonide anions (O_2^- and O_3^- , respectively) are the primary oxidants in these systems. They are commonly classified as reactive oxygen species (ROS).

Atmospheric chemistry is driven by a complex system of chain reactions of species, including nitrogen oxides, hydroxyl and hydroperoxide radicals, alkoxy and peroxy radicals, and ozone. HO_x radicals contribute to keeping air clean, but in polluted areas, the ozone concentration increases and creates a negative impact on plants and animals. Indeed, ozone concentration is used to assess air quality worldwide. Clouds have a direct effect on the chemical composition of the atmosphere. On one hand, cloud droplets absorb many trace atmospheric gases, which can be scavenged by rain and fog. On the other hand, ionic species can form in this medium, which makes the chemistry of the atmosphere richer and more complex. Furthermore, recent studies have suggested that air–cloud interfaces might have a significant impact on the overall chemistry of the troposphere.

Despite the large differences in molecular composition, concentration, and thermodynamic conditions among atmospheric, environmental, and biological systems, the underlying chemistry involving ROS has many similarities. In this Account, we examine ROS and discuss the chemical characteristics common to all of these systems.

In water treatment, ROS are key components of an important subset of advanced oxidation processes. Ozonation, peroxone chemistry, and Fenton reactions play important roles in generating sufficient amounts of hydroxyl radicals to purify wastewater. Biochemical processes within living organisms also involve ROS. These species can come from pollutants in the environment, but they can also originate endogenously, initiated by electron reduction of molecular oxygen. These molecules have important biological signaling activities, but they cause oxidative stress when dysfunction within the antioxidant system occurs. Excess ROS in living organisms can lead to problems, such as protein oxidation—through either cleavage of the polypeptide chain or modification of amino acid side chains—and lipid oxidation.



I. INTRODUCTION

Oxidation reactions are widespread in nature with the most fundamental processes being related to reactive oxygen species (ROS), including ozone (O_3), hydrogen peroxide (H_2O_2), hydrogen polyoxides (H_2O_x , $x > 2$), the associated hydroperoxide radicals (HO_x), and the superoxide and ozonide anions (O_2^- and O_3^- , respectively). The acronym ROS has been coined in the context of biological chemistry, but these species are also broadly involved in environmental and atmospheric chemistry.

In the troposphere, the gas-phase chemistry of the HO_x radicals and ozone prevails. However, there is increasing awareness of the important role played by water droplets and aerosols, where ionic species can readily form.^{1,2} Moreover, highly reactive oxygen species are increasingly being used in pollutant abatement as well as in oxidation reactions in natural

aquatic systems,^{3,4} and recent studies have shown that determining the mechanistic details of these processes is highly important from an environmental perspective.^{3,5} In living organisms, they have signaling functions, but the accumulation of ROS produces oxidative stress^{6–8} that can cause irreversible cell damage and is thought to be involved in aging and in many diseases, such as cancer, Alzheimer's, Parkinson's, and heart failure, among others. Moreover, ROS can also be used by the immune system to kill pathogens.^{6–9}

Figure 1 depicts a schematic representation of ROS in the atmosphere, including gas phase and cloud water droplet environments. The different species can react in the distinct phases as well as at the interface, can adopt ionic forms, and so

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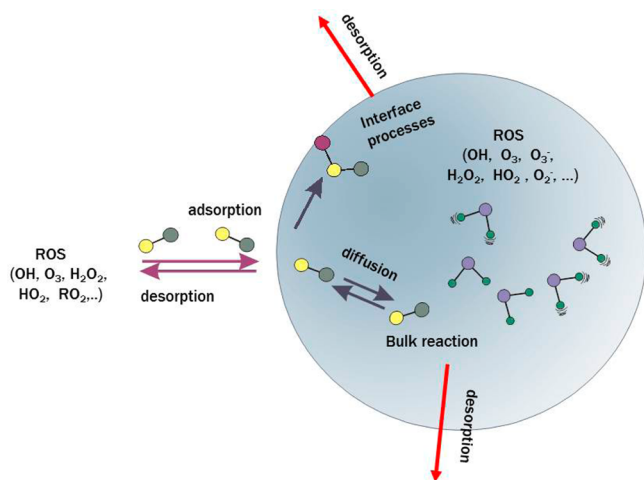


Figure 1. Representation of ROS in atmospheric gas phase and cloudwater droplet environments.

forth. A similar scheme could be drawn for these species in a variety of biological environments. Despite the apparent large differences in terms of molecular composition, concentration, and thermodynamic conditions that exist between atmospheric, environmental, and biological systems, the underlying chemistry has many similarities, which leads to interconnected reaction mechanisms. Much of this information is available in the literature but is scattered across the different communities. This Account brings all of this data together in one place with the aim of reviewing and examining common chemistry connections.

