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Preparation of Sulfur Trioxide and Oleum, by GARAGE CHEMIST

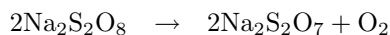
This is a new preparative pathway to sulfur trioxide, with completely over-the-counter chemicals and without the need for fancy apparatus, like catalyst tubes and such. Oleum, even if you can buy it, is horribly expensive from any of the known chemical suppliers (over \$100 per liter). Therefore, a good synthesis for SO_3 is necessary. The idea comes from the German Wikipedia page about sulfur trioxide. The pictures and process description below are from me. The only apparatus required is a ground-glass distillation setup, the same as you would use for the distillation of nitric acid.

Warning! Sulfur trioxide is extremely corrosive. It instantly carbonizes any organic matter it touches, including skin. A drop placed on wood instantly makes a black spot, under strong fizzing and fuming. The same happens when a drop falls on the skin.

Sulfur trioxide also reacts with water with explosive violence. When a drop of water falls into a flask containing SO_3 , the flask usually shatters because of the violent reaction and localized heating.

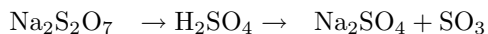
SO_3 fumes in air very strongly. The procedure must be carried out outside or under a fume hood.

When sodium persulfate is heated, it loses oxygen to form sodium pyrosulfate:



The evolved oxygen contains a small amount of ozone, which is identifiable by its smell.

Sodium pyrosulfate further decomposes into sodium sulfate and sulfur trioxide, but the reaction only takes place when sulfuric acid is present:



The sulfuric acid plays the role of a catalyst, it does not take part in the overall reaction, but without its presence, no SO_3 is formed.

Figure 1: apparatus prepared for distillation



Experimental

17.5 g dry sodium persulfate were put into a 100 mL round-bottom flask, and 2 mL concentrated sulfuric acid (of the highest obtainable strength, any water is very detrimental to the yield) were added. The flask was attached to the distillation setup, and heated by means of a bunsen burner. No water is run through the condenser, as the SO_3 would crystallize in the condenser. If necessary, the receiver is immersed in ice water for cooling (not necessary with this small batch). The initial setup is shown in Figure 1.

On heating, the mixture starts to rapidly generate oxygen, with some ozone as byproduct. When the oxygen evolution ceases, the mixture is heated stronger. It quickly melts into a clear liquid, and dense white fumes start to fill the setup.

Soon the first drops of liquid SO_3 will fall into the receiver. The thermometer registers a steam temperature between 45°C and 50°C during the process. If it becomes significantly higher than that (e.g. over 60°C) heating should be reduced a bit, since some H_2SO_4 could start to come over.

Residues of grease in the apparatus will be carbonized by the SO_3 ; this is normal and nothing to worry about. The SO_3 will also usually be colored brown due to this.

The flask will reach a very high temperature during this step (around 300°C). This is necessary for the sodium pyrosulfate to decompose.

Care must be taken to avoid the crystallizing SO_3 plugging the condenser outlet.

Figure 2: sulfur trioxide in receiver



This can be very dangerous. The solid SO_3 can be melted by means of a hot air gun if it is found to crystallize at the condenser outlet.

When no more SO_3 is coming over despite the reaction mixture still boiling, the reaction is over.

The SO_3 will most likely have partially or completely solidified in the receiver as shown in Figure 2.

My yield was only 1.4 g from the 17.5 g persulfate, but this was mostly due to the very small batch size. A yield of 100 g SO_3 from 200 g persulfate is claimed from another person. The ratio of persulfate to H_2SO_4 can also be varied and its effects on yield studied.

The distillation flask can be emptied, recharged with fresh sodium persulfate and H_2SO_4 and distilled again to increase the amount of SO_3 obtained. The batches should not be larger than 40 g persulfate at a time, because larger batches will be heated unevenly.

The combined portions of SO_3 can be redistilled for better purity. Pure SO_3 boils at 44°C and solidifies at 16.8°C .

The still is left in the fume hood until no more fuming is observed (all the SO_3 is turned into H_2SO_4 by atmospheric moisture), then it can be safely washed out with water.

SO_3 will quickly polymerize upon storage, evidenced by transformation into a

Figure 3: sulfur trioxide fuming in air



white amorphous mass (the polymerization starts within a few minutes to hours after preparation, depending on purity), but it depolymerizes again at ca. 66°C. Therefore, simple distillation gives normal SO₃ again.

The SO₃ can be dissolved in conc. H₂SO₄ to give oleum of any desired strength, but be warned, this process is exothermic, and with the very low boiling point of SO₃ it is very likely to start boiling. The liquid SO₃ should be slowly dripped into stirred, ice-cooled H₂SO₄ to avoid this. Polymerized SO₃ also dissolves in H₂SO₄, but slower and with less heat evolution.

Uses

Sulfur trioxide and oleum are exceptionally versatile reagents in the laboratory. Some of the most important uses shall be mentioned here:

With methanol or dimethyl ether, the powerful methylating agent dimethyl sulfate is formed. It is isolated by fractional distillation in vacuum. Diethyl sulfate is prepared analogously, by distilling SO₃ into dry diethyl ether, distilling away the ether and distilling the diethyl sulfate over Na₂SO₄ in vacuum.

By distilling SO₃ into SCl₂, the important chlorinating agent thionyl chloride is produced. This can be used for the production of acetyl chloride from acetic acid, and subsequently acetic anhydride.

By leading a stream of dry HCl gas through oleum until gas uptake stops, chlorosulfonic acid can be isolated by distillation. Chlorosulfonic acid is used for chlorosulfonations, by reaction with benzene, benzenesulfochloride (C₆H₅ – SO₂Cl) is obtained. Chlorosulfonic acid can also be used for an alternative preparation of dimethyl sulfate, as described in The War Gases by Mario Sartori.

Oleum is also employed as a condensing agent in organic chemistry, for example for the condensation of chloral with chlorobenzene to form DDT, the known powerful insecticide.