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Ozone, Bad guy or good guy?

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Abbreviation

CFS	chlorofluorocarbons
EGS	electronic ground state
NMHC	various reactive nonmethane-hydrocarbons
NPA(D)N	nitroperoxyalkyl nitrates and dinitrates
OLE	olefins
ODS	ozone-depleting substances
PacN	Peroxyacyl nitrates
RCHO	aldehydes

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Abstract

Ozone is a form of elemental oxygen containing three oxygen atoms. It's a relatively unstable, highly oxidative molecule. This article gave a review about the structure of ozone molecule, its chemical trait, typical reactions involved with ozone and the process in which ozone is generated and decomposed. The methods that how to detect the residue ozone in aqueous solution were also mentioned.

Introduction

Ozone, O_3 was first recorded by Van Marum (1785), who found that oxygen gas through which a stream of electric sparks had been passed, tarnished mercury and emitted a peculiar smell[1]. In 1840 C. F. Schonbein showed that this substance was also present in the oxygen liberated during the electrolysis of acidulated water, and gave it the name ozone (meanings odd smell)[1]. We know that ozone is what protects us from the most dangerous ultraviolet (UV) radiation from the sun. Ozone in the stratosphere, which lays 25 to 30 miles above the earth, blocks harmful ultraviolet light emitted from the sun[2]. Ultraviolet light can cause cataracts and certain skin cancers, warming of the earth's surface, and damage to plants and oceanic plankton. The stratospheric ozone layer serves as a protective filter against this type of radiation and is therefore considered "good ozone". Now, the good ozone is depleted by not only the chlorofluorocarbons (CFCs) and other ozone-depleting substances (ODS), but also the increase in UVB irradiation (280-320 nm) on earth’s surface [3, 4]. That raises a major environmental threat to the skin [5]. Bad ozone is that found in the earth's atmosphere (tropospheric ozone). Ozone is formed in our atmosphere as a result of complex reactions involving air pollutants from industrial, vehicular, chemical, and consumer products (i.c. hydrocarbons and nitrogen oxides) and ultraviolet radiation from sunlight. [6]

Structure Characteristic of Ozone

Ozone is a form of elemental oxygen. Its molecular weight is 47.9982 D. In its most stable form, elemental oxygen exists as diatomic molecule (O_2). The molecules of ozone contain three oxygen atoms (O_3) and is unstable with respect to O_2. Ozone is a very reactive gas, and even at low concentrations it is irritating and toxic. Consider that there are two possible ways to connect three atoms: in a "line" and in a "ring". (Figure 1)

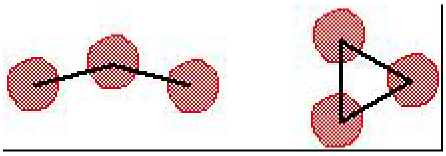
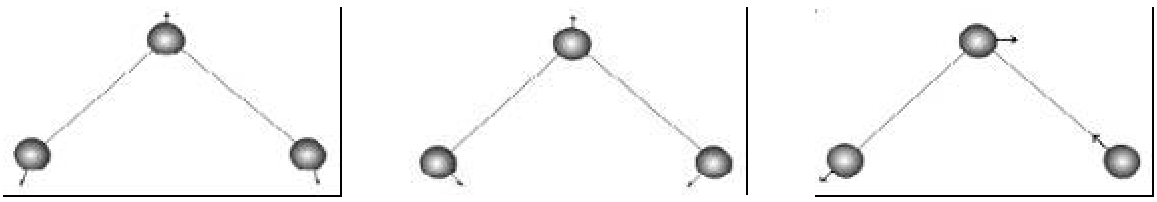


Figure 1. Two forms of possible ozone molecule.

The actual molecule is non-linear with a bond angle of 116° (Figure 2) [6].

Figure 2. Four resonance structures of the ozone molecule. Adopted from [6].

In contrast to oxygen, gaseous ozone is dimagnetic and possesses four resonance structures with (III) and (IV) accounting for its electrophilic nature[6]. When the all three oxygen atoms are the same isotopes, they form the isosceles triangle (apex angle t=116.7542°, two equal bonds r_e=1.27173 A°) [7] There are also three modes of vibration. (Figure 3)



'Stretching' symmetric vibration q1 'Bending' vibration q2 'Stretching' asymmetric vibration q3

Figure 3. Three modes of electronic ground state (EGS) vibration of ozone molecule.