II. GAS PHASE ROS CHAIN REACTIONS IN THE ATMOSPHERE

Hydroxyl radicals play a central role in the chemistry of the atmosphere and are linked to a strongly coupled system of reactions involving ROS species, such as HO_x , NO_x (NO and NO_2), O_3 , and alkoxy and peroxy radicals, among others.^{1,2} A simplified scheme of this system of chain reactions is displayed in Figure 2, and Table 1 collects the reaction enthalpies and reaction rate constants for some of the most important processes.

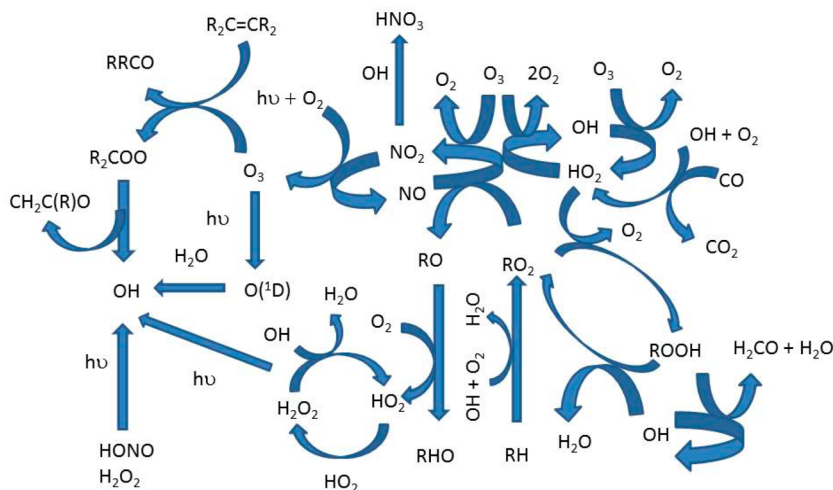


Figure 2. Primary reactions involving ROS in the atmospheric gas phase.

The primary source of OH in the atmosphere comes from the photolysis of ozone, producing atomic oxygen in its $^1\text{D}_g$ excited state, which reacts very fast with water vapor leading to the formation of two hydroxyl radicals (G1 and G2). Figure 2 shows additional sources of OH, such as photolysis of H_2O_2 and HONO (G16 and G27) or the unimolecular decomposition of carbonyl oxides formed from alkene ozonolysis (see below).

A closer look at Table 2 shows that many of these reactions have similar rate constants, and therefore, it is important to focus on reaction rates rather than rate constants. Consider, for example, the oxidation of CO and CH_4 , which are among species with high concentrations in the troposphere and are the primary consumers of OH. Their concentrations have been estimated to be uniform at 4.82×10^{13} molecules cm^{-3} for CH_4 and $(1.27\text{--}3.80) \times 10^{12}$ molecules cm^{-3} for CO.¹² The OH + CO reaction proceeds by the addition of a hydroxyl radical to carbon monoxide, leading to the formation of the HOCO radical prior to the production of a hydrogen atom and CO_2 ¹³ (G5, $k_{G5} = 1.5 \times 10^{-13}$ molecule $\text{cm}^{-3} \text{ s}^{-1}$). The OH + CH_4 reaction has a smaller rate constant (G7, $k_{G7} = 6.4 \times 10^{-15}$ molecule $\text{cm}^{-3} \text{ s}^{-1}$) and proceeds by transferring a hydrogen atom from methane to the hydroxyl radical, leading to the formation of CH_3 and H_2O . The corresponding reaction rates are given by eqs 1 and 2.

$$V_{G5} = k_{G5}[\text{OH}][\text{CO}] \quad (1)$$

$$V_{G7} = k_{G7}[\text{OH}][\text{CH}_4] \quad (2)$$

Although k_{G5} is 23.4 times greater than k_{G7} , under atmospheric conditions, V_{G5} is only between 0.62 and 1.85 times greater than V_{G7} , depending on the actual CO concentration. The H and CH_3 radicals formed through G5 and G7 react with molecular oxygen, leading to the formation of HO_2 and CH_3O_2 radicals (G6 and G8) and thus continuing the atmospheric oxidation chain.

Figure 2 shows that HO_2 can react with CH_3O_2 to form CH_3OOH (G17) or can alternatively produce H_2O_2 through a self-reaction (G11). Both reactions are mechanistically very similar, and theoretical studies from the literature^{14,15} show that they take place on a triplet potential energy surface. The products of these reactions can react further with OH. The hydroxyl radical abstracts one hydrogen atom from H_2O_2 to

