**CHEM 5142 - Reaction Mechanisms**

**Text:** Ralph G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, VCH, 1991. This text is out of print. We will use a copy (by permission from the publisher) which will be available soon.

**Grading:** the grade for the course will be determined from;

Two hour exams (100 points each) 50%

Exam I

Exam 2

Homework assignments 25%

Final exam (100 points) 25%

**Grading scale;**

A >90

A- 89-85 C 64-60

B+ 84-80 C- 59-55

B 79-75 D 54-50

B- 74-70 F <50

C+ 69-65

The course will focus primarily on the material in the text with additional assignments from the chemical literature. In addition, a list of other sources is given at the end of the syllabus. As a result of successfully completing this course you should be able to;

1. Understand the mechanisms involved in the various types of chemical processes involving transition metal complexes and organometallic compounds.

2. Understand the experimental aspects of determining the rate law for a chemical reaction.

3. Interpret the rate law in terms of possible mechanisms.

4. Understand how reactions of transition metal complexes relate to other areas such as the reactions of metalloenzymes in biological organisms and catalytic processes.

5. Critically read inorganic literature dealing with kinetic and mechanistic studies.

**Outline of Topics**.

I. Introduction: A general introduction to transition metal structure and bonding concepts. An overview of reaction patterns. Read chapter 1 in the text.

II. Experimental Determination of the Rate Law. Handouts

Assignment A. Handout I.

Read A. C. Melnyk, *et al. J. Am. Chem. Soc*. **1979**, *101*, 3232.

Assignment B. Handout II.

Read L. Helm, et, al. *Inorg. Chem*. **1985**, *24*, 1719. Use Figure 3 in this reference to obtain kb/t, s data and fit these to equation 4 to calculate kex at 323.8 K. How is kb obtained experimentally?

The Deduction of the Mechanism from the Rate Law.

Assignment. Handout III.

Read B. Perlmutter-Hayman & E. Tapuhi *Inorg. Chem.* **1977**, *16*, 2742-2745.

Experimental Techniques for Determination of the Rate of Reaction.

Read J. Barry DeRoos and J. P. Oliver *Inorg. Chem*. **1965**, *4*, 1741. Use their data to calculate the values of k1, k2Ke and Ea.

III. Substitution Reactions in Octahedral and Square Planar Complexes: D, ID, IA, A mechanisms. Chapters 2, 3.3, 4 of text.

Solvent Exchange

Acid Hydrolysis

Base hydrolysis

Anation

Read. J. G. Leipoldt, R. van Eldik, & H. Kelm, *Inorg. Chem.* **1983**, *22* , 4146-4149.

Fred Basolo, Hans H. Schmidt, and Ralph G. Pearson, J. Am. Chem. Soc. **1960,***82,* 4434-5. The Mechanism of Base Hydrolysis and Base Catalyzed Hydrolysis of Some Cobalt(III) Ammine Complexes.

IV. VIII. Isomerism and Stereochemical Changes in Complexes. Chapter 5 in text.

V. Substitution Reactions of Organometallic Compounds, Carbonyls and Related Substances. Chapter 6 in text.

VI. Oxidation-Reduction Reactions. Chapter 7 in text.

Outer Sphere mechanisms

Inner Sphere mechanisms

Read D. H. Macartney, A. McAuley, and O. A. Olubuyide *Inorg. Chem.* **1985,** *24,* 307-312. Answer the following questions about this article.

a) What is the main problem being investigated?

b) What is the authors explanation for the lack of agreement between the experimental results for the Fe(aq)2+/3+ electron exchange rate, k22, and the calculated value obtained from cross reactions by the Marcus theory?

c) What is the role of the sulfate ion in this reaction?

VII. Activation, Addition and Insertion Reactions and Catalysis.

CO Substitution Reactions.

Insertion Reactions

Oxidative Addition/Reductive Elimination Reactions

Catalysis of Organic Reactions/catalytic cycles

XI. Reactions of Metal Complexes with Oxygen and Hydrogen Peroxide.

Read. Robbins, M. H.; Drago, R. S. *J. Chem. Soc., Dalton* **1996,** 105-110. Redox Considerations for a Ruthenium Complex Catalysis of Substrate Oxidation by Hydrogen Peroxide in Aqueous Solution.

Rush, J. D.; Koppenol, W. H.  *J. Am. Chem. Soc.* **1988,** *110,* 4957-4963. Reactions of Fe(II)nta and Fe(II)edda with Hydrogen Peroxide.

XII. Charge Transfer and Photochemical Reactions of Transition Metal Complexes.

XIII. Selected Bio-inorganic Reactions.

Most Inorganic Chemistry texts contain chapters on the mechanisms of inorganic reactions. Some reference books which are particularly helpful are; These may be checked out from my office.

1. Jim D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole, 1985. A readable book focusing on reaction mechanisms of organometallic compounds.

2. F. Basolo and R. G. Wilkinson, *Mechanisms of Inorganic Reactions: A Study of Metal Complexes in Solution*. 2nd Edition, 1968, John Wiley & Sons, Inc. The classic text in this field. It provides a comprehensive summary of the early research results and theories of reaction mechanisms and is still relevant today.

3. Robert B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems*, Oxford, 1998.

4. Ralph G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, VCH, 1991