With respect to selection rules in vibrational spectra isotopic species of the ozone fall in two classes: (1) isotopomer with symmetric "ends", including $^{16}O_3$, $^{18}O_3$, $^{17}O_3$, $^{16}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{16}O^{17}O^{16}O$, etc; (2) isotopmer with asymmetric "ends", including $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{18}O$, $^{16}O^{17}O^{18}O$, etc [8]. The most abundant ozone isotopomer under natural condition is $^{16}O_3$ (99.27%) [8].

Sources of ozone

Ozone is produced naturally in the stratosphere. UV light splits oxygen molecules (O_2) into two single oxygen atoms (O) [1]:

1. O_2 + hv, (λ < 240nm) $\rightarrow$ 2O

Free oxygen atoms combine with further O_2 molecules to form ozone (O_3) [1] :

2. O + O_2 $\rightarrow$ O_3

Ozone can also be generated in photochemical smog [9]:

NMHC + NO_x + hv $\rightarrow$ O_3 + other pullutants

NO_x : NO + NO_2

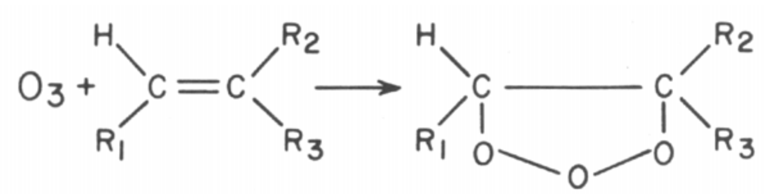
hv: λ <400 nm

In laboratory, common methods for ozone generation are ultraviolet radiation, electric arc discharge and electrolysis. Electric discharge on oxygen is the most common method for the production of ozone [2].

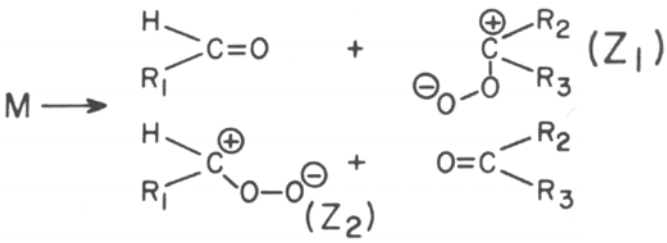
Typical reaction involved with ozone

Three oxygen atoms form a relatively unstable, highly oxidative molecule that serves as a strong oxidant for many commercial and industrial applications. Ozone is used as a bleach, a deodorizing agent, and a sterilization agent for air and drinking water. Ozone can do damage to many biological molecules including unsaturated fatty acid [10]. Ozone attacks the sulfur atom of methionone, cysteine, and glutathione, and reacts with some sterically hindered olefins to give singlet oxygen. [11] I use the reaction between ozone and olefin as an example: The ozone-olefin reaction has three steps [12]:

1. Initial reaction:



2. Molozonide splits:



3. Zwitterion reaction:

UNIMOLECULAR REARRANGEMENTS:

Z_1 → $R_2R_3 + CO_2$
→ R_2COOR_3 OR/AND R_3COOR_2

Z_2 → $R_1H + CO_2$
→ R_1COOH OR/AND $HCOOR_1$
→ $R_1OH + CO$
→ KETENE + H_2O

Not only fatty acid and protein, but also the nucleic acids are the target of ozone. For instance, tRNA can be degraded by ozone [13]. From the experiment data, we can see that the attack sites are all Gs. But the reason is still unclear (Figure 4).

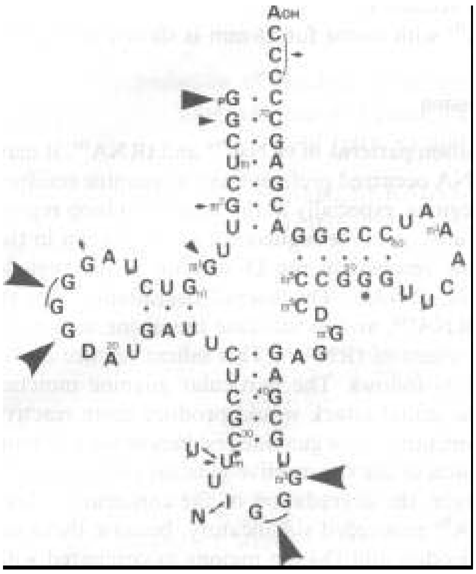


Figure 4. The mode of degradation of mouse tRNA^{pro} with ozone. Arrow heads show the degradation sites. (Adopted from [13]).

