Student Affiliates of the American Chemical Society (SAACS) February 4th, 2004 Meeting Minutes

Presenting:

Bruce S. Ault

Department of Chemistry, University of Cincinnati**,** Cincinnati, OH

Title: "High Temperature Chemistry Near Absolute Zero: The Interplay of Experiment and Theory"

Abstract: High valent transition metal compounds such as chromyl chloride, $CrCl_2O_2$, and $OMoCl_4$ are potent oxidizing agents capable of oxidizing many organic and inorganic compounds. While this has led to the use of these compounds as activating agents for C-H bands, they are also suspected carcinogens. The mechanisms by which these oxidation reactions occur are not fully understood, and intermediates in these reactions have not yet been identified. The matrix isolation technique, operating near 12 K, is uniquely suited for the isolation, identification and characterization of a wide range of reactive intermediates. Different methods may be used to deposit matrices, thereby allowing control over the time available for reaction between the precursors, as well as the available energy. Theoretical calculations using ab initio and density functional methods provide a powerful complement to the experimental studies. Using these approaches, the sequence of intermediates in the reactions of $OMoCl_4$ and $OVCl_3$ with small substrates will be discussed.

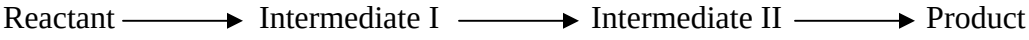
Meeting Minutes:

- Dr. Bruce S. Ault
  - Undergraduate studies: Caltech University in California
  - Graduate studies: Berkley University in California
  - Post-doc: University of Virginia

Matrix Isolation Concept:

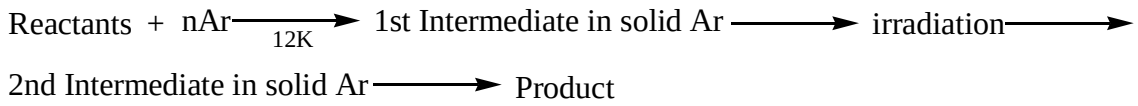
- The purpose of matrix isolation is to isolate chemical intermediates (free radicals, ions, molecular complexes, etc.) in reactions and to obtain their identities and characteristics, which will further provide information regarding the reaction mechanism.

Scheme:



- The chemistry in these experiments takes place around 12-13K, close to absolute zero (0K, -273.15ºC), which basically provides the chemical system with no thermal energy.
- The chemical reactions are done in an un-reactive gas such as argon (Ar), which is in its solid phase at 12K, allowing isolation, stabilization, and characterization of reaction intermediates. In addition, these reactions take place under vacuum because air would freeze at 12K.

Scheme:



Matrix Deposition:

- In twin jet deposition, samples are prepared in separate manifolds then sprayed from separate nozzles onto a cryogenic surface.
- In merged jet deposition or irradiation, samples are prepared in separate manifolds then sprayed from the same nozzle in order to allow the reactants to react longer than twin jet deposition, which can be used to isolate and characterize other reaction intermediates.

Goals:

- Isolate, identify and characterize initial intermediate in chemical reactions (twin jet).
- Isolate, identify and characterize secondary intermediates in chemical reactions (merged jet deposition or irradiation).
- Deduce reaction mechanism.
- Isolate, identify and characterize further intermediates when possible.

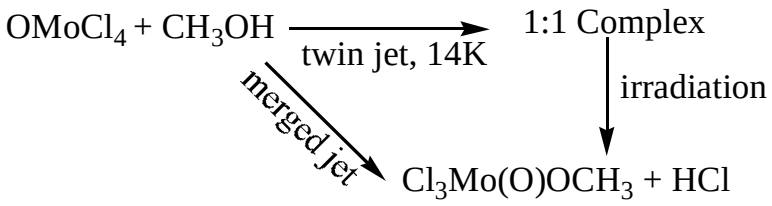
Systems of Interest:

- High valent transition metal oxo compounds including $OVCl_3$ and $CrCl_2O_2$ (strong oxidizing agents).

How would one observe the results?

- By isotopically labeling different atoms in a reaction and observing the shift changes in Infrared (IR) Spectroscopy.
- By using theoretical, molecular orbital theory calculations such as the Schrödinger equation.

Reaction:



Results:

- HCl was definitely formed and they believe that $Cl_3Mo(O)OCH_3$ was also formed in this reaction.
- Next, they used the computer program Gaussian '98 – B3LXP/6-322g* and the Schrödinger approximations in order to theoretically calculate the bond lengths and bond angles and stability of $Cl_3Mo(O)OCH_3$. The results showed that $Cl_3Mo(O)OCH_3$ was indeed a stable species.

Another Reaction:

$$OVCl_3 + NH_3 \longrightarrow HCl + Cl_2V(O)NH_2$$

Results:

- HCl was definitely a photoproduct and isotopic shifts and theoretical calculations support the formation of $Cl_2V(O)NH_2$.