

PHYSICAL AND CHEMICAL PROPERTIES OF OZONE

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Summary

In the present chapter, major physical and chemical properties of ozone shall be taken under examination. The molecular structure of ozone is going to be analyzed and discussed first, as it is the source and the explanation of all the other properties to be revealed after. The main physical constants concerning ozone shall be introduced, together with the data concerning the solubility of ozone in water and its dependence on temperature. Chemical properties that are going to be described here include the decomposition of ozone in aqueous and in gaseous phase and different reactions of molecular ozone with both inorganic and organic substances. Health and safety aspects regarding the use of ozone shall also be discussed.

1. Introduction

During the past decades, there has been a growing interest in the implementation of the advanced oxidation processes (AOPs) for air and water purification. According to their definition, the AOPs are processes involving the formation and reactions of hydroxyl radicals. The AOPs have been seen to be effectively used for the purification of both water and air, as pre-treatment or as treatment processes for contaminated media. It can be said that one of the first, if not the first one of these processes to be taken under thorough study was the use of ozone. Nowadays ozonation process is widely used all around the world with the main goal of drinking water purification.

To understand the process of water ozonation better, one must take into account all the properties of ozone that are involved. Generally speaking, the ozonation process consists of the following stages: generation of ozone, its introduction to the water, dissolution, and, subsequently, the chemical reactions between ozone and the dissolved substances. Dissolution of ozone in the water is governed by its physical properties, and the dissolution itself, as it shall be seen later, leads to partial ozone decomposition that initiates a chain of radical reactions, acting as a source of different oxidants, including the abovementioned hydroxyl radical. Then, the remaining dissolved molecular ozone steps into various reactions with the substances present in the water. Inorganic compounds mainly initiate its decomposition into radical species. Organic substances, on the other hand, react both directly with ozone and with radicals; if the latter reactions are out of our present scope, the former shall be discussed here. The reactions of ozone with organics proceed via several major pathways: in case of unsaturated bonds, the reactions of electrophilic substitution, nucleophilic addition and cycloaddition are possible depending on the properties of the substance under scope, especially on the character of atoms neighboring the unsaturated bond. Reactions of aliphatic organics, including amines, sulfur and carbon group heteroatom containing organic substances shall be also overviewed. In spite of their lower reaction rate when compared to the unsaturated hydrocarbons, the reactions of molecular ozone with saturated organic substances of different chemical structure are a point of interest that shall be elucidated.

Health and safety issues regarding the use of ozone shall be discussed here as a separate

point, as the wide use of ozonation and the properties of ozone make this topic important.

Finally, one must say that both physical and especially chemical properties of ozone can be understood much better through the knowledge of their ultimate source – the molecular structure of ozone. With this point we shall make our start.

2. Molecular Structure of Ozone

Ozone is a triatomic oxygen compound and its high reactivity is an outcome of its molecular structure. The structure of ozone molecule was established in 1952 as a hybrid of four resonance structures shown in Figure 1. The resonance structures are in a way extreme structures of a molecule that do not actually exist, but the real molecular structures lay in between of the resonance ones. These structures are used when no conventional structural formulae can actually describe the real chemical structure and the experimentally determined properties of the molecule are such that they correspond to those of all the different resonance structures simultaneously. This situation is well reflected in case of the investigation of ozone molecule structure. If the length of a single bond between two oxygen atoms in hydrogen peroxide is 1.49 Å and that of a double bond in oxygen molecule is 1.21 Å, the length of the bonds between oxygen atoms in ozone molecule has been determined to be 1.278 Å. This phenomenon is reflected by the hybrid of the first and the second resonance structures, as the bonds are longer than double bonds and yet considerably shorter than single bonds should be.

However, those two resonance structures alone do not yet give a precise overview of the molecular structure of ozone. They should give an O-O-O angle of 120°, due to the repelling between the atoms' electron clouds; the experimentally determined angle is, on the other hand, slightly lower, being 116.78°. The lower angle can be in its turn explained by the mutual attraction of positively and negatively charged oxygen atoms, as third and fourth resonance structures suggest. The latter peculiarity explains how the ozone molecule in reactions with unsaturated organics can act both as electrophilic and nucleophilic agent, depending on the character of the organic substrate; the mechanism of these reactions shall be discussed later.

