Ozone

CONTENT PRIMER

written by Isabella Priest and Joanna Goodey Pellois

The sun emits harmful ultraviolet (UV) radiation, which has shorter wavelengths than visible light and longer wavelengths than x-rays. The wavelength range for UV radiation is approximately 100 to 400 nm (1 nm = 10^{-9} m). The UV range can be further subdivided into UV-A (340 – 400 nm), UV-B (280 - 340 nm), and UV-C (100 - 280 nm) ranges.

When photons, packets of energy associated with electromagnetic radiation, of UV light interact with molecules, a process called photodissociation can occur. Photodissociation involves the breaking of a chemical bond. In the outermost layers (above 31 miles) of Earth's atmosphere, the mesosphere and thermosphere, most molecules have been dissociated into ions and atoms by high energy UV-C photons. For example, oxygen, O_2, molecules are photodissociated into two single oxygen (O) atoms according to (1) below. In (1), the reactant *hv* represents the energy associated with a UV-C photon that has enough energy to break a double bond in an oxygen molecule.

$$O{=}O(g) + hv \longrightarrow 2O(g) \qquad (1)$$

Reaction 1 explains why concentrations of molecular oxygen, O_2, are significantly lower than concentrations of atomic oxygen, O, at higher levels of the atmosphere.

Given that much of the bond breaking UV-C radiation from the sun is absorbed in the upper levels of the atmosphere, O_2 molecules are found in much higher concentrations in the lower level (below 9 miles) of the atmosphere, the troposphere. In the region between the troposphere and the mesosphere, the stratosphere (9 miles to 31 miles), O_2 molecules from the lower levels of the atmosphere react with single O atoms from the upper levels of the atmosphere to form ozone, O_3. The formation of ozone, O_3, in the stratosphere is a relatively fast reaction (2).

$$O(g) + O_2(g) \longrightarrow O_3(g) \qquad (2)$$

The concentration of ozone in the stratosphere can be decreased by one of two chemical reactions. Ozone, O_3, molecules can absorb a photon of UV-B light and dissociate into atomic oxygen, O, and molecular oxygen, O_2 (3).

$$O_3(g) + hv \longrightarrow O(g) + O_2(g) \qquad (3)$$

Ozone molecules, O_3, can also react with atomic oxygen, O, to form molecular oxygen, O_2 (4).

$$O_3(g) + O(g) \longrightarrow 2O_2(g) \tag{4}$$

Overall, the photodissociation (3) and the reaction (4) of ozone occur at a much slower rate than the formation of ozone (2). Because ozone is forming faster than it is being reacted or dissociated, the concentration of ozone in the stratosphere is high and is known as the ozone layer. The highest concentration of ozone is found between 12 and 15 miles above Earth.

The absorption of UV-B radiation by ozone (3) reduces the amount of harmful radiation that reaches the lower levels of the atmosphere. The UV-B radiation absorbed by ozone damages biological tissue and can mutate DNA in a manner that causes skin cancers. Higher energy UV-C photons are significantly more damaging than UV-B photons, however they are absorbed in the upper levels of the atmosphere.

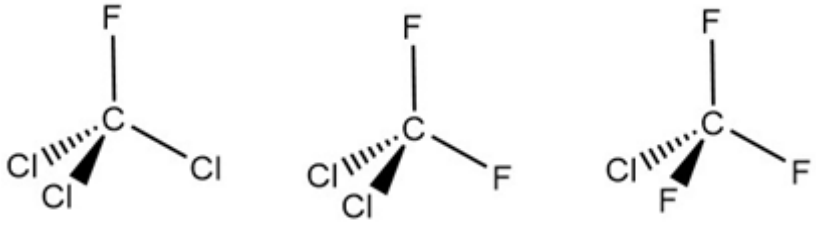
Depletion of the ozone layer leads to higher concentrations of UV-B radiation in the troposphere and therefore higher incidences of skin cancer. Depletion of the ozone layer occurs when the rate of reaction of ozone, O_3, with atomic oxygen, O, (4) is significantly increased. In other words, depletion occurs when ozone is disappearing at a faster rate than it is being produced. Rates of reactions, like (4), increase in the presence of a chemical species called a catalyst. In the 1970s, scientists proposed that a growing hole in the ozone layer was due to the presence of atomic chlorine, Cl. The unstable chlorine atoms catalyze or speed up (4) via a two-step chemical process (5, 6).

$$Cl(g) + O_3(g) \longrightarrow ClO(g) + O_2(g) \tag{5}$$

$$ClO(g) + O(g) \longrightarrow Cl(g) + O_2(g) \tag{6}$$

The net chemical equation, the combination of (5) and (6), is the conversion of ozone, O_3, into molecular oxygen, O_2 (4). After further investigation, it was determined that the source of the atomic chlorine, Cl, that catalyzes the decomposition of ozone was a class of compounds called chlorofluorocarbons.

Many chlorofluorocarbons (CFCs) are tetrahedral compounds that have a total of 4 fluorine or chlorine atoms attached to the central carbon atom. Examples of three common CFCs are drawn below.



Freon 11 Freon 12 Freon 13

CFCs have been used as propellants in aerosol cans and refrigerants. The trade names of CCl_3F, CCl_2F_2 and $CClF_3$ are Freon-11, Freon-12, and Freon-13. These CFC compounds are inert (relatively unreactive) in the troposphere and were not initially thought to pose a risk to the environment. For decades, millions of tons of CFCs were released into the troposphere. Given that CFCs are inert, they remain intact and slowly migrate from the troposphere up to the stratosphere. Once in the stratosphere, CFCs are exposed to UV-B

and UV-C radiation that breaks the bond between the carbon atom and a chlorine atom in a CFC. For example, when Freon-12 (CCl_2F_2) absorbs photons with wavelengths less than 290 nm, a chlorine atom, Cl, is released (7).

$$CCl_2F_2(g) + hv \longrightarrow CCl_2F(g) + Cl(g) \quad (7)$$

The chlorine atom, Cl, is highly reactive and reacts rapidly with ozone, O_3, producing chlorine monoxide, ClO, and molecular oxygen, O_2 (5). In addition to this rapid depletion of ozone, the chlorine atom, Cl, is regenerated as a product of the reaction of chlorine monoxide, ClO, with atomic oxygen, O (6). The regenerated atom, Cl, can react with many other ozone, O_3, molecules. This means that a single molecule of a CFC compound can be responsible for rapidly decomposing many ozone molecules. CFCs are therefore responsible for accelerating the depletion of the ozone layer in the stratosphere.