Part 2: The Chemistry of Ozone Gas.

Abstract: In Part 2 of Ozonated Liquids in Dental Practice, the chemistry of ozone gas and its reactivity is examined. The manufacture of ozone and applications are discussed. The formation of radicals is of concern in animal cells, and early research that is sued to ‘prove’ the dangerous nature of ozone is examined. Examination of the original research shows the current FDA position concerning ozone and its usage in health care to be flawed. Ozone gas is used extensively in commercial applications to sterilise water, to remove organic compounds from products and to control water effluent pollution.

Introduction.

Ozone (Fig 2.1) is a pale blue-coloured gas with a chemical formula O$_3$. It plays an important role as a natural constituent in the higher layer of the earth's atmosphere.

The word for ozone comes from the Greek word "ozein" which means "to smell" since ozone was first noticed because of its characteristic pungent odor. The odor is detectable in air at levels of about 0.1 parts per million, and it is postulated that exposure to ozone becomes fatal to humans at around levels of 100 ppm for 10,000 minutes or 10,000 ppm for 30 seconds.

Ozone, O$_3$, is a blue-coloured gas at ambient temperatures, but this colour is not noticed at the low concentrations at which it is usually generated. In the liquid and solid states, ozone is dark blue. Liquid ozone boils at -111.3 °C and solid ozone melts at -192.5 °C.

Ozone has the unique feature of decomposing to harmless, non-toxic and environmentally safe oxygen, chemical formula O$_2$. Ozone is naturally produced by the energy of sunlight in the upper atmosphere. It is heavier than air and thus prone to gravitational pull towards the earth's crust. As it falls towards the earth, it reacts with any pollutant in the atmosphere that it comes into contact with, thereby cleaning the air. If ozone binds water molecules in water vapour in the atmosphere, it forms hydrogen peroxide, a component of rainwater.
There are three natural ways that ozone is created:

1. The first is by lighting, which provides the wonderful fresh smell after a thunderstorm. The high-energy discharge from the lightning strike provides the energy to combine three molecules of oxygen (O₂) into two molecules of ozone (O₃).

2. The second is through waterfalls and crashing surf, which accounts for the energetic feeling and calm experienced near these sites.

3. The third way is by photons from the sun breaking apart nitrous oxide, a pollutant formed by the combustion of hydrocarbons in the internal combustion engine. This type of ozone accumulates in smog due to temperature inversions and is a lung and eye irritant. It is this harmful effect of ozone that the media focuses on and why the healing property of ozone tends to be ignored. This is despite the plethora of research that shows ozone to be possibly the best way forward to eliminate bacterial, fungal and viral infections.

About 40 kilometres above the earth’s surface, there is a layer of ozone blanketing the earth and protecting the life on earth from the harmful effects of ultra violet rays emanating from the sun. Environmentalists are concerned about the holes in the ozone layer due to dense pollution. These holes allow harmful ultra-violet rays to reach the earth’s surface. Ironically, this ozone layer is produced by the action of ultra violet rays on oxygen in the air. In addition to protecting life from the harmful effects of UV rays, ozone also acts on the hydrocarbons and other chemical pollutants destroying them. The resulting oxides are not toxic but they could be an irritant to the respiratory mucous membrane lining the windpipe and bronchi. These oxides resulting from ozone’s oxidative power in destroying these toxins will certainly not cause cancer and other degenerative disorders, but the unoxidised chemicals and hydrocarbons may do so.

The air that is breathed in during respiration is a mixture of oxygen, nitrogen and traces of a number of other gases. When humans evolved into an oxygen dependant species, the air had about 30% concentration of oxygen. This gradually decreased to 21% and then to 17%. Man evolved and adapted to these lowered concentrations of oxygen in the air. However in dense industrial cities the oxygen concentration can be as low as 14%. Pessimists claim that oxygen concentration in some areas may be as low as 11%. At these concentrations the human physiology cannot adapt adequately. It is not an exaggeration to say we are all oxygen starved. This drastic reduction of oxygen in the air is due to increased industrial pollution released into the atmosphere. In some cities, for example, Tokyo, oxygen is available at street corners. And in
others, hyperbaric oxygen clinics are gaining in popularity, London and San Francisco being examples.