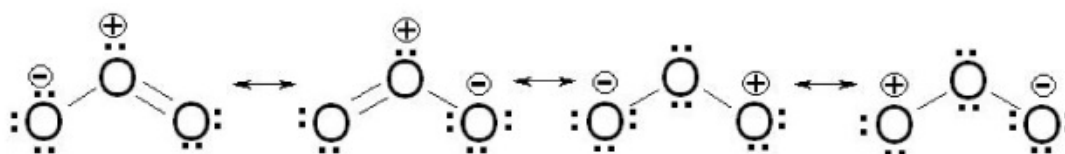


Figure 1. Resonance structures of ozone molecule

An alternative structure of ozone molecule could be a cyclic one with electrically neutral oxygen atoms connected by single bonds. This structure, although being synthesized in laboratory conditions using high-frequency lasers, does not occur frequently in the nature. One of the main reasons for this is the angle strain in triangular structure, as in case with cyclopropane, ethylene oxide or aziridine. In case of three atoms of the same electronegativity the O-O-O angle should be close to 120° as mentioned above for energetic reasons; however, in case of cyclic structure a triatomic

molecule is shaped in form of an equilateral triangle, where the angles can be only 60°. This way the electron clouds that form σ -bonds are severely bent outward from straight lines of the triangle. This situation is often referred to as bent bond or banana bond. Such bonds are far less stable due to the abovementioned strain and at receiving relatively small amounts of energy the cycle is easy to open.

3. Physical Properties of Ozone

3.1. Basic Physical Data

At standard conditions ozone is a pale blue gas; at concentration levels in the Earth's atmosphere it is colorless. The density of ozone is over 1.5 times greater than that of the air. Gaseous mixtures of ozone with oxygen, nitrogen or air are by their properties close to ideal mixtures. At concentrations of over approximately 10-11% by volume or greater ozone-air mixtures are explosive, as ozone decomposes with emission of large quantities of energy. Working with ozone at lower concentrations is considered to be safe in that respect (for other working safety issues considering the use of ozone, see Section 5). Main physical constants concerning ozone are summarized in Table 1.

| Parameter | Value |
|---------------------------------|--|
| Molecular mass | 47.998 g mol ⁻¹ |
| Density at 273.15 K | 2.144 kg m ⁻³ |
| Melting point at 1 atm | 80.7 K |
| Boiling point at 1 atm | 161.3 K |
| Critical temperature | 261.05 K |
| Critical pressure | 54.62 atm |
| Critical density | 463 kg m ⁻³ |
| Density at 90.15 K | 1751 kg m ⁻³ |
| Viscosity at 90.15 K | 1.55±0.02 mPa s ⁻¹ |
| Electron affinity | 1.9-2.7 eV |
| Dipole moment | 0.53±0.02 D |
| Dielectric constant at 273.15 K | 1.0019 |
| Dielectric constant at 90.15 K | 4.75 |
| Heat of evaporation | 0.71 J mol ⁻¹ |
| Free energy of formation | 6.89 J mol ⁻¹ |
| Heat of dissolution | 0.93 J mol ⁻¹ |
| Diffusion coefficient in water | 1.74 × 10 ⁻⁹ m ² s ⁻¹ |
| Van der Waals' constants: | |
| <i>a</i> | 3.545 atm L ² mol ⁻² |
| <i>b</i> | 0.04903 L mol ⁻¹ |

Table 1. Physical constants of ozone

3.2. Solubility of Ozone

Ozone, like oxygen, is not readily soluble in water. Solubility of ozone in water as the dependence on water temperature at pressure of 1 atm can be characterized by Figure 2. The values of solubility are presented as a solubility ratio (S), i.e. as a ratio of ozone

concentration in water (given in mg L^{-1}) to ozone concentration in the air (given in mg L^{-1}). As Figure 2 shows, the dependence of the solubility ratio on the temperature at the range examined in the available literature can be fairly enough approximated by an exponential function with sensible value of the coefficient of determination.

