Box 1.1. Ozone chemistry

Stratospheric ozone is produced naturally by photolysis of molecular oxygen (O_2) at ultraviolet wavelengths below 242 nm,

$$O_2 + h\nu \rightarrow O + O \quad [1]$$

The atomic oxygen produced in this reaction reacts rapidly with O_2 to form ozone (O_3),

$$O + O_2 + M \rightarrow O_3 + M \quad [2]$$

where M denotes a collision partner, not affected by the reaction. O_3 itself is photolyzed rapidly,

$$O_3 + h\nu \rightarrow O + O_2 \quad [3]$$

O_3 and O establish a rapid photochemical equilibrium through Reactions [2] and [3], and together are called 'odd oxygen'. Finally, in this sequence of reactions (known as the Chapman reactions), ozone is removed by

$$O + O_3 \rightarrow 2O_2 \quad [4]$$

Destruction by Reaction [4] alone cannot explain observed ozone abundances in the stratosphere and it is now known that, away from polar latitudes, the ozone production through Reaction [1] is largely balanced by destruction in catalytic cycles of the form

$$\begin{aligned}
&XO + O \rightarrow X + O_2\\
&X + O_3 \rightarrow XO + O_2\\
&\text{Net: } O + O_3 \rightarrow 2O_2 \qquad \text{[Cycle 1]}
\end{aligned}$$

The net reaction is equivalent to Reaction [4]. Note that, because O and O_3 are in rapid photochemical equilibrium, the loss of one oxygen atom also effectively implies the loss of an ozone molecule, so that the cycle destroys two molecules of 'odd oxygen'. Notice also that the catalyst, X, is not used up in the reaction cycle. The most important cycles of this type in the stratosphere involve reactive nitrogen (X = NO), halogen (X = Cl) and hydrogen (X = H, OH) radicals. In the lower stratosphere, cycles catalyzed by Br also contribute to the ozone loss. Owing to the large increase of O with altitude, the rates of these cycles increase substantially between 25 and 40 km, as does the rate of ozone production.

In polar regions, the abundance of ClO is greatly enhanced during winter as a result of reactions on the surfaces of polar stratospheric cloud particles that form at the low temperatures found there. However, atomic oxygen, O, has very low concentrations there, which limits the efficiency of Cycle 1. In that case, two other catalytic cycles become the dominant reaction mechanisms for polar ozone loss. The first, the so-called ClO dimer cycle, is initiated by the reaction of ClO with another ClO,

$$\begin{aligned}
&ClO + ClO + M \rightarrow (ClO)_2 + M\\
&(ClO)_2 + h\nu \rightarrow ClOO + Cl\\
&ClOO + M \rightarrow Cl + O_2 + M\\
&2\,(Cl + O_3 \rightarrow ClO + O_2)\\
&\text{Net: } 2O_3 \rightarrow 3O_2 \qquad \text{[Cycle 2]}
\end{aligned}$$

and the second, the ClO-BrO cycle, is initiated by the reaction of ClO with BrO:

$$\begin{aligned}
&ClO + BrO \rightarrow Cl + Br + O_2\\
&Cl + O_3 \rightarrow ClO + O_2\\
&Br + O_3 \rightarrow BrO + O_2\\
&\text{Net: } 2O_3 \rightarrow 3O_2 \qquad \text{[Cycle 3]}
\end{aligned}$$

The net result of both Cycle 2 and Cycle 3 is to destroy two ozone molecules and to produce three oxygen molecules. Both cycles are catalytic, as chlorine (Cl) and bromine (Br) are not lost in the cycles. Sunlight is required to complete the cycles and to help maintain the large ClO abundance. Cycles 2 and 3 account for most of the ozone loss observed in the late winter-spring season in the Arctic and Antarctic stratosphere. At high ClO abundances, the rate of ozone destruction can reach 2 to 3% per day in late winter-spring. Outside the polar regions the ClO-BrO cycle is of minor importance because of much lower ClO concentrations, and the effect of the ClO dimer cycle is negligible as the cycle is only effective at the low polar temperatures.