Ozone is the only agent which can deal with this state of dense pollution, and also super oxygenate the body. Ozone is a gas with half-life of about 5 – 30 minutes depending on the temperature and the pH of the media. It is a natural trace element of the atmosphere. Because of its reactivity and short half-life it cannot be bottled and stored: neither can it be made into pills.

Ozone generated from oxygen is a triatomic molecule. Three molecules of oxygen will form two molecules of ozone. Ozone is generated from oxygen, the gas that sustains our life. Oxygen (O₂) is a diatomic molecule i.e. each molecule of oxygen contains 2 atoms of O. Each atom O has a nucleus containing 8 neutrons and 8 protons. 2 orbits surround the atoms. Each one of the orbit has 4 electrons i.e. the two orbits have 8 electrons. This makes the oxygen molecule made up of two atoms with 16 electrons orbiting around the nuclei. The two atoms are strongly bonded and the gas oxygen is stable and can be bottled and stored.

In ozone, two of the atoms are bonded strongly like in oxygen and the third atom is loosely bonded. This makes gas ozone ten times more soluble in water than oxygen. Compared to oxygen, ozone has 24 protons, 24 neutrons and 24 electrons. The atomic weight of ozone is 48. The oxygen molecule is straight where as the ozone molecule is curved as in Fig 2.1. This configuration makes the ozone molecule most reactive.

**Ozone Generation.**

There are three main types of ozone generators that mimic the electrical discharge in lightning that are used to create ozone gas on demand from air or oxygen gas:

1. The use of ultra-violet light: The production of ozone from oxygen is carried out as the stream of oxygen moves through a tube illuminated with a narrow frequency bandwidth of ultraviolet light.

2. Corona Discharge: Oxygen is passed through a tube containing a hot cathode surrounded by a screen anode. This system tends to have a limited life time due of the effect of ozone on the hot plates, and as the heat from these plates heats the gas, a proportion of the ozone formed reverts to oxygen. This in turn causes further damage to the anode and cathode.

3. Cold Plasma: This is a similar design to the corona discharge tube, but the anode and cathode are encased in glass rods filled with a noble gas. In this design the voltage jumps between the anode and cathode rods, forming an electrostatic or ‘plasma’ field. The advantage of the cold plasma system is that no heat is imparted to the gas as it passes through the electrostatic field. It has an almost infinite life-time due to this design. The cold plasma generator, originally invented by Nikola Tesla in the 1920s, is still in use today.
In the atmosphere, ozone is produced by photo-dissociation of molecular oxygen into activated oxygen atoms, which then react with further oxygen molecules (equations 1 and 2).

\[
\begin{align*}
O_2 & \xrightarrow{(\text{solar energy / uv})} 2O \quad (1) \\
O_2 + O & \rightarrow O_3 \quad (2)
\end{align*}
\]

Photo-dissociation is where the molecular bonds are broken by light energy. Halliwell and Gutteridge described the two oxygen-oxygen bonds in the ozone molecule as being of equal length and intermediate in nature between those of oxygen-oxygen single and double bonds (Gutteridge and Halliwell 1989). Ozone decomposition forms oxygen, and energy is released. This reaction is termed exothermic. In absence of catalysts or ultraviolet light, the rate of this decomposition is very slow, even at high temperatures. Ozone decomposition is caused by solar ultraviolet radiation in the range 240-300 nm, as shown in equation 3.

\[
O_3 \rightarrow \frac{3}{2} O_2 \quad \Delta H = -142 \text{kJ mol}^{-1} \quad (3)
\]

The reaction of water-soluble electron donors with ozone produces the ozone radical anion due to the high redox potentials (equation 4) (Jacobs, 1986). This transient radical anion is rapidly protonated, generating HO$_3^\cdot$. This HO$_3^\cdot$ decomposes to the hydroxyl radical (equation 5).

\[
\begin{align*}
X^\cdot + O_3 & \rightarrow X^\cdot + O_3^- \quad (4) \\
O_3^- + H^+ & \rightarrow HO_3^\cdot \rightarrow \cdot OH + O_2 \quad (5)
\end{align*}
\]

Reactions 4 and 5 convert ozone to an even more powerful oxidant, the hydroxyl radical (OH).

