10.4: Atmospheric Chemistry and Photochemical Reactions

Atmospheric chemistry describes chemical processes that occur in the atmosphere. One notable aspect of atmospheric chemistry is that it occurs in the gas phase where molecules are relatively far apart, so a molecule or a fragment of a molecule may travel some distance before bumping into another species with which it reacts. This is especially true in the highly rarefied regions of the stratosphere and above.

A second major aspect of atmospheric chemistry is the occurrence of **photochemical reactions** that are initiated when a photon (essentially a packet of energy associated with electromagnetic radiation) of ultraviolet radiation is absorbed by a molecule. The energy of a photon, E, is given by E =*h*ν where *h* is Planck's constant andνis the frequency of the radiation. Electromagnetic radiation of a sufficiently short wavelength breaks chemical bonds in molecules, leading to the formation of reactive species that can participate in reaction sequences called **chain reactions.**

An example of an important chain reaction sequence that begins with photochemical dissociation of a molecule is the one that occurs when chlorofluorocarbons get into the stratosphere. Chlorofluorocarbons are given the trade name of Freons and consist of carbon atoms to which are bonded fluorine and chlorine atoms. Noted for their extreme chemical stability and low toxicities, they were once widely used as refrigerant fluids in air conditioners, as aerosol propellants for products such as hair spray, and for foam blowing to make very porous plastic or rubber foams. Dichlorodifluoromethane, CCl_2F_2, was used in automobile air conditioners. Released to the atmosphere, this compound remained as a stable atmospheric gas until it got to very high altitudes in the stratosphere. In this region, ultraviolet radiation of sufficient energy (*h*ν)is available to break the very strong C-Cl bonds,

$$\mathrm{CCl_2F_2} + h\nu \rightarrow \cdot\mathrm{CClF_2} + \mathrm{Cl}\cdot \tag{10.4.1}$$

releasing Cl atoms. The dot represents a single unpaired electron remaining with the Cl atom when the bond in the molecule breaks. Species with such unpaired electrons are very reactive and are called **free radicals**. As discussed in Chapter 2 Section 2.13 and shown by reactions 2.13.1 and 2.13.2, in addition to molecular O_2 there are oxygen atoms and molecules of ozone, O_3, also formed by photochemical processes in the stratosphere. A chlorine atom produced by the photochemical dissociation of CCl_2F_2 as shown in Reaction 10.4.1 can react with a molecule of O_3 to produce O_2 and another reactive free radical species, ClO•. This species can react with free O atoms which are present along with the ozone to regenerate Cl atoms, which in turn can react with more O_3 molecules. These reactions are shown below:

$$\mathrm{Cl}\cdot + \mathrm{O_3} \rightarrow \mathrm{O_2} + \mathrm{ClO}\cdot \tag{10.4.2}$$

$$\mathrm{ClO}\cdot + \mathrm{O} \rightarrow \mathrm{O_2} + \mathrm{Cl}\cdot \tag{10.4.3}$$

These are chain reactions in which ClO• and Cl• are continually reacting and being regenerated, the net result of which is the conversion of O_3 and O in the atmosphere to O2. One Cl atom can bring about the destruction of as many as 10,000 ozone molecules! Ozone serves a vital protective function in the atmosphere as a filter for damaging ultraviolet radiation, so its destruction is a very serious problem that has resulted in the banning of chlorofluorocarbon manufacture.

Very small particles of the size of a micrometer or less called **aerosols** are important in atmospheric chemical processes. Photochemical reactions often result in the production of particles. Particle surfaces can act to catalyze (bring about) atmospheric chemical reactions. Some particles in the atmosphere consist of water droplets with various solutes dissolved in them. Solution chemical reactions can occur in these droplets. One such process is believed to be the conversion of gaseous atmospheric sulfur dioxide (SO_2) to droplets of dilute sulfuric acid (H_2SO_4), which contribute to acid rain. Some very small particles, such as sea salt crystals entrained into the atmosphere by wind-blown seawater spray droplets and formed by evaporation of water from the droplets, act as **condensation nuclei** around which raindrops form.

The Ionosphere

An important kind of photochemical reaction that occurs at altitudes generally above the stratosphere (50 km and higher) is the formation of ions by the action of ultraviolet and cosmic radiation energetic enough to remove electrons (e^-) from molecules as shown by the example below:

$$\mathrm{N_2} + h\nu \rightarrow \mathrm{N_2^+} + \mathrm{e^-} \tag{10.4.4}$$

The ions formed are very reactive, but air is so rarefied at the altitudes at which they form that they persist for some time before reverting to neutral species. This results in an atmospheric layer called the **ionosphere** in which ions are constantly being formed and neutralized. At night when the solar radiation responsible for ion formation is shielded by Earth, the predominant process is recombination of positive ions with electrons, a phenomenon that proceeds most rapidly in the lower, denser regions of the ionosphere. The result is a lifting of the ionosphere, a phenomenon first hypothesized in 1901 when Marconi, attempting to bridge the Atlantic ocean with shortwave radio discovered that radio waves could be propagated over long distances, especially at night, making long distance shortwave radio transmission possible. For a time in the 1900s until made obsolete by satellite and fiber optics, the ionosphere was a useful part of the atmosphere's natural capital (see Section 10.12) by making possible long-distance shortwave radio broadcasts.