



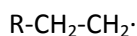
Decomposition of Volatile Organic Compounds by Atmospheric Hydroxyl Free Radicals: Understanding the “Cascade” Effect

Although it may be difficult to visualize how hydroxyl radicals can totally decompose volatile organic compounds (VOCs), both within the irradiation chamber of the Odorox® machine and throughout the treatment space, it is a process that is very well understood and documented in over 25 years of chemical literature.¹⁻⁵ The decomposition of volatile organic and inorganic compounds by hydroxyl radicals involves a complex series of free radical oxidation steps that gradually result in the loss of individual carbon atoms to eventually form carbon dioxide (CO₂). HGI, the manufacturer of the Odorox® technology, describes this process for simplicity as the “cascade” effect.

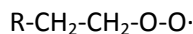
The process is very complex but continues to completion because the reactions involved are highly favored thermodynamically and kinetically. This means that substantial energy is released when hydroxyl radicals gain an electron. Nature favors reactions that result in lower energy states. It also means that the rates of reactions of hydroxyls with VOCs are very fast; a characteristic essential to efficiency. If the kinetics is not favorable, reactions are just too slow to be useful. You need both factors in your favor for an efficient sanitizing system.³

The hydroxyl radical is one of the most powerful oxidants found in nature, surpassed only by atomic fluorine in its oxidation potential. As an efficient oxidant, hydroxyls are driven to regain one electron to restore their very stable valence configuration. The most facile way to accomplish this in an environment rich in VOCs is to abstract a hydrogen atom with its single electron, leaving behind an organic free radical. Hydroxyls are such oxidants that they accomplish this within 22-44 milliseconds.

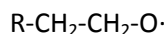
The newly formed organic free radical has an unpaired electron that is initially localized on the carbon atom.



This moiety rapidly reacts with ambient oxygen to form a peroxy free radical in which the free electron is now localized on an oxygen atom.



This species is a powerful oxidant in its own right, and will react with VOCs and inorganic gases. It is more stable than the hydroxyl radical and able to travel further away from the reaction chamber to react with VOCs and microorganisms in the treatment area. Peroxy radicals can also rapidly form oxy radicals in ambient air.



Oxy radicals are powerful oxidants and even more stable than their peroxy counterparts, and therefore are able to travel even further throughout the treatment space to react with microorganisms and other VOCs. Other down-stream oxidants are even more stable.

Hydroxyl radicals are also generated throughout the treatment space by continued reactions of intermediate compounds. For example, peroxy compounds decompose to form hydroxyls. Ozone is formed inside the chamber during photolysis, but the Odorox[®] technology is designed so that only small amounts of ozone exit the machine. This ozone is quickly decomposed in the treatment space and is another component of the many complex chemical reactions that occur. In fact, hydroxyls are known to eliminate ozone and the ozone can help create even more hydroxyls. Hydroxyls and these types of intermediate oxidants are the means by which Odorox[®] systems are able to penetrate and treat structures and contents at a distance from the device.

HGI describes this ongoing free radical chain reaction sequence and the formation of a series of intermediate oxidants as the cascade effect to enable non-scientists to visualize the complex chemistry. The free radical transfer reactions essentially 'unzip' carbon chains rapidly. As long as hydroxyls are continuously formed, both thermodynamic and kinetic factors favor continued oxidation of VOCs. Hydroxyls have a very high oxidation potential and high reaction rates with most VOCs; characteristics that are well documented in the chemical literature.¹⁻⁴ In the cascade effect, successive generations of oxidants continue to decompose and dissociate VOC carbon chains. This is driven by the nature of the oxidation process, which introduces oxygen into the carbon chains. In oxygenated VOCs, the hydrogen atoms near the oxygen atoms are much more reactive because of polarization. Oxygen attracts electrons away from less electronegative atoms and makes them more reactive. As such, hydroxyls next to carbon bearing oxygen(s) are more readily abstracted by another hydroxyl...and so on until that carbon atom is cleaved from the chain as stable CO₂.