Table 1. Relevant Gas Phase Reactions Occurring in the Earth's Atmosphere with Associated Reaction Enthalpies (ΔH_{rxn}) and Rate Constants (k) at 298 K

number	reaction	ΔH_{rxn}^a (kcal mol ⁻¹)	k^b
G1	$\text{O}_3 + h\nu$ ($\lambda < 320$ nm) \rightarrow $\text{O}(^1\text{D}) + \text{O}_2(^1\Delta)$	93.49 ± 0.01	5.1×10^{-5}
G2	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	-29.09 ± 0.02	2.0×10^{-10}
G3	$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O}(^3\text{P})$	-45.24 ± 0.00	
G4	$\text{O}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \rightarrow \text{O}_3$	-25.69 ± 0.01	2.81×10^{-12}
G5	$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	-24.49 ± 0.02	1.5×10^{-13}
G6	$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	-49.17 ± 0.04	7.5×10^{11}
G7	$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	-13.93 ± 0.05	6.4×10^{-15}
G8	$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	-32.13 ± 0.23	1.8×10^{-12}
G9	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	-39.08 ± 0.07	7.30×10^{-14}
G10	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	-27.85 ± 0.06	2.0×10^{-15}
G11	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	-38.32 ± 0.08	1.60×10^{-12}
G12	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	-47.52 ± 0.04	1.8×10^{-14}
G13	$\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$	-24.30 ± 0.07	3.5×10^{-17}
G14	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	-7.61 ± 0.08	8.8×10^{-12}
G15	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	-31.38 ± 0.05	1.7×10^{-12}
G16	$\text{H}_2\text{O}_2 + h\nu$ ($\lambda < 355$ nm) \rightarrow 2OH	50.38 ± 0.01	7.7×10^{-6}
G17	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	-36.36 ± 0.47	5.2×10^{-12}
G18	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	-11.30 ± 0.33	7.7×10^{-12}
G19	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{OH} + \text{H}_2\text{O}$	-53.34 ± 0.26	1.9×10^{-12}
G20	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	-33.33 ± 0.45	3.6×10^{-12}
G21	$\text{NO}_2 + h\nu$ ($\lambda < 420$ nm) \rightarrow $\text{NO} + \text{O}(^3\text{P})$	73.21 ± 0.03	8.8×10^{-3}
G22	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	-49.16 ± 0.06	2.1×10^{-11}
G23	$\text{H}_2\text{CO} + h\nu$ ($\lambda < 340$ nm) \rightarrow $\text{H} + \text{HCO}$	88.19 ± 0.05	3.3×10^{-5}
G24	$\text{H}_2\text{CO} + h\nu$ ($\lambda < 360$ nm) \rightarrow $\text{H}_2 + \text{CO}$	-0.33 ± 0.03	4.4×10^{-5}
G25	$\text{H}_2\text{CO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	-30.67 ± 0.07	8.5×10^{-12}
G26	$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$	-33.48 ± 0.07	5.1×10^{-12}
G27	$\text{HONO} + h\nu$ ($\lambda < 400$ nm) \rightarrow $\text{OH} + \text{NO}$	49.66 ± 0.04	1.9×10^{-3}
G28	$\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_3 + \text{O}_2$	-20.93 ± 0.25	
G29	$\text{O}_3 + \text{isoprene} \rightarrow \text{products}$		1.3×10^{-17}
G30	$\text{OH} + \text{isoprene} \rightarrow \text{products}$		1.0×10^{-10}

^aReaction enthalpies obtained taking ΔH_f values at 298 K from reference 10. ^bRate constants are in cm³ molecule⁻¹ s⁻¹ for bimolecular reactions and s⁻¹ for unimolecular reactions; values were taken from reference 11.

produce H₂O and regenerate HO₂ (G15). CH₃OOH can react with OH in two different ways: 34.5% produces H₂CO regenerating OH (G19), and 65.5% leads to the back formation of CH₃O₂ (G20). Note that in reaction G19, the hydroxyl radical acts as a catalyst because there is no net consumption of OH.

In polluted areas where the concentration of NO is high, both HO₂ and CH₃O₂ (or RO₂ in general) oxidize NO to NO₂, which in daylight photolyzes to regenerate NO and produce O(³P) (G21). Atomic oxygen then adds to molecular oxygen to produce ozone (G4). This is one of the most important sources of atmospheric O₃. However, in situations with high concentrations of NO₂, this radical reacts with OH to produce HNO₃ (G22) in a process that contributes to an effective atmospheric loss of both the hydroxyl radicals and nitrogen

Table 2. Relevant Reactions Occurring in Water Solutions that Involve ROS with Reaction Free Energies (ΔG_r) and Reaction Rate Constants (k) at 298 K

