

# Q9

## What are the chlorine and bromine reactions that destroy stratospheric ozone?

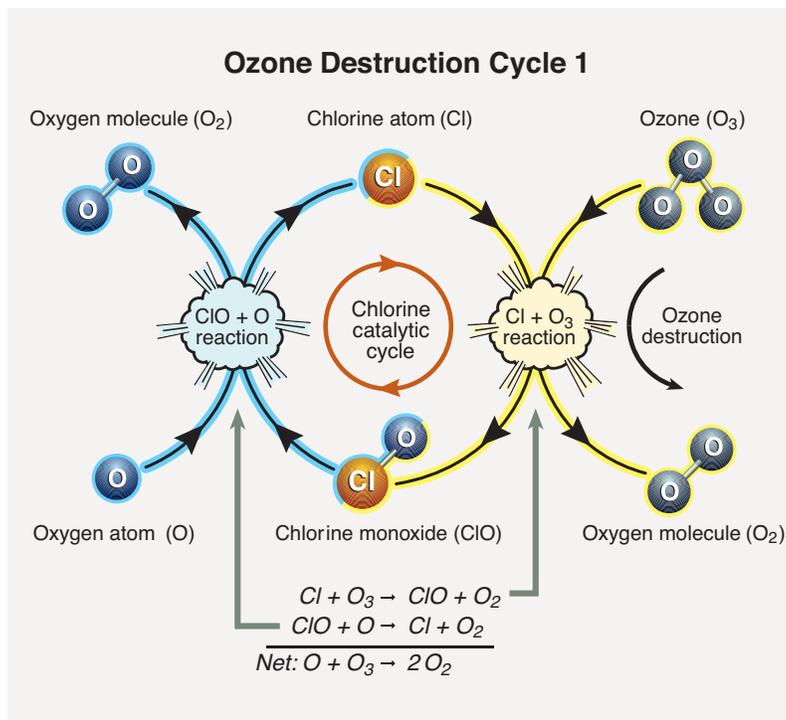
Reactive gases containing chlorine and bromine destroy stratospheric ozone in “catalytic” cycles made up of two or more separate reactions. As a result, a single chlorine or bromine atom can destroy many thousands of ozone molecules before it leaves the stratosphere. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. A special situation develops in polar regions in the late winter/early spring season where large enhancements in the abundance of the most reactive gas, chlorine monoxide, leads to severe ozone depletion.

Stratospheric ozone is destroyed by reactions involving **reactive halogen gases**, which are produced in the chemical conversion of *halogen source gases* (see Figure Q8-1). The most reactive of these gases are chlorine monoxide (ClO), bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). These gases participate in three principal reaction cycles that destroy ozone.

**Cycle 1.** Ozone destruction Cycle 1 is illustrated in Figure Q9-1. The cycle is made up of two basic reactions:  $\text{Cl} + \text{O}_3$  and  $\text{ClO} + \text{O}$ . The net result of Cycle 1 is to convert one ozone molecule and one oxygen atom into two oxygen molecules. In each cycle, chlorine acts as a *catalyst* because ClO and Cl react and are re-formed. In this way, one Cl atom participates in many cycles, destroying many ozone molecules. For typical stratospheric conditions at middle or low latitudes, a single chlorine atom can destroy hundreds of ozone molecules

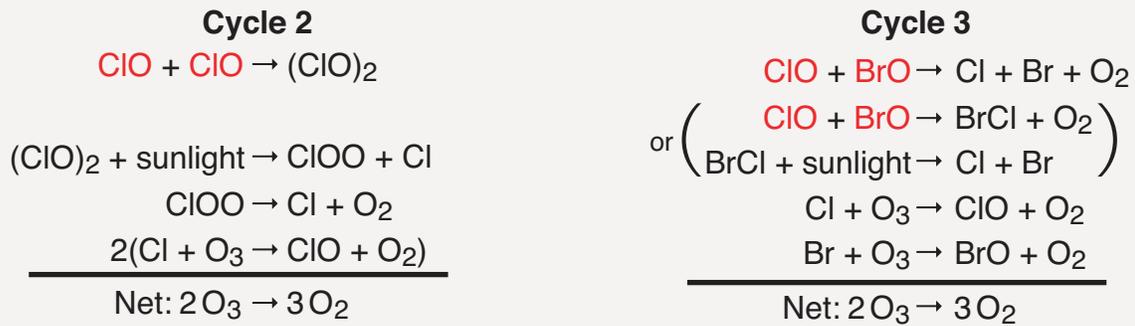
before it happens to react with another gas, breaking the catalytic cycle, and up to tens of thousands of ozone molecules during the total time of its stay in the stratosphere.