Odorox[®] systems were designed to be innately safe by replicating nature's sanitizing process. They do this by using the same range of UV radiation to generate the same chemicals in the same concentrations when they are distributed around the treatment space. The rate of formation of hydroxyls and decomposition of VOCs within the photolysis chamber is high since the chemicals that are formed within the chamber are effectively diluted throughout the treatment space. All of the chemicals generated in the Odorox[®] chamber as part of the cascade effect are also generated in nature. The Odorox[®] system replicates the constant cleansing action of the sun by circulating the treatment area air constantly back through the photolysis chamber along with injecting hydroxyls into the treatment space. This is how the system effectively imitates what happens in nature.

The overall concentrations of by-products produced by Odorox[®] systems and in nature are in the low parts-per-billion (ppb) range. We have evolved to tolerate low concentrations of these chemicals because we are surrounded by them every day. Understandably, Occupational Safety & Health Administration (OSHA) and other regulatory agencies are concerned about high levels of chemicals in the environment. Most any chemical in high concentrations would be toxic. The Lovelace Respiratory Research Institute (LRRI) and Columbia Labs studies, along with a very significant number of field experiences, have confirmed that the Odorox[®] systems safely and effectively reduce ambient odor and VOC concentrations indoors.

There is an abundance of literature documenting the complexity of the reactions of hydroxyls with VOCs and inorganic gases in our atmosphere. The reactions described here are a small subset of the cascade effect, which is well characterized in the atmospheric chemistry literature as this is the primary way in which the atmosphere remains safe to breathe. Without hydroxyls, VOCs and inorganic gases would build up and render our atmosphere unsuitable for life as we know it.

HGI did not need to repeat these extensive chemical studies to validate the way by which its Odorox® systems are both safe and effective. What HGI chose to do was conduct definitive, third party studies to prove that it produces sufficient concentrations of free atmospheric hydroxyl radicals to be able to react with mid to high parts per billion levels of VOCs; concentrations that are typically found in remediation environments and other similar situations. HGI has done so in its studies with LRRI, the results of which have been further validated by independent analysis by Dr. David Crosley, a physical chemist well known for his years of studies and publications on atmospheric hydroxyl chemistry. The analytical methods used to do these studies involved very sophisticated methods and test chambers designed specifically to study hydroxyls as well as the industry's most sensitive analytical equipment (gas chromatograph-mass spectrometers sensitive to concentrations of a few parts per billion).

These studies verify that Odorox® systems generate optimal levels of free hydroxyl radicals that result in concentrations of hydroxyls and other oxidants throughout the treatment space that correspond to those found in nature. They also further verify that Odorox® hydroxyls rapidly react with VOCs reducing their concentration throughout the treatment space at rates of reaction that match those published in the literature; a definitive result for the confirmation that hydroxyls are the reactive species.

Selected References:

1. D. R. Crosley, The Measurement of HO and HO₂ in the Atmosphere, *J. Atm. Sci.* 52, 3299 (1995).
2. B.J. Finlayson Pitts and J. N. Pitts, Jr., *The Chemistry of the Upper and lower Atmosphere*, Academic Press, San Diego, 1999.
3. W. B. Demore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, NASA Report JPL 97-4, 1997.
4. Y. Yang and L. Zhu, Wavelength-Dependent Photolysis of n-Hexanal and N-Heptanal in the 280-330 Region, *J. Phys. Chem.* 108, 8307 (2004).
5. *Analytical Techniques for Atmospheric Measurement*, Edited by D. E. Heard, University of Leeds, Blackwell Publishing, (2006).
6. C. J. Weschler and H. C. Shields, Production of the Hydroxyls Radical in Indoor Air, *Environmental Science and Technology/ Vol. 30, NO. 11* 3250-58, 1996.

Odorox and the HGI Logo are trademarks or registered trademarks of HGI Industries Incorporated, Boynton Beach, Florida USA.