number	reaction	ΔG_r^a (kcal mol ⁻¹)	k^b (M ⁻¹ s ⁻¹)
S1	$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_2^- + \text{HO}_2$	4.63	
S2	$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_3^- + \text{HO}$	20.6/10.9	
S3 ^c	$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_2(^3\Sigma_g^-) + \text{HO}_2^-$	-16.19	40/70
S4	$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_2(^1\Delta_g) + \text{HO}_2^-$	6.67	
S5	$\text{O}_3 + \text{O}_2^- \rightarrow \text{O}_3^- + \text{O}_2$	-26.88	1.6×10^9
S6	$\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{O}_2(^3\Sigma_g^-) + \text{H}_2\text{O}$	-59.49	0.065
S7	$\text{O}_3 + \text{HO}_2^- \rightarrow \text{OH} + \text{O}_2(^3\Sigma_g^-) + \text{O}_2^-$	-7.78/-10.79	5.5×10^6
S8	$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	-42.85	1.1×10^8
S9	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	-26.95	8.3×10^5
S10	$\text{HO}_2 + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$	-71.08	9.7×10^7
S11	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	-60.02	1.0×10^{10}
S12	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	-41.19	4.2×10^9
S13	$\text{OH} + \text{O}_2^- \rightarrow \text{O}_2 + \text{OH}^-$	-47.48	1.0×10^{10}
S14	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	-33.07	2.7×10^7
S15	$\text{OH} + \text{HO}_2^- \rightarrow \text{HO}_2 + \text{OH}^-$	-26.66	7.5×10^9
S16	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH} + \text{OH}^-$		53
S17	$\text{Fe}^{3+} + \text{O}_2^- \rightarrow \text{Fe}^{2+} + \text{O}_2$		$(0.12-3.6) \times 10^5$
S18	$\text{Fe}^{2+} + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 + 2\text{OH}^-$		
S19	$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+$		
S20	$\text{Fe}^{2+} + \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$		3.3×10^8
S21	$\text{Fe}^{2+} + \text{HO}_2 \rightarrow \text{Fe}^{3+} + \text{HO}_2^-$		1.2×10^6
S22	$\text{Fe}^{2+} + \text{O}_3 \rightarrow \text{Fe}^{\text{IV}}\text{O}^{2+} + \text{O}_2$		8.2×10^5

^aObtained taking ΔG_f values at 298 K listed in reference 24 and references therein. ^bValues taken from references 25–27. ^cSpin forbidden.

oxides. These examples illustrate the high complexity of the gas phase chemistry of the atmosphere, which cannot be understood without considering the whole chain of reactions.

Beyond its key role as a precursor of hydroxyl radicals, ozone also acts as a pollutant in the atmosphere. From this point of view, three reactions involving ozone deserve to be highlighted, namely those with OH, HO₂, and unsaturated compounds.²

The first two reactions (G9 and G10) are important in chemistry of the atmosphere because they form a catalytic cycle that destroys two ozone molecules to generate three oxygen molecules with no net consumption of HO or HO₂ (G31 = G9 + G10).²



Reaction G9 takes place by the addition of OH to O₃ to produce HO₄, which decomposes into HO₂ and O₂.¹⁶

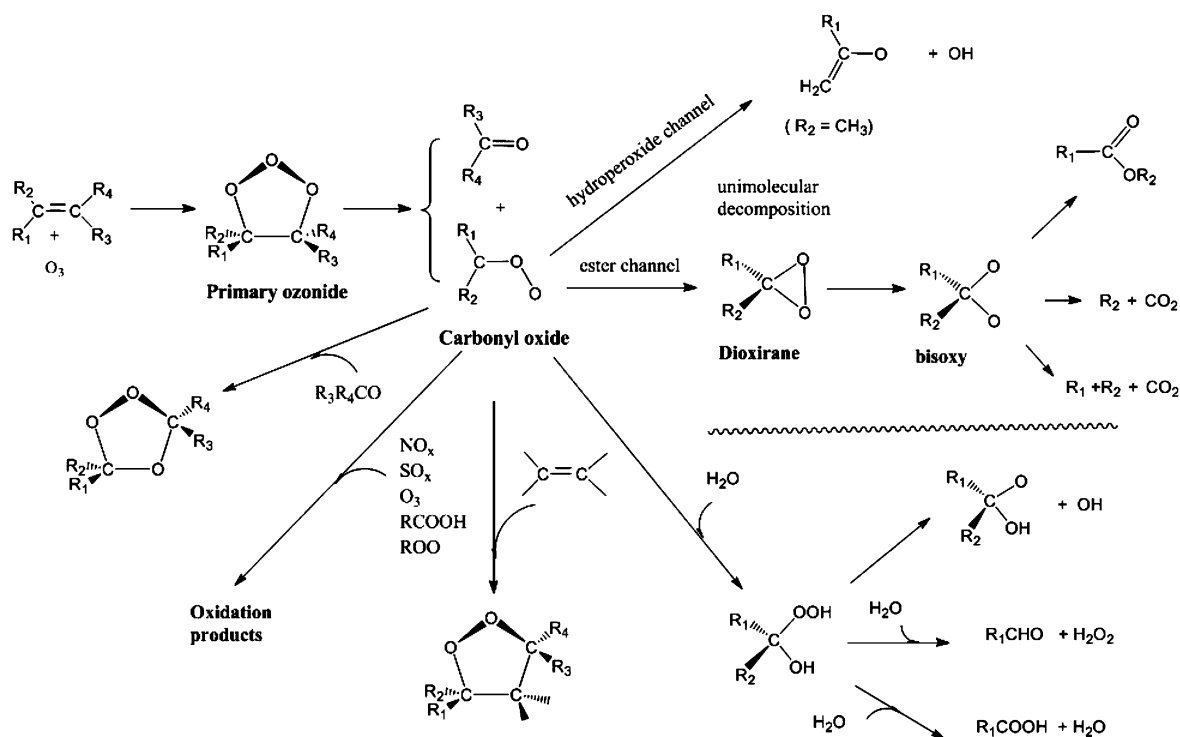


Figure 3. Schematic mechanism of gas phase alkene ozonolysis.