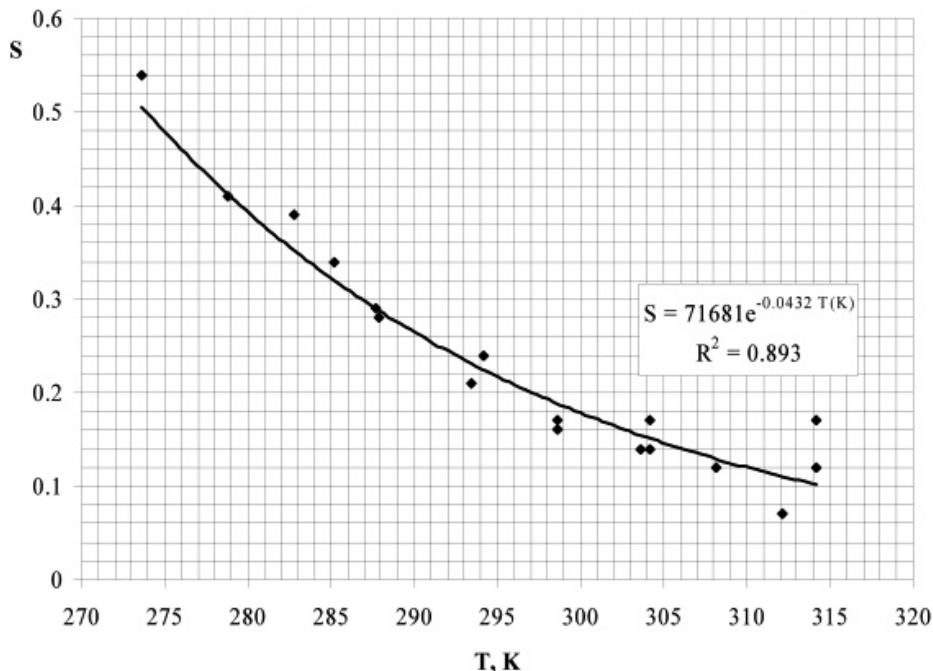


Figure 2. Temperature dependence of the solubility of ozone in water

As the available experimental data suggests, the dissolution of ozone follows Henry's law, i.e. the concentration of dissolved ozone at fixed temperature is consistently growing with the increase of the partial pressure of ozone in gaseous phase and the trend is close to linear, as in Henry's law.

4. Chemical Properties of Ozone

4.1. Ozone-initiated Radical Reactions in Water

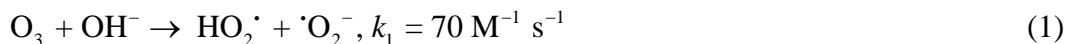
Ozone-initiated radical reactions are oxidation-reduction or, simpler, redox reactions, i.e. reactions involving the transfer of electrons between reacting species and the changes in the oxidation state of the reagents. In these reactions, ozone is effectively decomposed, although it may thus act as a precursor for the formation of far more powerful oxidants than itself, e.g. hydroxyl radical, which, as an oxidizing agent, is even more powerful than fluorine.

Generally speaking, the decomposition of ozone as a result of its dissolution in water that initiates the formation of various radical species can proceed according to two basic mechanisms. They are, respectively, Hoigné-Staehlin-Bader and Gordon-Tomiyasu-Fukutomi mechanisms, named thus after the authors of respective models. The former pathway is considered to be the most widely accepted; however, at higher pH values the latter one is far more accurate.

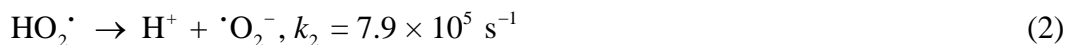
As it is common with radical reactions, their mechanism of ozone decomposition in water can be divided into three principal stages: the initiation of the reaction, chain reactions proper and the breakdown of radical reaction chain. Radicals formed in the initiation step trigger the formation of more radicals from reaction precursors, and the formed radicals serve themselves as the initiators of continuing reactions. With sufficient amounts of reaction substrate radical reaction can be considered (at least for a certain period of time) to be self-fuelled. The inhibition and breakdown of radical chain may take place in various ways: the on-going radical reaction can be inhibited by the depletion of reaction substrate, by the continuous formation and accumulation of less reactive species, or by the introduction of an agent that can adsorb the radicals without being effectively oxidized, i.e. a radical scavenger. The examples of radical scavengers can be carbonate anion, humic substances or *tert*-butyl alcohol. In case of radical scavengers the radicals are added to the substance molecule without the successive continuation of the reaction chain.

