

Q8

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, lead 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 Q7-1). 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.

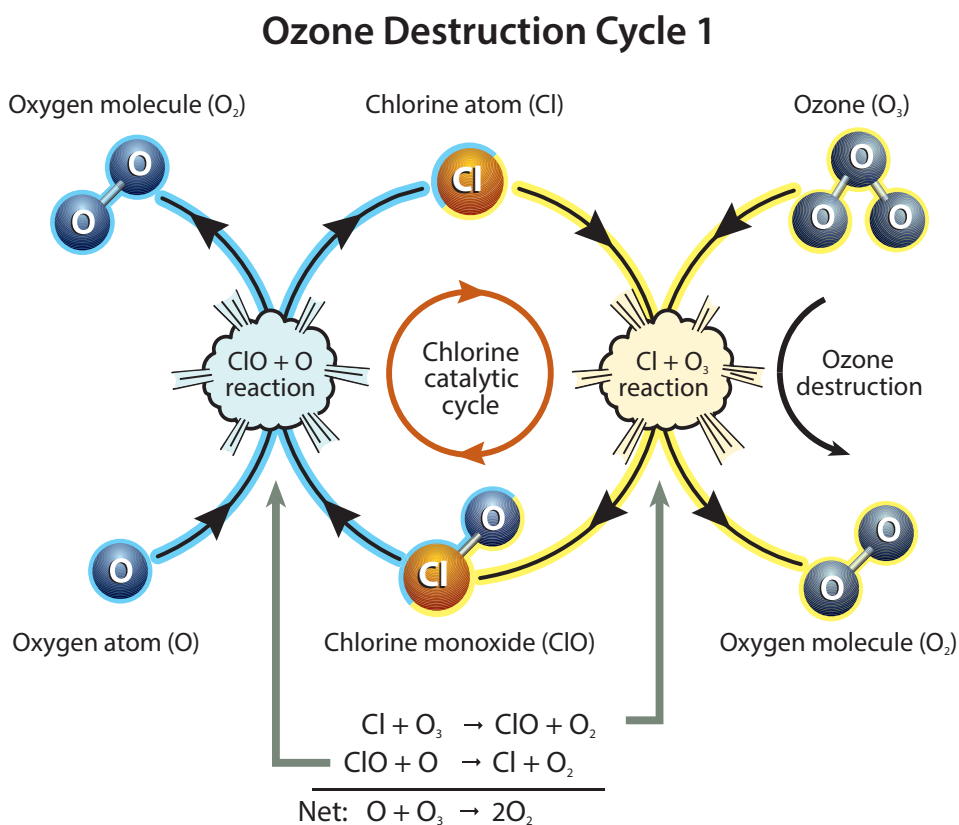
Cycle 1. Ozone destruction Cycle 1 is illustrated in **Figure Q8-1**. The cycle is made up of two basic reactions: $\text{Cl} + \text{O}_3$ and $\text{ClO} + \text{O}$. The net result of Cycle 1 is to convert one ozone molecule and one oxygen atom into two oxygen molecules. In each cycle,

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 thousands of ozone molecules before it happens to react with another gas, breaking the catalytic cycle. During the total time of its stay in the stratosphere, a chlorine atom can thus destroy many thousands of ozone molecules.

Polar Cycles 2 and 3. The abundance of ClO is greatly increased in polar regions during late winter and early spring, relative to

Figure Q8-1. Ozone destruction Cycle 1

The destruction of ozone in Cycle 1 involves two separate chemical reactions. 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 and O_2 . Then, Cl reacts with O_3 and re-forms ClO, consuming O_3 in the process and forming another O_2 . The net or overall reaction is that of atomic oxygen (O) with ozone (O_3), forming two oxygen molecules (O_2). 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 hence available for further destruction of ozone. Atomic oxygen is formed when solar ultraviolet (UV) radiation reacts with O_3 and O_2 molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes, where solar UV radiation is most intense.



other seasons, as a result of reactions on the surfaces of polar stratospheric clouds (see Q7 and Q9). Cycles 2 and 3 (see **Figure Q8-2**) 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 that 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 stratosphere over the Arctic and Antarctic regions in the late winter/early spring season (see Q10 and Q11). At high ClO abundances, the rate of polar ozone destruction can reach 2 to 3% per day.