Conversely, ozone reacts with HO_2 by abstracting the hydrogen atom to produce O_2 and HO_3 , which decomposes into OH and O_2 .¹⁷

Alkene ozonolysis is an important sink for unsaturated compounds. This chemistry leads to the formation of organic acids, radicals, and secondary organic aerosols. This reaction mechanism is displayed in Figure 3. The reaction follows the concerted addition of ozone across the alkene double bond according to the Criegee mechanism.^{18,19} This produces the primary ozonide, which decomposes to yield a carbonyl oxide, or Criegee intermediate (CI), and a carbonyl compound. In the gas phase, CIs are formed with excess vibrational energy and can either decompose unimolecularly or be stabilized by collision with other atmospheric gases. Figure 3 shows that there are two different pathways for the unimolecular decomposition of CI, namely, ester and hydroperoxide channels. The ester channel produces CO , CO_2 , organic acids, and radicals, whereas the hydroperoxide channel yields hydroxyl radicals.²⁰

Stabilized CIs react mostly with water vapor, which is one of the most abundant trace tropospheric gases. The reaction proceeds upon the addition of water to carbonyl oxide to form hydroxy hydroperoxides, which react with a second water molecule to produce H_2O_2 and organic acids.^{21,22} However, CIs can also react with other trace atmospheric gases (see Figure 3).²³

III. ROS IN AQUATIC SYSTEMS

The aqueous phase provides an important chemical environment for ROS. About 50% of the Earth's troposphere is covered by clouds, and many atmospheric gases are absorbed into cloud droplets. Therefore, chemical reactions occurring inside a cloud droplet (as depicted in Figure 1) play an important role and impact the entire atmospheric chemical composition. ROS play a key role in oxidative abatement in wastewater and drinking

water processes. In aerobic biological organisms, ROS are formed as byproducts of the metabolism of molecular oxygen, and many of the reactions involving these species take place in water environments inside cells.

A number of reactions involving ROS in solution have been collected in Table 2 along with their corresponding reaction free energies. Many reactions involving radicals take place in a manner that is similar to how they occur in the gas phase. For instance, OH can react by hydrogen abstraction through addition to double bonds or by electron transfer, though solvent effects can enhance the reaction rates by up to a factor of 20.²⁸ However, ionic species are formed, which is the key difference relative to the gas phase chemistry. Indeed, many compounds are implicated in acid–base equilibria. An important example is HO_2 ($\text{p}K_a = 4.8$). For systems in which both the acid and its conjugated base react with a given species, the reaction rate depends on pH; von Sonntag and von Gunten use the term “reactivity $\text{p}K$ ” for these types of reactions.³ Computer simulations, on the other hand, have been carried out to analyze the specific interactions of many ROS with water in solution and to evaluate their hydrophilic or hydrophobic character.^{29,30}

ROS in Clouds

As mentioned above, many atmospheric gases are absorbed into cloud droplets. The efficiency of the absorption process depends on the water solubility, which is directly related to Henry's law constant (K_H). Species such as H_2O_2 and HO_2 ($K_H = 1.4 \times 10^5$ and $9.0 \times 10^3 \text{ M atm}^{-1}$, respectively³¹) are efficiently scavenged by cloud droplets.³²

Clouds in different atmospheric areas have different pH values that range between 2.3 and 7.3,³² and inside the clouds, HO_2 can coexist with its conjugated base O_2^- . Under very acidic conditions, HO_2 predominates, and in less acidic or basic conditions, O_2^- predominates. Consequently, the chemistry

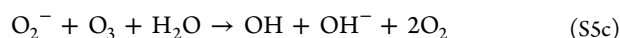
triggered by hydroperoxide and superoxide radicals changes significantly according to the pH. For instance, the formation of H_2O_2 can occur by HO_2 self reaction (S9) or by reaction between HO_2 and O_2^- (S10). The mechanism of reaction S9 has the same features as in the gas phase. However, the mechanism underlying reaction S10 is not well understood.

The uptake of HO_2 by cloud droplets has important atmospheric consequences. Such a process reduces the HO_2 concentration in the gas phase, diminishing the NO to NO_2 conversion (G14). Consequently, the formation of O_3 through reactions G21 and G4 decreases, as does the formation of OH through G1 and G2.³² It has been estimated that in the presence of aerosols, the global mean tropospheric OH concentration decreases by 3%;³³ although an additional source of OH radicals can be related to the photolysis of ozone adsorbed at the surface of the aerosols (see below). These data clearly demonstrate that the tropospheric gas phase chemistry and cloud chemistry are not only strongly interrelated but are also strongly coupled.