In the atmosphere, ozone reacts with nitrogen oxides, undergoing the following reactions:

$NO + O_3 \longrightarrow NO_2$

$NO_2 + RO_3^{\cdot} \longrightarrow PacN$

$NO_2 + OH^{\cdot} \longrightarrow HNO_3$

$NO_2 + O_3 \longrightarrow NO_3$

$NO_3 + NO_2 \longrightarrow N_2O_5 \xrightarrow{H2O} HNO_3$

$NO_3 + RCHO \longrightarrow HNO_3$

$NO_3 + OLE \longrightarrow NPA(D)N$

Application of Ozone

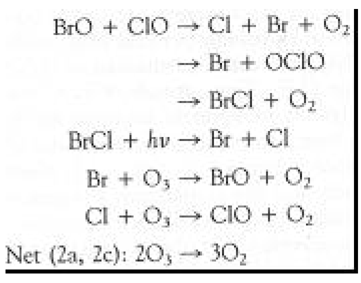
The antipathogenic effects of ozone have been substantiated for several decades. Its killing action upon bacteria, viruses, fungi, and in many species of protozoa, serve as the basis for its increasing use in disinfecting municipal water supplies in cities worldwide. It also can be used as a bleach, a deodorizing agent. All these usage are due to its highly oxidative reaction ability. Specific therapeutic applications of ozone include the treatment of vascular disease such as stroke, obstructive arteriopathy, venous insufficiency, cancer, acute and chronic viral diseases, ulcers, infected wounds, gangrenes, burns, inflammatory bowel disease such as Crohn's disease, ulcerative colitis and spinal disc problems. Ozone is also excellent for topical treatment of bacterial, fungal and viral infections, wounds, decubitus ulcers, lymphatic diseases, nail afflictions, radiodermatitis, frostbite and burns, especially those that are difficult to heal [14].

Decomposition of ozone

Ozone is destroyed in reactions with oxides containing chlorine, bromine, and iodine, which exist naturally[1]. Ozone also can decompose via reaction with UV irradiation. At λ >310 nm, O_3 photolysis leads to production of oxygen atoms in the ground stste, at λ <310 nm, $O(^1D)$ is formed[9]:

$O_3 + hv\ (\lambda > 310\ nm) \longrightarrow O_2 + O\ (^3P)$

$O_3 + hv\ (\lambda < 310\ nm) \longrightarrow O_2 + O\ (^1D)$



Chlorofluorocarbons (CFCs) are the principal man-made pollutants which have the effect of depleting the ozone level. CFCs were produced world-wide and widely used as refrigerants and foaming agents. In stratosphere, solar UV radiation releases chlorine species which attack ozone catalytically [9].

After the ozone level was reduced, skin cancer and other UV induced diseases increased[5].

Detection of ozone

Residual aqueous ozone can by determined by direct UV absorption at 259 nm is proportional to ozone concentration[12]. Another method is using indigo or iron terpyridine as a reporter reagent [15]. When they react with ozone, the change of color (fade) is proportion to the ozone concentration. Figure 5.

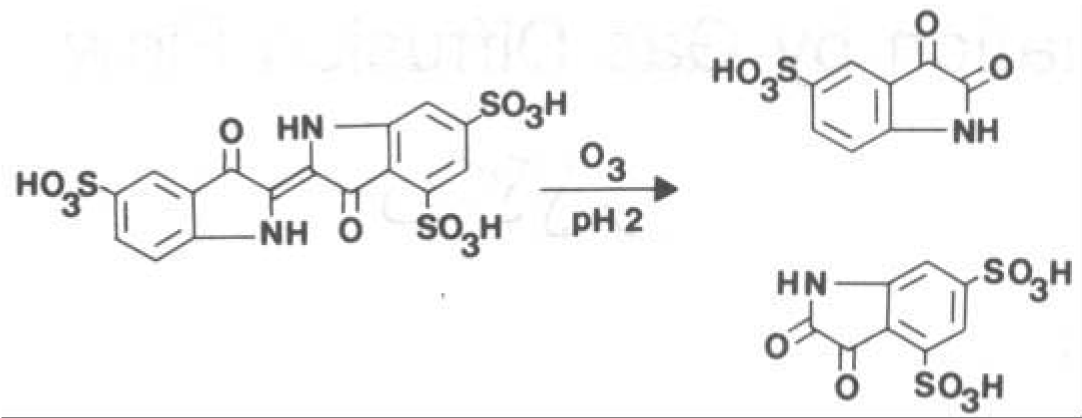


Figure 5. Structure and reaction equation for the indigo reagent decolorization by ozone. (Adopted from [15])

Summary

Ozone has highly oxidizing which is the chemical basis of its application. If it used as a bleach, a deodorizing agent or even in therapy, it is a good guy. But it also can be contribute to smog causing air pollution, or can damage to biological molecule that are essential for life, it is a bad guy.

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