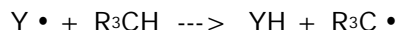


# CHLORINATED HYDROCARBONS, RADICALS AND POLLUTION

## REACTIONS OF HYDROCARBONS

Unactivated CH and CC bonds are the least reactive parts of organic compounds, with non-polar bonds, 90 - 100 kcal/mole. These bonds are unreactive to polar reagents, but succumb to homolytic cleavage (one electron with each atom) when provided the bond dissociation energy. CH and CC bond cleavage occurs in extreme heat, such as in the cracking of petroleum (no oxygen, pyrolysis), or in a flame (with oxygen, combustion). It can also occur if the hydrocarbon is exposed to atoms or molecules with unpaired electrons (radicals); if the radical itself (Y•) carries with it enough energy to break a CH bond, it forms a Y-H bond while leaving a carbon radical.



Oxygen (a diradical), halogens (except for F, split into atoms by less than 60 kcal/mole) and sometimes peroxides (split into oxygen radicals by less than 50 kcal/mole) can abstract (remove) a hydrogen atom from a complex molecule, leaving a reactive carbon radical (tertiary more stable than secondary, etc.). The cascade of exothermic free radical chain reactions that ensues can sometimes result in useful products such as polymers but usually produces complex mixtures.

By exciting the electrons of a radical generator such as halogen or oxygen, light can initiate free radical reactions. The energy of the light available determines the strength of the bond it can break.

Radical chain reactions are only terminated when two radicals combine to form a stable covalent bond. The bond must be strong to terminate the chain since the energy available may break it again; for halogenation, the formation of a carbon - halogen bond is enough, but if high energy ultraviolet radiation is available, even CH bonds can be rebroken.

## ABSORPTION OF LIGHT

Like atoms, molecules absorb ultraviolet (< 380 nm) and visible (380 - 780 nm) light, but unlike atoms, the absorptions are broad. The most common (and lowest energy) absorption seen is that exciting an electron in the highest bonding orbital or a non-bonding orbital to an antibonding orbital. The nuclei are in constant motion relative to each other in the molecule and the energy needed to excite the electron depends on the precise nuclear positions at the moment of absorption; the sum of all the possibilities for electron energies produces the broad absorption band.

## OZONE

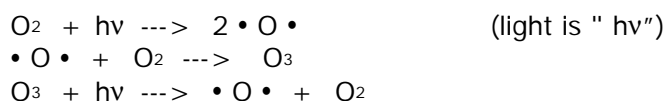
Dioxygen, the normal form, is a diradical and thus quite reactive. Ozone, trioxygen, has its electrons paired but is very polar: none of the contributors to its resonance hybrid structure have neutral atoms with eight electrons. Ozone reacts vigorously with alkenes and other double bonds (thereby destroying rubber and damaging tissues) and is a much more vigorous oxidant than oxygen itself; usually its multistep reactions add an oxygen to the substrate and release dioxygen. Ozone is produced in the high temperature combustion of modern automobile engines along with oxides of nitrogen, carbon or both) and is one of the indicator pollutants monitored in cities. Clean air below 20 km has no ozone - it's only source in the troposphere (lower atmosphere) is lightning - but dirty city air may have more than 1 part per million, enough to cause sore lungs and long term damage.

Dioxygen absorbs far ultraviolet light (maximum about 150 nm, cutoff about 200 nm) from the sun, as does dinitrogen, but little in the atmosphere absorbs the nearer ultraviolet. Ozone in the stratosphere (about 25 km) can serve that function, since ozone's absorption maximum is 250 nm with a cutoff about 350 nm.

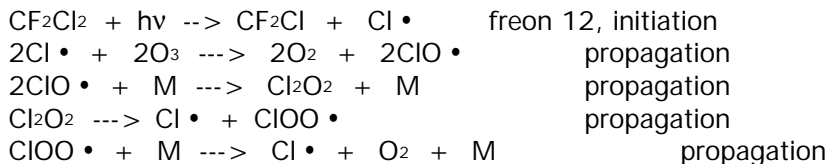
## DESTRUCTION OF OZONE BY CHLORINE AND BROMINE RADICALS

Little protection from the far ultraviolet of the sun is available for the molecules of the stratosphere and its high energy is sufficient to break any covalent bonds. Moreover, the low pressure in the stratosphere reduces the rate of chemical reactions (fewer collisions) and permits atoms and reactive

molecules like ozone to survive for some time. Ozone is formed and destroyed continuously, creating a "steady state", like pouring water into a sink at the same rate it flows out; because of the delicate balance needed, the amount of ozone stays constant only in a band in the lower stratosphere near 25 km above the surface.



Several activities of man conspire to upset this balance. The first to make headlines was the supersonic transport (SST), whose exhaust releases radicals such as nitrogen oxides (try to write structures for NO and NO<sub>2</sub> to convince yourself) and hydrocarbon fragments directly into the stratosphere where they react with O• radicals, interrupting the formation but not the destruction of ozone. The second activity is less obvious. Most of the organics released by man and nature are destroyed in the troposphere, but completely halogenated hydrocarbons such as the chlorofluorocarbons (CFC's or freons) survive until they reach the stratosphere. The ultraviolet light breaks the carbon-chlorine and carbon-bromine (but not C-F) bonds to release halogen atoms which react with ozone. In most parts of the world the concentration is low and no detectable problems ensue. But in the dark polar winter the reactive chlorine species condense onto the fine nitric acid-rich ice-clouds creating a reservoir of ozone-destroying capacity. In the spring, these reactive chlorine compounds are mobilized over the space of a few weeks, creating a free radical chain reaction and a catastrophic drop in the ozone concentration (to about 1/4 of its normal levels) now called "the ozone hole". Many of the reactions take place on the surface of the ice crystal, designated by "M".



The overall result of the propagation steps is  $2\text{O}_3 \longrightarrow 3\text{O}_2$  !

Termination requires production of a less reactive chlorine species and its precipitation from the stratosphere. Any source of chlorine in an oxidation state above -1 is a threat to the ozone layer, including the perchlorates used as solid rocket fuel for the space shuttle. Bromine atoms are more stable than chlorine and are even more persistent catalysts for ozone destruction; fortunately they are rare.

The proposed replacements for CFC's, HCFC's, differ only in being incompletely halogenated, i.e. they have CH bonds as well as CX. The CH bonds are much more likely to be broken in the troposphere.

The chain reaction that follows breaking of the CH bond converts chlorine to chloride which is washed out of the atmosphere by rain before it reaches the stratospheric ozone layer.

#### FOR FURTHER READING

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