O_2^- can oxidize ozone, contributing to the aqueous phase loss of O_3 and production of hydroxyl radicals (S5). The mechanism involves an electron transfer from O_2^- to O_3 . The anion O_3^- is in fast equilibrium with O_2 and O^- (S5a, with $K_{\text{eq}} = 2.5 \times 10^6 \text{ M}$),³ and the oxygen atom anion is in equilibrium (S5b) with its conjugated acid OH^- .³



such that the whole reaction can be written as



S5c constitutes the dominant source of hydroxyl radicals in cloud droplets, and it is estimated that the OH formed through these reactions is between 5 and 50 times larger than the scavenging of OH from the gas phase.³⁴ The reaction is obviously pH sensitive with the production of hydroxyl radicals being enhanced at higher pH values.

A further source of hydroxyl radicals in clouds arises from Fenton-like reactions of Fe^{2+} and Cu^+ , which can account for 9–41% of OH production in droplets.³² Details on Fenton mechanisms are discussed in the next section.

ROS in Water Abatement Processes

Reactions involving O_3 , H_2O_2 , and/or UV radiation in water form a subset of reactions in so-called advanced oxidation processes (AOPs). Glaze et al.⁴ defined AOPs as those processes that lead to the generation of hydroxyl radicals in sufficient quantity to affect water purification. The main processes include ozonation at high pH, simultaneous addition of ozone and hydrogen peroxide (peroxone chemistry),^{3,35} and Fenton reactions.³⁶

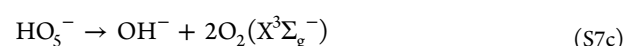
Different $\text{O}_3 + \text{OH}^-$ reactions can be envisaged (S1–S4). From them, only S3 is exergonic, but it is spin forbidden, thereby ruling out the possibility of it playing an important role. It has been suggested that S1 takes place through an HO_4^- intermediate (S1a), which then decays into $\text{O}_2^- + \text{HO}_2$ (S1b).³ Theoretical calculations,²⁴ however, predict the formation of the HO_4^- anion to be endergonic regarding $\text{O}_3 + \text{OH}^-$ and $\text{O}_2^- + \text{HO}_2$, thus lessening the importance of this intermediate.



The simultaneous addition of O_3 and H_2O_2 to a water solution is named the “peroxone process”,³ and it favors the production of hydroxyl radicals. However, O_3 does not react with H_2O_2 directly ($K_{\text{S6}} = 0.065 \text{ M}^{-1} \text{ s}^{-1}$) but rather with its conjugated base HO_2^- ($K_{\text{S7}} = 5.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) via S7.³⁵ This is a pH-dependent reaction ($\text{p}K_{\text{a}(\text{H}_2\text{O}_2)} = 11.6$), which dominates over a wide range of pH values with an observed rate constant given by eq 6 (reaction S7 should have minor to no relevance in acidic media, however).³

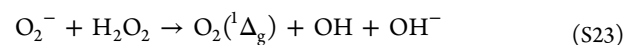
$$K_{\text{obs}} = K_{\text{S7}} \times 10^{(\text{pH} - \text{p}K_{\text{a}})} \quad (6)$$

The most plausible reaction mechanism involves the addition of O_3 to HO_2^- , forming the HO_5^- adduct S7a, which decomposes through reactions S7b and S7c.³

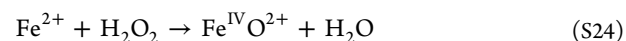


Reaction S7b leads to hydroxyl radical formation because HO_2 deprotonates to O_2^- , which follows the set of reactions S5–S5c as discussed in the previous section.

The Fenton reaction involves the production of hydroxyl radicals from the oxidation of ferrous ion by hydrogen peroxide (S16). The Fe^{3+} ions formed are then reduced to Fe^{2+} by the superoxide anion (S17). The overall reaction (S23) is commonly known as the Haber–Weiss reaction.³⁷



Fe^{2+} can also be oxidized by HO and HO_2 (S20 and S21), whereas Fe^{3+} can be reduced by HO_2 and O_2^- (S17), and even by H_2O_2 (S19), making Fenton chemistry a very complex system.²⁶ The Fenton reaction has been known for more than 100 years, and yet the whole detailed reaction mechanism is still not well understood. In addition, and depending on the specific conditions, there is competition between the one electron transfer process (S16) and the two electron oxidation process via O atom transfer (S24).³⁸



This competition is pH dependent, and as the pH increases, the reaction mechanism follows reaction S24.

It is interesting to point out that ozone can also oxidize Fe^{2+} in a similar manner as H_2O_2 does in reaction S24³⁹ with a computed rate constant of $8.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$,²⁷ suggesting that S22 can be an important sink of ozone in clouds.

