Odorox® System Chemistry – Formaldehyde Decomposition

Introduction

Atmospheric hydroxyl radicals (HO·) are continuously produced by the action of the sun's radiated energy on oxygen and water vapor in our atmosphere. There are, on average, two million hydroxyl radicals (hydroxyls) in each cubic centimeter of ambient outdoor air during daylight hours. They are the main driving force behind the daytime reactions with hydrocarbons in the troposphere and neutralize most natural and man-made pollutants including greenhouse gases like formaldehyde, methane, hydrogen sulfide and ozone.

Atmospheric hydroxyls are also proven to kill bacteria, virus, and mold because they are able to penetrate their permeable cell membranes. Hydroxyls react with and damage the lipids and proteins that form the cell membranes, which results in leakage and cell death. Conversely, humans, animals and plants have developed symbiotically with atmospheric hydroxyl radicals and thrive in their presence. Atmospheric hydroxyls are a critical component of nature's dynamic ability to provide environments that are free of harmful chemicals and pathogens. (D. E. Heard, "Analytical Techniques for Atmospheric Measurement", Blackwell Publishing, 2006 – professor at the University of Leeds, UK).

As our indoor environments have become increasingly closed off from the outdoors, indoor air builds up chronic, unhealthy levels of Volatile Organic Compounds (VOC's), ozone and pathogens. This is because hydroxyls are very short-lived and cannot survive long indoors. Indoor air sanitizing systems that produce hydroxyl radicals can decompose these contaminants and recreate naturally purified air indoors.

Hydroxyl Chemistry

The HGI Odorox® irradiation process is fundamentally very simple. High energy spectrum UV irradiation of various wavelengths interacts with the oxygen and water vapor in ambient air. Reactive oxygen species, such as ozone and atomic oxygen are generated. Atomic oxygen reacts with the water vapor present to generate atmospheric hydroxyl radicals by removing a hydrogen atom. Additional hydroxyl radicals are formed when ozone is decomposed in HGI systems by selective UV irradiation. Ozone is further consumed when it reacts with volatile organic compounds with a carbon-carbon double bond (C=C), which are plentiful indoors. So ozone is both created and destroyed in the HGI process. Alkenes are very common in nature as they are produced by plants, animals and humans – we respire parts per billion (ppb) levels of an alkene called isoprene. Indoors, alkenes are generated by the outgassing of fabricated wood products, fabric, solvents, cleaning products (Pine Sol), etc. and steady state levels in the mid-ppb range are common. Over time the ozone levels are reduced to a low ppb steady state that depends on ventilation rates, hydroxyl radical formation rates, humidity, temperature, room size, etc..

Studies at a major respiratory research center, noted for its atmospheric chemical studies, have verified that high level of hydroxyls, similar to those found in nature, are produced by an HGI Odorox® Boss™ system and that they react with airborne VOC's. Measured reaction rates are incredibly fast; on the order of 20-50 milliseconds. These studies have been further analyzed, interpreted and substantiated by a leading industry expert in atmospheric hydroxyl radical chemistry.

Airborne hydroxyls are the perfect sanitizing agent. They react with a broader range of chemicals and do so over one million times faster than ozone, bleach or other sanitizing agents. This means that, where hydroxyl radicals are formed, they preferentially decompose most chemicals they encounter – even when ozone and other oxidizing agents are present. These high energy hydroxyls rapidly react with organic chemicals principally by removing a hydrogen and forming an organic radical that is subsequently decomposed by continued oxidation. The organic radicals formed set up a complex chain reaction of many radical by-products, including peroxy radicals (H-O-O· and R-O-O·, where R is an organic moiety) and oxy radicals (R-O·) that are themselves good oxidizing, sanitizing and deodorizing agents. The by-products are much more stable than the original hydroxyl radical and able to penetrate large volumes of air. As in nature, the individual steps grow exponentially in complexity. The net result is that organic compounds are reduced in size and oxidized until they eventually form carbon dioxide and water. As long as the system is running, the chain reactions persist.

Formaldehyde Formation and Decomposition

In nature, formaldehyde is produced from a variety of sources and by the action of hydroxyl radicals as they decompose VOC's. As hydroxyls decompose larger VOC's, smaller and smaller hydrocarbon compounds are formed. Formaldehyde is the smallest; it contains one carbon bonded to oxygen ($H_2C{=}O$) and represents the last step before the final oxidation to produce carbon dioxide – carbon bonded to two oxygen atoms (O=C=O).

Formaldehyde is a common contaminant in indoor air as it outgases from fabricated wood products, paints, adhesives, fabrics etc. It is toxic and the Occupational Safety & Health Administration (OSHA) guideline for formaldehyde exposure is less than 750 ppb (0.75 parts-per-million (ppm)) over an 8-hour period. Short term exposure cannot exceed 2 ppm. Formaldehyde reacts rapidly with hydroxyl radicals, so hydroxyl radical generators used indoors are very effective in decomposing it.

During the use of HGI systems, formaldehyde will be formed and decomposed along with other VOC's present by both the reaction with hydroxyls and with ozone, although reaction with hydroxyls is over a million times faster. The reaction of hydroxyls with formaldehyde initiates a sequence involving nitric oxide, oxidizing the formaldehyde to CO and H_20, the NO to NO_2 and regenerating a hydroxyl radical. There are intermediate steps that involve the formyl radical and the peroxy radical. There is no net loss of hydroxyls as they are regenerated by the reaction of the peroxy radical with oxygen. The net reaction is:

$$HO + H_2CO + NO \rightarrow CO + NO_2 + H_2O$$

The reaction rate of formaldehyde with the hydroxyl is the rate limiting step and is twice as fast as the reaction of a hydroxyl with a typical VOC like n-heptane. Even 100 parts-per-trillion (ppt) of NO (which is considered a very clean environment), is sufficient to promote the reaction sequence.

Over time a steady state level of formaldehyde is reached that is based on a variety of variables including the output of the hydroxyl generator, concentration of the influx of VOC's, ambient formaldehyde levels, room ventilation rate, humidity, system fan speed, etc.. Using reaction rate data from HGI studies and the literature, in a typical 12' x 12' x 9' room that is minimally ventilated, a concentration of 100 ppb of formaldehyde would react with the amount of hydroxyls produced by and HGI Boss™ system so that 48 ppb will remain after 1 hour, 23 ppb after 2 hours, and so on.

If we started at the high end of the OSHA formaldehyde scale at 750 ppb, and assumed a background concentration of VOC's of 10 ppb, using the same system, there would be 370 ppb remaining after 1 hour, 180 ppb after 2 hours, 90 ppb after 3 hours and so on. If the background VOC levels are higher, the rate of formaldehyde decomposition could be somewhat slower. Since formaldehyde reacts so much faster with hydroxyls than most VOC's it is be preferentially removed over time.

References.

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