PubMed, the WWW On-Line reference data base, lists over 8,000 references to ‘Ozone’. The research covers atmospheric ozone holes, to water purification, waste disposal to blood sterilisation, and use in dentistry, to cleaning micro-processors.

**Ozone: Is This Gas A Health Hazard?**

Personal exposure to ozone and its effects to these people have been investigated by Brauer and Brook (Brauer and Brook, 1995) and this paper is often used by detractors to support the assertion that ozone should be regarded as a dangerous gas.

Brauer and Brook measured exposure to ozone using personal monitoring conducted with a nitrite-coated filter passive ozone sampler described by Koutrakis et al., 1994 (Koutrakis et al., 1994) in two groups of 25 healthy people. These two groups had occupations that were spent entirely outside. Even with low summer ozone levels of 35 ppb and less over a 24-hour time period on average, the values exhibited a strong dependence upon collated UV absorption and ozone readings. The volunteers in this study ozone samplers for their workdays only. Duplicate samplers were also used to assess their performance.

Brauer and Brook estimated that values with more than 35% variation were associated with true differences in exposure, and these values reflected the time spent outdoors. A body plethysmograph was used to assess lung function, and additional data was collected on subjective sensation and physiological responses of 40 subjects. These subjects were exposed to lower and higher ozone concentrations. Irritation of the eyes and airways was collected. Subjects drawn from senior citizens, juvenile asthmatics, forestry workers, athletes and office clerks were pre-assessed. They were grouped as ozone-risk groups or as a control group. Each group was
examined over an 8-day period, in the morning and in the afternoon, with average ozone concentrations ranging from 0.001 to 0.100 ppm.

Brauer and Brook’s study demonstrated no relevant ozone-induced effects for senior citizens, the group with the lowest ventilation rate, and only marginal reductions of respiratory flows and volumes for athletes. Forestry workers and clerks were exposed to the lowest ozone concentrations, and this group showed significantly higher airway resistance on ozone ventilation days.

Although Brauer and Brook concluded that ozone had a minor influence (author’s emphasis) on pulmonary responses relative to other constituents of the air in selected locations, for example in outdoor forestry or indoor office and domestic environments, this study has been used to hold up ozone as a dangerous gas with no part in modern health care. Yet research published by Hoppe et al showed air constituents or pollutants could be reaction products of ozone from exhaust fumes from forestry equipment, or pollutants deposited on interior surfaces (Hoppe et al., 1995) as a natural pathway as nature attempts to rid the air of man-made toxins.

Bocci (Bocci V, 1994) has emphasised that the known toxicity of ozone should not prevent its usage for medical purposes. Ozone has been shown, at carefully selected dose levels, to be of therapeutic value in the management of circulatory disorders, viral diseases and cancer. Gliner et al., (Gliner et al, 1979) investigated the effects of increasing concentrations of ozone from 0.25, 0.50 and 0.75 ppm, on visual and auditory attentive tasks to assess vigilance performance. The analysis of EEG data showed that ozone concentrations as high as 0.75 ppm did not alter the performance of visual and auditory tasks. However, a deficit in performance beyond that of the normal vigilance decline was observed during exposure to 0.75 ppm of ozone.

In 2004, Young and Setlow (Young & Setlow 2004) determined that ozone does not kill spores by DNA damage. Rather, ozone seems to render the spores defective in germination, perhaps because of damage to the spore's inner membrane. The Young and Setlow study would seem to suggest concerns that ozone may cause mutations in cells may be unfounded, despite the production by ozone of radicals in water and fluids.

After 125 years of usage, ozone therapy in medicine and various other fields is widely accepted in many nations around the world, including Germany, France, Italy, Russia, Romania, Czech Republic, Poland, Hungary, Bulgaria, Israel, Cuba, Japan, Mexico, and in some U.S. states.

Ozone is neither a killer nor a toxic gas when used in controlled environments. It is an effective therapeutic agent, in addition to being a deodorising and sterilising agent. No therapy can be in use all these years if it was dangerous or harmful.

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