ROS in Biological Systems

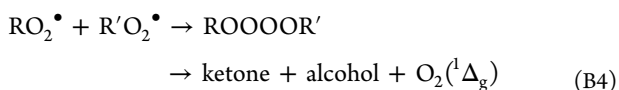
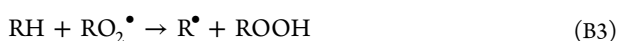
In aerobic biological organisms, ROS are formed as byproducts of the metabolism of molecular oxygen. However, ROS can also come from pollutants in the environment, from food, or even from processes induced by the sun’s UV radiation absorbed through the skin. Living organisms have an efficient antioxidant system to neutralize the damage produced by ROS.⁶ However, a dysfunction in the antioxidant system can cause oxidative stress, which can result in an imbalance between the rate of the oxidant production and degradation.⁸

Among the endogenous ROS, O_2^- is one of the primary species that is formed by 1 electron reduction of molecular oxygen. Most O_2^- is reduced to H_2O_2 by superoxide dismutase (SOD) at almost diffusion limited rates.⁴⁰ The remaining

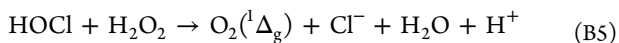
fraction can add to other radicals such as NO-producing peroxynitrite (ONOO^-),^{6,40} a potent biological oxidant, but it can also inactivate several enzymes containing iron–sulfur clusters.⁶ This leads to the release of iron, which triggers the production of OH radicals through the Haber–Weiss reaction (see S16, S17, and S23 in the previous section).

Moreover, at pH 6.8, ~1% of the superoxide is found as a hydroperoxyl radical, which can react with O_2^- to produce H_2O_2 , as discussed in the previous section (S11). The HO_2 radical is highly reactive, and it has a high membrane permeance such that, despite its low concentration, it has been assumed to play a central role in mediating the toxic side effects of aerobic respiration.⁴¹

Similar to its role in the atmosphere, the OH radical is a key oxidant and reacts with a nearly diffusion-controlled rate constant. Hydroxyl radicals react with biomolecules through hydrogen abstraction, addition to double bonds, and electron transfer in the same manner as discussed in the previous sections, and it can produce DNA damage and modify proteins and lipids.^{8,44} As an example, let us consider the oxidation of cell membranes that causes changes in the structural organization and packing of their lipid components. Hydroxyl radicals abstract a hydrogen atom from polyunsaturated fatty acids in the membrane. This process produces a carbon-centered radical, which reacts fast with O_2 -generating peroxy radicals (RO_2) (B1–B2) in a manner similar to that in the atmospheric gas phase (Figure 2). The RO_2 radical can further react through B3 or B4. In B4, another peroxy radical ($\text{R}'\text{O}_2$) produced by the oxidation of another lipid chain is involved. The tetraoxide formed decomposes according to the Russell mechanism, yielding a ketone, an alcohol, and an excited oxygen molecule $\text{O}_2(^1\Delta_g)$ (B4).^{6,42}



Further sources of $\text{O}_2(^1\Delta_g)$ in living organisms are the Haber–Weiss reaction, the Fenton reaction (S16, S17, and S23), and the reaction between H_2O_2 and HOCl (B5) that takes place in neutrophils.⁴² $\text{O}_2(^1\Delta_g)$ is involved in Diels–Alder reactions, ene-reactions, 2 + 2 cyclo-additions, and the formation of peroxides, and constitutes an important defense mechanism against microorganisms.^{8,42}



Ozone is one of the most important tropospheric pollutants, and it has an important health impact on living organisms in both animals and plants.⁷ Ozone is capable of reacting with almost every biomolecule (lipids, proteins, nucleic acids, carbohydrates, thiols, tocopherols, etc.). It does not penetrate far into cells but reacts mainly in the apoplast in plants, in the pulmonary epithelial lining fluid (ELF) layer, in epithelial cell membranes, and it can react with human skin lipids.^{7,43} Indeed, in both plant apoplasts and the ELF, there coexist a number of antioxidants, such as ascorbic acid, uric acid, and glutathione, which constitute the first line of defense against O_3 .⁴⁴ Thus, cellular damage does not originate from a direct reaction with

ozone but rather from species formed in the reaction of ozone with antioxidants or with the double bonds of the lipids found in the ELF, cell membranes, and skin.^{7,43} In these processes, the reaction of ozone with lipid double bonds follows the Criegee mechanism as displayed in Figure 3 and leads mostly to the formation of H_2O_2 through the reaction of the carbonyl oxide intermediate with water.

Wentworth and co-workers have suggested that O_3 could also be generated endogenously in human atherosclerotic arteries and by activated antibody-coated neutrophils.⁴⁵ Their conclusions were supported by theoretical calculations regarding the reaction of O_3 with H_2O_2 ⁴⁶ and $\text{O}_2(^1\Delta_g)$ with H_2O .⁴⁷ Evidence for ozone formation has been indirectly inferred from the identification of signature products.⁴⁵ These results are however controversial because other studies concluded that such signature products are not univocal, and that endogenous O_3 formation should be taken with caution.⁴⁸ The question remains open as very recent work supports ozone formation in biological systems with the overall mechanism remaining unclear.⁴⁹

IV. ROS AT AQUEOUS INTERFACES

In recent years, several experimental and theoretical investigations have focused on chemistry at the air–water interface, suggesting enhanced reactivity in this environment.