4.1.1. Hoigné-Staehlin-Bader Mechanism

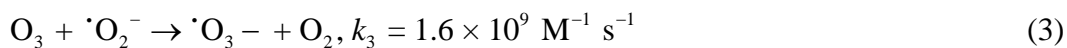
Ozone decomposition and the initiation of radical species formation according to Hoigné-Staehlin-Bader model begin with the reaction of ozone with hydroxide anion found in water primarily as a result of water molecule hydrolysis (see Eq. (1)). As a result, hydroperoxide radical and superoxide radical ion are formed.



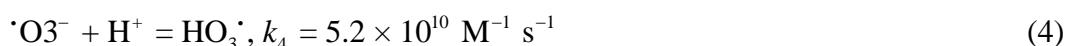
As it can be seen from the value of reaction rate constant k_1 , the initiation step is somewhat slow, making it the limiting stage of ozone decomposition. Hydroperoxide radical formed in the course of reaction (1) may also dissociate to form proton and superoxide radical ion, as suggested by Eq. (2):



Superoxide radical ion, formed in course of these reactions, serves as the initiator of the continuous chain reaction, transferring its excess electron to ozone molecule. Equation (3) shows its reaction with ozone, during which ozonide radical ion is formed:



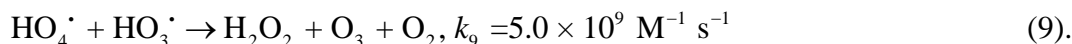
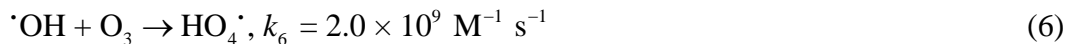
Ozonide radical ion can consequently step into reaction (4), which lead to the formation of a powerful and renowned oxidant, hydroxyl radical, as it can be seen from reaction Eq. (5):



$$k_{-4} = 2.3 \times 10^2 \text{ s}^{-1}$$



Hydroxyl radical can initiate following reactions (6-9):



Reactions (8) and (9) can be considered as an inhibition stage of the radical reaction chain; not only radical species are not formed as their products, but also ozone is at least partially regenerated.

Table 2 presents the oxidation potentials of major oxidizing species formed in the process of ozone decomposition in water compared to that of molecular ozone.

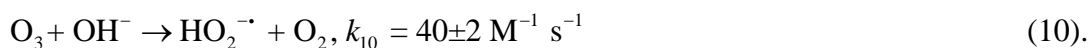
It should be added here that the values presented in Table 2 were obtained at neutral and acidic pH; in basic conditions the oxidation potential of ozone is lower, being 1.24 V.

| Oxidant | Oxidation potential, V |
|-------------------------------|------------------------|
| •OH | 2.80 |
| O ₃ | 2.07 |
| H ₂ O ₂ | 1.78 |
| HO ₂ • | 1.70 |

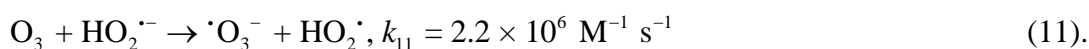
Table 2. Oxidation potentials of radical species formed during ozone dissolution in water

4.1.2. Gordon-Tomiyasu-Fukutomi Mechanism

In this scheme, the initiation reaction is somewhat different from the previous one, as only hydroperoxide anion radical is formed due to different electron transfer pattern:



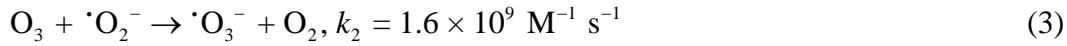
Hydroperoxide anion radical subsequently reacts with ozone molecule to form ozonide ion radical and hydroperoxide radical:



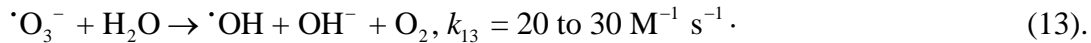
Hydroperoxide radical can also react with hydroxide anion, as the following reaction equation suggests:



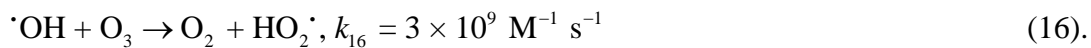
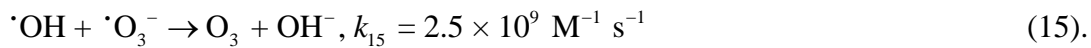
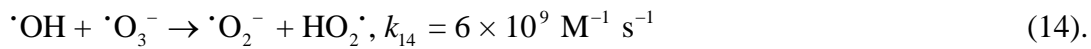
Superoxide radical, thus formed, reacts accordingly to Eq. (3):



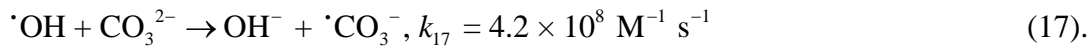
Ozonide radical ion, formed in course of reactions (3) and (11) interacts with water molecule to form hydroxyl radical:



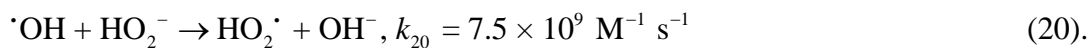
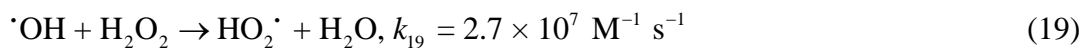
Hydroxyl radical can consequently step into reaction with ozonide anion radical or molecular ozone (Eqs. (14) to (16)):



The radical reaction pattern as presented above is effectively inhibited by dissolved carbonate-ions that have a good reputation as radical scavengers. Their action can be described by Eqs. (17) and (18):



There have been numerous suggestions that reactions (17) and (18) as they are cannot be fully considered as inhibiting the ozone decomposition, as according to reaction (18) superoxide ion radical is formed which was seen to initiate the decomposition of ozone (see Eq. (3)). Thus the current mechanism can be slightly improved by adding another two reactions:



Hydroperoxy anion in reaction (20) is formed as a result of the dissociation of hydrogen peroxide.

Even though hydrogen peroxide can act as an initiator for ozone decomposition (see section 4.2.5), it can inhibit the latter at higher concentrations due to the mass transfer becoming the limiting stage of the reaction. Hydroperoxide radicals formed during these reactions are also known to be less active than hydroxyl radicals (see Table 2).

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Biographical Sketch

Deniss Klauson was born in Tallinn, Estonia, on the 24th of March, 1983. The academic degrees received are as follow: Bachelor of Science, *cum laude*, 2005, and Master of Science, 2006. Both were received at Tallinn University of Technology (TUT), Estonia. Currently, the author is a first year PhD student at TUT, Department of Chemical Engineering; Chemical and Environmental Protection Technology is the author's major field of studies.

From August 2006 he is a Research Scientist at the Department of Chemical Engineering at TUT; also, he holds a Junior Specialist position at Tallinn Water Ltd. (a part of United Utilities, Ltd.) from 2005. Previous job experiences include: Research Associate at TUT (2002-2006) and Laboratory Assistant at Tallinn Water Ltd. (2004-2005). For two months in 2004 the author was a IAESTE scholar at Lappeenranta University of Technology, Finland. Previous publications are as follow:

1. Klauson, D., Portjanskaja, E., Kachina, A., Krichevskaya, M., Preis, S. and Kallas, J., The influence of ferrous/ferric ions on the efficiency of photocatalytic oxidation of pollutants in groundwater. *Environmental Technology*, 2005, vol. 26, no. 6, pp. 653-662(10)
2. Klauson, D., Preis, S. The influence of ferrous ions on the efficiency of aqueous photocatalytic oxidation of 2-ethoxy ethanol. *International Journal of Photoenergy*, 2005, vol. 7, no. 4, pp. 175-180
3. Klauson, D., Preis, S., The influence of iron ions on the aqueous photocatalytic oxidation of de-icing agents. *International Journal of Photoenergy*, 2007, vol. 2007, Article ID 89359, 7 pages

The author's research interest is the photocatalytic oxidation of organic pollutants, mainly oxygenated motor and jet fuel additives, using as a catalyst commercial titanium dioxide and ultraviolet irradiation. Presently, the use of various doped titania catalysts that utilize visible light for their performance is under investigation, together with solar irradiation-using photocatalysis.