

A. This is a Masters Degree Project:

Oxygen effects in the reactions of Organosulfur Compounds

Oxygen is the most important reagent in the reactivity of organic sulfur compounds, especially in the formation of metal-ion mediated free radical formation. What does oxygen determine? Some reactions will be degassed with argon for complete anaerobic environments and some will be saturated with oxygen. This saturation is performed by basically bubbling oxygen gas into the reaction solutions before the start of reaction and then capping the reaction solutions until the reaction is over (fixed batch oxygen concentrations). Some experiments will be carried out under a constant flow of oxygen gas in a CSTR-type of configuration. We have a spectrophotometric cell mount in a UV-Vis spectrophotometer with a gaseous oxygen inlet as well as an outlet. The results should be extremely interesting. We also have, in our laboratories, a stopped-flow ensemble with a complete anaerobic kit such that we can run a whole series of experiments without introducing oxygen. In aerobic conditions, oxygen measurements will be very important in determining extent of reaction as well as postulating a possible mechanism. Dithionite is a well-known product of the decomposition of sulfinic acids, but, dithionite is not formed in strictly anaerobic conditions. The oxygen probe we use is a complete polarographic system consisting of a platinum cathode, silver anode, and KCl solution sealed around the electrodes by a Teflon membrane fastened with an O-ring. The response time is 90% in 10 seconds and it takes 30 s to reach steady state mainly because of the membrane. Since the probe is a complete system by itself, it is relatively unaffected by, and does not offset, its external environment. Adequate stirring will eliminate reading error due to oxygen depletion in the vicinity of the membrane. Oxygen uptake measurements will be performed at either 25 °C or 37 °C on a Gilson Oxy 5/6 oxygraph. A YSI 5331 oxygen probe will be inserted into a stirred, thermostatically controlled reaction vessel coupled to an amplifier and recorder.

B. This is a Masters Degree Project:

Autoxidations in Environmental Chemistry.

Under field conditions, autoxidations have proved difficult to contain. The problems of acid mine drainage arise from autoxidations. Effluent of high sulfide content like *black liquor* from tannery extracts and acid mine drainage are normally allowed to sediment and oxidize before being drained into the natural water system. The study of autoxidation of the thiols, sulfide, sulfenic, sulfinic and sulfonic acids will be performed by following the pH changes. Any additional oxygen atom on the sulfur atom comes stoichiometrically with a release of two protons¹. Most important and yet unexplored area of autoxidations should involve metal ion catalysts. There is evidence to confirm that the mineral content in a region can play a role in the rate of autoxidations of sulfide liquors. Apart from acknowledging that autoxidations occur in organic sulfur compounds, no-one has as yet worked on the mechanistic details. Partly the reason could be that these reactions are extremely slow and require a lot of patience to study. Autoxidations can also be followed by oxygen concentrations or the absorbance of the organic sulfur compound. For the oxidation of a sulfonic acid to sulfate, we found that conductimetric techniques work very well. The formation of the sulfate after cleavage of the C-S bond results in a large increase in conductivity of the reaction solution. We have already constructed batch and flow reactors of volume 33.6 ml equipped with ports for oxygen, pH and platinum electrodes to study the slow oxidations of organic sulfide compounds and the free sulfide by molecular oxygen. The reactors have inlets for controlled oxygen delivery (batch or flow). The complete studies will involve adjustments of pH, and addition of metal ions (and sequestering using standard chelators).