**Polar Cycles 2 and 3.** The abundance of ClO is greatly increased in polar regions during winter as a result of reactions on the surfaces of polar stratospheric clouds (PSCs) (see Q8 and Q10). Cycles 2 and 3 (see Figure Q9-2) become the dominant reaction mechanisms for polar ozone loss because of the high abundances of ClO and the relatively low abundance of atomic oxygen (which limits the rate of ozone loss by Cycle 1). Cycle 2 begins with the self-reaction of ClO. Cycle 3, which begins with the reaction of ClO with BrO, has two reaction pathways to produce either Cl and Br or BrCl. The net result of both cycles is to destroy two ozone molecules and create three oxygen molecules. Cycles 2 and 3 account for most of the ozone loss observed in the Arctic and Antarctic stratospheres



**Figure Q9-1. Ozone destruction Cycle 1.** The destruction of ozone in Cycle 1 involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen with ozone, forming two oxygen molecules. The cycle can be considered to begin with either ClO or Cl. When starting with ClO, the first reaction is ClO with O to form Cl. Then, Cl reacts with ozone and re-forms ClO, consuming ozone in the process. The cycle then begins again with another reaction of ClO with O. Chlorine is considered a catalyst for ozone destruction because Cl and ClO are re-formed each time the reaction cycle is completed, and ozone is simply removed. Atomic oxygen (O) is formed when solar ultraviolet radiation (sunlight) reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar ultraviolet radiation is most intense.

### Ozone Destruction Cycles in Polar Regions



**Figure Q9-2. Polar ozone destruction Cycles 2 and 3.** Significant destruction of ozone occurs in polar regions because ClO abundances reach large values. In this case, the cycles initiated by the reaction of ClO with another ClO (Cycle 2) or the reaction of ClO with BrO (Cycle 3) efficiently destroy ozone. The net reaction in both cases is two ozone molecules forming three oxygen molecules. The reaction of ClO with BrO has two pathways to form the Cl and Br product gases. Ozone destruction Cycles 2 and 3 are catalytic, as illustrated for Cycle 1 in Figure Q9-1, because chlorine and bromine gases react and are re-formed each time the reaction cycle is completed. Visible sunlight is required to complete each cycle and to help form and maintain ClO abundances. During polar night and other periods of darkness, ozone cannot be destroyed by these reactions.

in the late winter/early spring season (see Q11 and Q12). At high ClO abundances, the rate of polar ozone destruction can reach 2 to 3% per day in late winter/early spring.

**Sunlight requirement.** Sunlight is required to complete and maintain Cycles 1 through 3. Cycle 1 requires sunlight because atomic oxygen is formed only with solar ultraviolet radiation. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar ultraviolet radiation (sunlight) is most intense.

Cycles 2 and 3 require visible sunlight to complete the reaction cycles and to maintain ClO abundances. In the continuous darkness of winter in the polar stratosphere, reaction Cycles 2 and 3 cannot occur. It is only in late winter/early spring when sunlight returns to the polar regions that these cycles can occur. Therefore, the greatest destruction of ozone occurs in the partially to fully sunlit periods after midwinter in the polar stratosphere. The visible sunlight needed in Cycles 2 and 3 is not sufficient to form ozone because this process requires solar ultraviolet radiation (see Q1). In the stratosphere in the late winter/early spring period, solar ultra-

violet radiation is weak at low Sun angles. As a result, ozone destruction by Cycles 2 and 3 in the sunlit winter stratosphere greatly exceeds ozone production.

**Other reactions.** Global ozone abundances are controlled by many reactions that both produce and destroy ozone (see Q2). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens. The sources of reactive hydrogen and nitrogen gases are the naturally occurring gases methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O), respectively. The importance of reactive hydrogen and nitrogen gases relative to reactive halogen gases is expected to increase in the future, because the atmospheric abundances of the reactive halogen gases are decreasing as a result of the Montreal Protocol, while CH<sub>4</sub> and N<sub>2</sub>O abundances are projected to increase substantially due to human activities.

### Replacing Lost Ozone in the Stratosphere

The idea is sometimes put forth that humans could compensate for lost global stratospheric ozone by replacing it. Ozone could be manufactured, stored, transported to the stratosphere, and released in depleted regions. Unfortunately, the idea has substantial practical limitations.

Ozone amounts in the stratosphere reflect a continual *balance* between chemical production and destruction (see Q2). The addition of chlorine and bromine to the stratosphere from human activities has changed the natural balance by increasing ozone destruction and, thereby, lowering stratospheric ozone amounts. Chlorine and bromine destroy ozone in catalytic reactions that allow each atom to destroy many thousands of ozone molecules (see Q9). A one-time injection of manufactured ozone to the stratosphere would not restore the natural balance because the added ozone would be destroyed in the same chemical reactions with chlorine and bromine within about a year. Thus, ozone additions would need to be large and continuous as long as stratospheric chlorine and bromine amounts remained enhanced above natural amounts, a condition expected to persist for several decades (see Q16). Continuous replacement for decades would pose unprecedented technical and resource challenges that will likely be unacceptable to decision makers in the international community.

Specific technical difficulties in replacing stratospheric ozone are the large amounts of ozone required and the delivery method. The total amount of atmospheric ozone is approximately 3,000 megatons (1 megaton = 1 billion kilograms) with most residing in the stratosphere. Compensating for the average global ozone loss, currently about 3%, would require 90 megatons of ozone to be distributed regularly throughout the stratosphere many kilometers above Earth's surface. The energy required to produce this amount of ozone would be a significant fraction of the electrical power generated annually in the United States, for example, which is now approximately 4 trillion kilowatt hours. Processing and storing requirements for ozone, which is explosive and toxic in large quantities, would increase the energy requirement. In addition, methods suitable to deliver and distribute large amounts of ozone to the stratosphere have not been developed. Concerns for a global delivery system would include further significant energy use and unforeseen environmental consequences.