Plastic Sulfur

If molten liquid sulfur is quenched from 350 °C rapidly to 20 °C by spraying into cold water, the resulting solid sulfur is known as "plastic sulfur". Fibers obtained this way have helical S_∞ chains with ten sulfur atoms for every helix repeat length. In addition, this type of sulfur is a composite material, having cyclic S_8 molecules packed into cavities between the fibers.

When liquid sulfur is discharged into cold seawater in an undersea volcanic eruption, probably the form of sulfur generated is plastic sulfur.

Sulfur Rings

Most of the allotropes of sulfur consist of molecular rings, S_n, where n = 6-20. The most stable of these rings is S_8, a molecule having S–S interatomic distances of 2.05 Å and belonging to the D_{4d} point group. Commercially available sulfur consists mostly of S_8 molecules, but it typically has a bright yellow color (characteristic of elemental sulfur) that comes from a small amount of S_7 impurity. Pure S_8 is pale yellow-green.

Another impurity that may be present in volcanic sulfur is S_7Se, where one of the sulfur atoms in the eight-membered ring is replaced with selenium.

Hexasulfur

Molecular hexasulfur has been synthesized in various ways. One way is via the thermal decomposition of S_2I_2, itself being generated by reaction of 2 KI with S_2Cl_2, analogous to the organic Finkelstein reaction. Using this method, it is possible to obtain S_6 in ca. 36% yield after separation from other S_{2n} molecules by fractional precipitation.

Of course, it would be desirable to have a reaction for selective generation of S_6, and the organometallic reagent known as titanocene pentasulfide has been developed for this purpose. It has the formula Cp_2TiS_5, and a molecular structure featuring a six-membered TiS_5 ring that effectively acts as a source of S_5^{2-} because of the polarity (sulfur negative, titanium positive) of the Ti–S bonds. Accordingly, S_6 has been synthesized in 87% yield by the reaction of Cp_2TiS_5 with SCl_2, giving titanocene dichloride (Cp_2TiCl_2) as the organometallic co-product of the reaction. Additionally generated in the reaction are small amounts of S_{12}. The sulfur dichloride reagent, SCl_2, does not have a long shelf life; it must be generated, distilled, and used while still fresh.

Heptasulfur, Nonasulfur, and Decasulfur

The seven-membered ring compound S_7 can also be generated in a selective reaction employing titanocene dichloride together with S_2Cl_2. Pure S_7 is not thermally stable and must be stored below −50 °C.

The molecular S_9 ring has been prepared similarly, by reaction of Cp_2TiS_5 with S_4Cl_2

In the case of S_{10}, the synthesis method is different. Here SO_2Cl_2 is employed effectively as a source of chlorine and SO_2 gas as a leaving group. The balanced reaction uses 2 Cp_2TiS_5 + 2 SO_2Cl_2 to provide S_{10}, 2 $SO_2\uparrow$, and 2 equiv of titanocene dichloride.

Sulfur as a Crystalline Mixture of Rings

When equal amounts of S_6 and S_{10} are recrystallized together from CS_2, the crystals so obtained consist of equal amounts of S_6 and S_{10} molecules. These crystals have a melting point of 92 °C. It has been said that this is the only solid allotrope of an element containing molecules of different sizes, but this use of the term "allotrope" is probably not appropriate here given our accepted definition.

Twelve- and Twenty-Membered Rings

The S_{12} molecule provides a nice example of D_{3d} symmetry, while S_{20} molecules take on a D_4 structure.

Vulcanization

An important application of elemental sulfur is its combination with natural and synthetic rubber in the process known as vulcanization. The most important synthetic polymer processed this way is polystyrene/polybutadiene, which when vulcanized is used to make automobile tires and other products. The vulcanization process installs $–SS_nS–$ cross-links between the polymer chains, making the rubber hard and not sticky.

The S_2 Molecule

Just like when comparing nitrogen and phosphorus, in the case of oxygen and sulfur the light element is a gas while the heavier element adopts a variety of solid allotropes. What are the properties of S_2? One way this has been approached is by the synthesis of a bicyclic disulfide molecule, $C_5H_6S_2$, that could release S_2 in a thermal retro Diels-Alder reaction. The S_2 so-generated in the presence of 2,3-dimethylbutadiene led to detectable formation of a new cyclic disulfide product, interpreted as evidence for the intermediacy of S_2 as a reactive transient.

Where is S_2 found in nature? The very close approach to earth of comet IRAS-Araki-Alcock 1983 VII led to the observation of UV emission spectra showing the presence of S_2 close to the cometary nucleus!