Sunlight requirement. Sunlight is required to complete and maintain these reaction cycles. Cycle 1 requires ultraviolet (UV) radiation (a component of sunlight) that is strong enough to break apart molecular oxygen into atomic oxygen. Cycle 1 is most important in the stratosphere at altitudes above about 30 km (18.6 miles), where solar UV-C radiation (100 to 280 nanometer (nm) wavelengths) is most intense (see Figure Q2-1).

Cycles 2 and 3 also require sunlight. In the continuous darkness of winter in the polar stratosphere, reaction Cycles 2 and 3 cannot occur. Sunlight is needed to break apart $(\text{ClO})_2$ and BrCl, resulting in abundances of ClO and BrO large enough to drive rapid ozone loss by Cycles 2 and 3. These cycles are most active when sunlight returns to the polar regions in late winter/early spring. Therefore, the greatest destruction of ozone occurs in the partially to fully

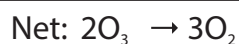
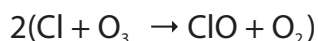
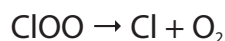
sunlit periods after midwinter in the polar stratosphere.

Sunlight in the UV-A (315 to 400 nm wavelengths) and visible (400 to 700 nm wavelengths) parts of the spectrum needed in Cycles 2 and 3 is not sufficient to form ozone because this process requires more energetic solar UV-C solar radiation (see Q1 and Q2). In the late winter/early spring, only UV-A and visible solar radiation is present in the polar stratosphere, due to low Sun angles. As a result, ozone destruction by Cycles 2 and 3 in the sunlit polar stratosphere during springtime greatly exceeds ozone production.

Other reactions. Global abundances of ozone are controlled by many other reactions (see Q1). Reactive hydrogen and reactive nitrogen gases, for example, are involved in catalytic ozone-destruction cycles, similar to those described above, that also take place in the stratosphere. Reactive hydrogen is supplied by the stratospheric decomposition of water (H_2O) and methane (CH_4). Methane emissions result from both natural sources and human activities. The abundance of stratospheric H_2O is controlled by the temperature of the upper tropical troposphere as well as the decomposition of stratospheric CH_4 . Reactive nitrogen is supplied by the stratospheric decomposition of nitrous oxide (N_2O), also emitted by natural sources and human activities. The importance of reactive hydrogen and nitrogen gases in ozone depletion 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 abundances of CH_4 and N_2O are projected to increase due to various human activities (see Q20).

Ozone Destruction Cycles in Polar Regions

Cycle 2



Cycle 3

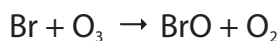
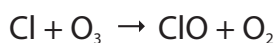
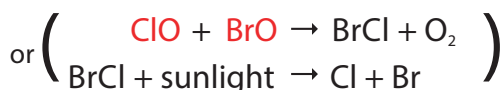


Figure Q8-2. Polar ozone destruction Cycles 2 and 3. Significant destruction of ozone occurs during late winter and early spring in the polar regions when abundances of ClO reach large values. In this case, the cycles initiated by the reaction of ClO with another ClO (Cycle 2) or the reaction of ClO with BrO (Cycle 3) efficiently destroy ozone. The net reaction in both cases is two ozone (O_3) molecules forming three oxygen (O_2) molecules. The reaction of ClO with BrO has two pathways to form the Cl and Br product gases that lead to loss of ozone. The destruction of ozone by Cycles 2 and 3 is catalytic, as illustrated for Cycle 1 in Figure Q8-1, because chlorine and bromine gases react and are re-formed each time the reaction cycle is completed. Sunlight is required to complete each cycle and to help form and maintain elevated abundances of ClO. During polar night and other periods of darkness, ozone cannot be destroyed by these reactions.