

Introduction

- Dimethyl Sulfoxide (DMSO, $[(CH_3)_2SO]$) is an important organosulfur compound with a lot of source and degradation pathways found in the environment.
- It is mainly produced in marine boundary layer and has been thought as a possible source of sulfur dioxide, (SO_2) an important air pollutant. The production of SO_2 has been speculated to occur with the oxidation of DMSO with common acids like oxalic acids, succinic acids and malonic acids.
- Oxalic acid is the most abundant dicarboxylic acid in the atmosphere and is used here to study the oxidation of DMSO to produce SO_2 . Oxalic acid exists in three forms (fig 1).

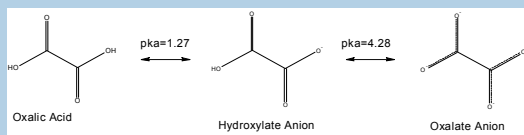


Figure 1: Oxalic acid exists in three forms in the marine environment. Oxalic acid is present in low pH (<1) Hydroxylate anions in pH 1-3 and oxalate anion in higher pH (>3). Collectively all three species are referred to as oxalic acid.

- The proposed reduction of DMSO by oxalic acid forms methyl sulfonic acid (MSA) and dimethyl sulfide (DMS) (Fig 2), as a first step towards the formation of SO_2 .

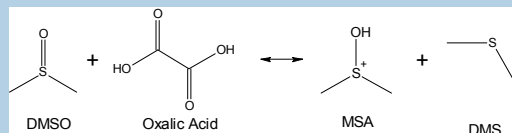


Figure 2: This is the proposed reaction, where oxalic acid reduces DMSO to form methyl sulfonic acid and dimethyl sulfide, compounds found in the marine boundary layer.

- The reaction of DMSO with oxalic acid is investigated here using ion chromatography.

Instrument Conditions

- Ion chromatography has been used to separate DMSO, oxalic acid, and known DMSO oxidation products (dimethyl sulfide, and methylsulfonic acid) based on charge densities.
- By using IC we are able to monitor the concentrations of oxalic acid, DMSO, and any other products that may form.
- Ion Chromatograph under the following conditions:
 - 1.8 mL flow rate
 - CS9-HC column with 0.5mM succinic acid eluent.
 - ARS -300, 4 mm regenerating suppressor
 - 25 μ L sample size, DS-4 conductivity meter.

Experimental procedure

- Each solution contains 5 mL of 0.5 M DMSO and 3mL of an oxalic acid (0.01-0.5M) in a scintillation vial.
- Five calibration standards (0.1-0.8M) of DMSO and oxalic acid were made before analyzing mixtures of DMSO and oxalic acid.
- Each solution of DMSO and oxalic acid was run three times in succession.

Calibration curve- ion chromatograph

Two calibration curves were made with various amounts of analyte compounds. One calibration standard was DMSO (fig 3), so we could observe the amount of DMSO left in solution after reaction. Oxalic acid was also used as a calibration standard to monitor the amount of oxalic acid left in solution. The shift in the DMSO peaks suggests that DMSO forms larger species at higher concentrations.

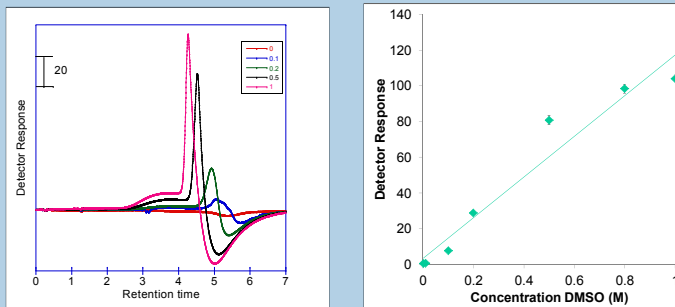


Figure 3: (right) Chromatograms of the various concentrations tested. (left) Calibration curve, with error bars. Error bars are one standard deviation from the mean of five replicate measurements. Each calibration standard was taken in triplicate to find the error bars. Concentrations are from 0.1 - 1 M DMSO solutions.