Computational studies of molecules at the air–water interface have provided valuable information for improving our understanding of chemistry at the surface of atmospheric clouds and have concurrently raised new questions about such chemistry. In this context, a fundamental property is the accommodation free energy profile as well as the solvation free energy difference between the interface and the bulk, $\delta\Delta G_{\text{solv}} = \Delta G_{\text{solv,interface}} - \Delta G_{\text{solv,bulk}}$, which are connected with an air–interface–bulk partition. Molecular dynamics (MD) simulations on important ROS, such as O_2 , O_3 , OH, HO_2 , and H_2O_2 , have concluded that all of these species display thermodynamic stabilization, and thus enriched concentration, at the interface.⁵⁰

Calculated free energy differences can also be used to estimate equilibrium constants. Using elaborated quantum mechanics/molecular mechanics (QM/MM) simulations for the HO_2 radical at the air–water interface (Figure 4), a net increase of the pK_a by 1–2 units, and a decrease of the O_2/O_2^- redox potential by ~0.3 V, have been predicted.^{51,52} Moreover, these QM/MM simulations have allowed solvation effects on thermal reactions at the interface to be rationalized. A

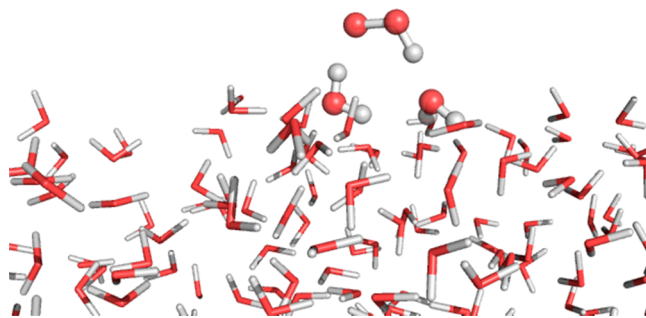


Figure 4. Snapshot of a combined QM/MM molecular dynamics simulation of the HO_2 radical at the air–water interface. The radical, and the two water molecules forming a hydrogen-bond with the radical, are represented in a ball and stick model.

key issue is the stabilization/destabilization of the reactant frontier orbitals (HOMO, LUMO), which in turn depends on the proton acceptor or proton donor character of the species.⁵¹

Photochemical processes can also be significantly impacted by interactions with the interface. Indeed, the combination of computer simulation results for the UV–visible absorption spectrum of ozone with experimental data for quantum yields and actinic flux have led to the prediction that the production rate of OH radicals at the interface is increased by as much as 3–4 orders of magnitude relative to the equivalent reactions in the gas phase (G1 and G2).⁵³

In line with these theoretical results, enhanced reactivity (compared to bulk) has been observed in the reactions between Fe^{2+} and H_2O_2 or O_3 (Fenton chemistry via reactions S16, S17, and S22–S24)⁵⁴ and the photochemistry associated with FeOH^{2+} and H_2O_2 .⁵⁵

Other studies have focused on processes of biological relevance. Ozonolysis of antioxidants, such as ascorbic acid and uric acid, resulted in $\text{O}_2(^1\Delta_g)$ productions at the interface that were different than those of the bulk solution and in significant production of different ozonides, which diffuse through biomembranes to trigger degradation of the membrane surface.^{56,57} In addition, theoretical simulations have predicted that the HO_2 acid–base equilibrium is increased by more than 1 order of magnitude with respect to that of bulk water,⁵⁸ reinforcing the importance of hydroperoxyl radicals in biological systems.

V. CONCLUSIONS

This account summarizes the most relevant chemical features of ROS in atmospheric, water treatment, and biological environments. These species have different functions in the distinct environments, but the underlying chemistry is very similar. Many gas phase reactions driven by hydroxyl radicals and ozone that take place in the atmosphere have the same electronic features and similar mechanisms as reactions that occur in liquid water, noting that solvation effects can enhance the reaction rate significantly. In solution, the acid–base equilibrium of HO_2 , H_2O_2 , and HO and the redox properties of O_2 , O_3 , H_2O_2 , and OH play a major role, and the pH conditions in different environments are the origin of the main differences seen in atmospheric chemistry (mainly acidic in clouds), water treatments (wide range), and living organisms (close to 7).

Less known are the processes that take place at the air–water and water–hydrophobic interfaces. Recent results from the literature have shown enhanced reactivity of ROS at these interfaces and predict significant changes in properties such as pK_a and redox potentials of some species. These studies suggest that the air–water and water–hydrophobic interfaces are environments of their own and constitute an emerging area of important research that branches and bridges across the gas and liquid phase environments.

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