Short communication

Detrimental impact of triplet oxygen in biosphere

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Oxygen is essential for the existence of all forms of life since it is an important constituent of almost all biologically important compounds including DNA and serves as blood purifier. Simultaneously oxygen also induces a number of degradation processes through the generation of reactive oxygen species like superoxide radical anion, singlet oxygen, hydroxyl radical, hydrogen peroxide etc. The reactive oxygen species also cause serious health hazards. In this paper an attempt has been made to discuss various methods of generation of triplet oxygen, its reaction, its detrimental effects, and some protective measures to nullify the catastrophic effect of triplet oxygen.

Key words: Oxygen, molecular triplet oxygen, superoxide radical anion, singlet oxygen, hydroxyl radical, hydrogen peroxide.

INTRODUCTION

At normal temperature and pressure, oxygen exists as a colourless and odourless gas with molecular formula O_2 . The molecular orbital electronic arrangement of the molecule is:

 $\sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2 \, \sigma 2p_x{}^2 \, \pi 2p_y{}^2 \, \pi 2p_z{}^2 \, \pi^* 2p_y{}^1 \, \pi^* 2p_z{}^1$

The molecular oxygen in its ground state contains two unpaired electrons with parallel spin and hence molecular oxygen is known as molecular triplet oxygen (${}^{3}O_{2}$). Its bond order is two and it exhibit paramagnetic behavior. It has bond length of 121 pm and bond energy of 498 kJ/mol (Pauling, 1960). This is an important species which sustains live on earth and forms a major part of the atmosphere.

Generation of triplet oxygen

1. By Photosynthesis: Oxygen is produced by photo induced splitting of water during oxygenic photosynthesis. For example green algae and cyan bacteria in marine environment generate about 70% of the free oxygen produced on earth surface and the rest is produced by terrestrial plants (Raven et al., 2005).

 $6CO_2 + 6H_2O$ (chrophyll) $\xrightarrow{h_V}$ $C_6H_{12}O_6 + 6O_2$

2. Photolytic Oxygen evolution: Photolytic oxygen occurs

by the decomposition of water in presence of light and a complex enzymatic system (Raval et al., 2005).

$$2H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e$$

3. Photochemical reactions of ozone: Ozone can undergo photodecomposition in presence of species like NO, Cl^{\circ} *etc.* to give molecular oxygen (Dey, 1999; Sharma, 2001). Ozone absorbs ultraviolet radiation with wavelengths as long as 290 nm. This radiation causes the ozone to decompose into O₂ molecules and oxygen atoms.

 $O_3 (g) \xrightarrow{UV (<290 nm)} O_2 (g) + O (g) (light wavelength < 290 nm)$

This, too, is an exothermic reaction. The overall effect of this reaction and the previous reaction is the conversion of light energy into heat.

Thus, ozone in the stratosphere prevents highly energetic radiation from reaching the Earth's surface and converts the energy of this radiation to heat. These compounds are so inert that they, like N₂O survive in the atmosphere until they eventually reach the stratosphere, where intense UV radiation from the sun liberates chlorine atoms from them. The chlorine atoms, like NO, catalytically destroy ozone.

$$2NO + O_3 \rightarrow N_2O + 2O_2$$

 $CI^{\circ} + O_3 \rightarrow CIO^{\circ} + O_2$

 $CIO^{\circ} + O \rightarrow CI^{\circ} + O_2$

Reactions of oxygen

1. Reaction with active metals: Oxygen reacts spontaneously with active metals to give either their oxide or peroxide or superoxide, depending upon electro positivity of the metal. Some bases can be prepared by the direct combination of a metal with oxygen.

Metal + Oxygen \rightarrow Basic oxide

4Li + $O_2 \rightarrow 2Li_2O$ (Lithium oxide)

 $4Na + O_2 \rightarrow 2Na_2O$ (sodium oxide)

 $2Na + O_2 \rightarrow Na_2O_2$ (Sodium peroxide)

 $K + O_2 \rightarrow KO_2$ (Potassium superoxide)

2. Reaction with non metals: Oxygen reacts with non metals corresponding oxides.

 $S + O_2 \rightarrow SO_2$

$$P + O_2 \rightarrow P_2 O_5$$

3. Reaction with nonmetal oxides: Oxygen reacts with toxic nonmetal oxides like NO SO_2 etc which subsequently undergo some other reactions and get eliminated from the environment (Panda, 2007; Pani, 2007).

$$2NO_{(g)} + O_2 \rightarrow 2NO_2(g)$$

 $2NO_{(g)} + O_{(g)} \rightarrow N_2O_5_{(g)}$

 N_2O_5 (g) + H_2O (l) \rightarrow 2HNO₃ (l)

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

 SO_3 (g) + H₂O (l) \rightarrow H₂SO₄ (l)

4. Photochemical decomposition followed by combination: Oxygen in stratosphere decomposes to atomic oxygen by absorbing UV radiation of wavelength less than 240 nm which subsequently combine with O_2 molecule to give ozone, an important reactive oxygen species (Dey, 1999).