Chromatogram of Reaction between DMSO + oxalic acid

The chromatogram of several DMSO and oxalic acid mixtures are shown below (fig 4). Peak one at 1.5 min, is oxalic acid, the peaks at 4.8 minute is DMSO. The peak shift of DMSO from higher concentration suggests a chelate effect to form larger products which have a longer retention time.

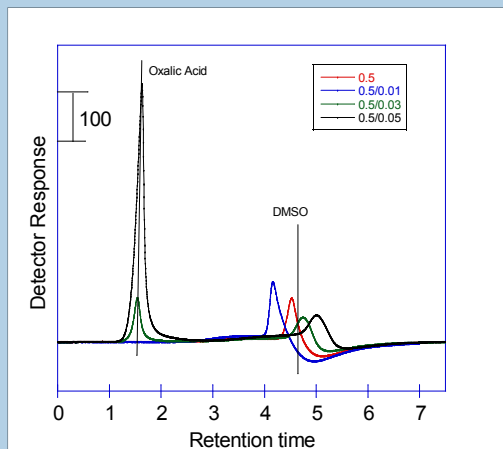


Figure 4: Chromatogram of each of the various concentrations of DMSO + oxalic acid mixture. The concentrations are noted in the key.

The peaks showing before and after DMSO peaks are thought to be degradation products when DMSO chelates. It is also thought that the peaks could be a result of DMSO reaction with the Oxalic acid. Further studies are ongoing to separate and identify each of these peaks separately.

Results

The amount of DMSO observed in solution follows a sigmoidal curve (fig. 5). If no reaction occur, the amount of Oxalic before and after the reaction would be the same (blue line). If a reaction occur, oxalic acid would be the limiting reagent and no peaks would be observed at this concentration range, the graph would show a flat line at zero.

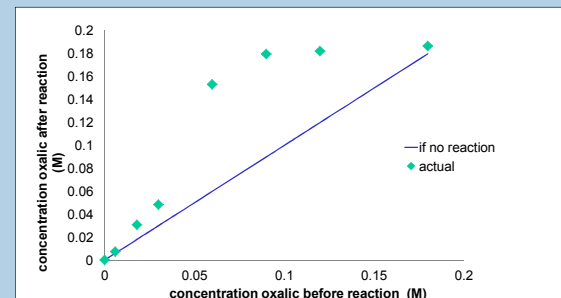


Figure 5: Graph of concentration of oxalic acid before and after reaction. The amount of oxalic acid in solution follows a sigmoidal curve which suggests that oxalic acid may act as a DMSO sink in low concentrations. The blue line indicates the predicted trend if no reaction or chelate were observed.

We can analyze the sigmoidal curve assuming steady state approximation (all other variables except concentration of DMSO and oxalic acid are constant) by taking the double reciprocal (fig 6). The asymptote is $\frac{x-intercept}{slope} = 0.03M$, observed in (fig 5).

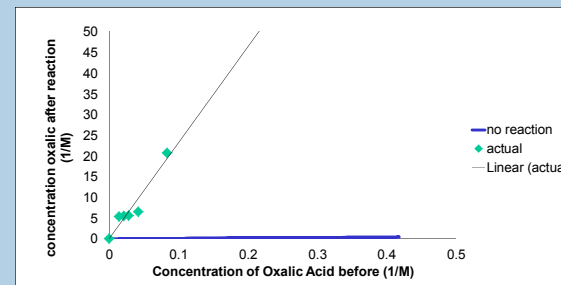


Figure 6: Concentration of oxalic acid before and after the reaction. Values represent the double reciprocal. Line of best fit $y=231.62x + 0.0347$, $R^2=0.92$. The blue line shows the trend if no chelate or reaction were observed, the blue line is near x-axis

SUMMARY

- The reaction of DMSO with Oxalic acid is producing some interesting chemistry, as evident by the appearance of more than one product peak. It may be the chelate effect, where at high and low concentrations oxalic acid is released.
- Observed trend may be due to a pH effect. Oxalic acid can chelate with DMSO causing a higher concentration of oxalic acid to be observed.
- No variation in concentration of oxalic and DMSO observed after solutions interact for ten minutes.

Acknowledgements

This research was done as part of the Arkansas State University Experiential Learning Fellowship (ELF) Program (NSF grant no. 1060209) research initiative.