 $O_2 + O \rightarrow O_3$

5. Reduction to a number of ROS: Oxygen becomes a

very good electron acceptor from the electron transport chain during cellular respiration (mitochondria) and light reaction of photosynthesis (Han et al., 2001; Panda et al., 1986). Such an electron acceptance converts oxygen to other reactive oxygen species in a step wise manner as shown below:

 $O_2 + e \xrightarrow{etc.} O_2^- \circ (superoxide anion)$

 $O_2^- \circ + 2H^+ + 2e^- \rightarrow H_2O_2$ (Hydrogen peroxide)

 $H_2O_2 \rightarrow 2O \circ H$ (Hydroxyl radical)

 $H^+ + O_{\circ}H + e^- \rightarrow H_2O$

Detrimental effects of oxygen gas

Oxygen is essential for all forms of life since it is a constituent of DNA and almost all other biologically important compounds. But if a species is exposed to large amount of oxygen for a longer period of time, the oxygen becomes highly detrimental.

1. Breathing 50 to 100% oxygen at normal pressure over a prolonged period causes lung damage that is, "Paul– Bert effect".

2. Highly concentrated sources of oxygen promote rapid combustion and therefore cause fire and explosion hazards in presence of fuel. The combustion hazards also apply to the compounds of oxygen with a high oxidation potential such as chlorate, perchlorate, dichromate etc.

3. High concentration of oxygen damages cells mainly through the formation of a number of ROS which attack unsaturated sites of lipids causing their peroxidation. ROS also attacks DNA and other cell components.

4. Taking oxygen gas at a higher pressure than normal atmospheric pressure for a longer period of time causes hyperoxia which is manifested by dizziness, nausea, twitching on the face, coughing and irritation of the throat etc.

5. Liquid oxygen spills, if allowed to soak in to organic matter, cause these materials to detonate unpredictably with subsequent mechanical impact.

6. Higher concentration of oxygen can cause corrosion of metals and nonmetals by forming the corresponding oxides and thereby causing their destruction.

7. Conversion of oxygen to other reactive oxygen species like ${}^{1}O_{2}$, O₃, ${}^{\circ}OH$, O $_{2}^{-}{}^{\circ}$ *etc.* result in senescence of plants and animals, prematuring of leaves etc.

Protective measures

Since life on earth exists in presence of oxygen, it has

been associated with a number of antioxidant systems to nullify the detrimental effect of oxygen. The antioxidants may be enzymatic or non-enzymatic nature.

Enzymatic antioxidants

Mainly three groups of enzymes play significant role in protecting biological system from oxidant stress.

Superoxide dismutase

(SOD) These enzymes convert superoxide radical anion to hydrogen peroxide (H_2O_2) which comparatively less toxic than superoxide radical anion. (Johnson and Giulvi, 2005; Nozik et al., 2005)

$$O_2^-\circ + O_2^-\circ \rightarrow O_2 + O_2^{2-}$$

 O_2^{2-} + $2H^+ \rightarrow H_2O_2$

SOD accelerates detoxifying reaction roughly 10,000 times over non-catalyzed reaction.

Catalase

It degrades H₂O₂ to water and oxygen

$$2H_2O_2 \xrightarrow{catalase} 2H_2O + O_2$$

Glutathione peroxidases

These enzymes degrade hydrogen peroxide and also reduce organic peroxides in to alcohol.

 $2H_2O_2 \xrightarrow{Glutathion en \cdot peroxidase s} 2H_2O + O_2$

 ROO^{-} ______ *Glutathion en peroxidase s* \rightarrow $R-OH + O_2$

Besides the above three major classes of enzymes, other enzymes like glutathione transferase, hemoxgenase etc also participate in enzymatic control of oxygen radicals and their products (Bjelakovic, 2007).

Non-enzymatic antioxidants

Three nonenzymatic antioxidants of particular importance are:

1. Vitamin E: It traps peroxyradicals in cellular membrane there by protecting them from oxidative damage.

2. Vitamin C: It traps reactive oxygen species from a variety of sources.

3. Glutathine: It is a tripeptide (glutamyl–cysteinyl– glycine) with exposed sulfhydryl group (SH). The SH group is very good target for the trapping of free radicals (Matill, 1947).

Besides the above three, other non enzymatic antioxidants may be carotenoids, flavonoids, uricacid, bilrubin etc.

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