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AFOSR 51367

64-2

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"Mechanism of Inorganic Reactions: Bridge Mechanism
in Electrochemical Oxidation and Reduction of Metal Ions."

University of Kansas

Reynold T. Iwamoto

Director
Project Contract/Grant
AFOSR 61-8

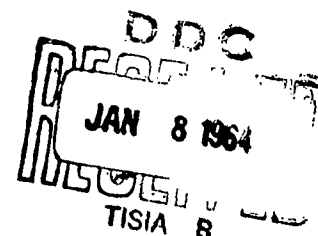
Grant No. AFOSR 61-8

Final Report

October 1, 1961 - December 31, 1962

Date of Report

November 11, 1963



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The following report covers the research supported by this grant over the one and a half year period from June 1, 1961 to December 31, 1962.

The chief problem in studying ligand effects in redox reactions of metal ions in aqueous system is that "only when certain conditions are fulfilled with respect to the substitution lability of the redox partners has it been possible to draw fairly definite conclusions as to the nature of the activated complexes." In order to obtain information fundamental to understanding better the mechanism of inorganic oxidation-reduction reactions, in particular of those involving a bridged activated complex, we have proposed the use of nonaqueous solvents and of an electrode in place of either the oxidant or reductant to study these reactions. Through such an approach, we hope to simplify greatly the design of experiments.

The attractiveness of utilizing nonaqueous solvents for the proposed electrochemical study is that the desired electron mediator can readily be placed in the coordination sphere of the metal ion by using it, if it is a liquid, as the solvent or by working in an "inert" nonaqueous solvent if it is a solid. There was, however, one serious problem; no simple method was available for comparing the electromotive force series in various solvents. Because the proposed electrochemical study would be of little value unless we were able to ascertain the magnitude of the liquid-junction potentials included in the potentials obtained, we undertook a careful examination of the problem of evaluating liquid-junction potential. The results of the investigation are described in Anal. Chem., 33, 1795 (1961) and Anal. Chem., 35, 867 (1963).

At the same time, we began an investigation of various carboxylic acids as electron mediators in inorganic electrochemical oxidation-reduction reactions. Unfortunately, this investigation has taken a back seat to an interesting reaction between copper(II) ion and copper metal in acetic acid that was uncovered in our

study of the electrochemical behavior of copper ions in acetic acid. When copper metal is added to an acetic acid solution of copper(II) perchlorate, the color of the solution changes almost immediately from a pale blue to an intense violet. Because of the unusual nature of this reaction, we have spent a considerable amount of time studying the reaction and trying to isolate the purple product. Although we encountered a great deal of difficulty in isolating the purple species, we were continuously encouraged by the great interest of a number of notable inorganic chemists, such as Professor Taube and Professor Kleinberg, in the reaction. We finally succeeded this past year in isolating the purple product, and are now in the midst of characterizing the material. A very interesting feature of the purple species is that it contains a copper(II) and a copper(I) ion.

Knowledge of the make-up of the coordination sphere around an ion is indeed indispensable in understanding the properties of the ion and the mechanism of the chemical processes which the ion undergoes in a particular medium. The study of the polarographic behavior of nickel(II) in acetonitrile in the presence of chloride, J. Electroanal. Chem., 6, 234 (1963), was our first attempt to obtain information on how the make-up of the coordination sphere around an ion influences the behavior of the ion in solution.

Because even the most careful purification of an organic solvent leaves a surprisingly appreciable amount of water in the solvent, e.g., a solvent which is 99.98% pure, i.e., 0.02% in water, is 0.01M in water, one of the most important problems with regard to the interpretation of experimental results on studies dealing with the nature and behavior of inorganic ions in nonaqueous media is the effect of residual water. Our continued interest in this problem has resulted in an examination of the formation constants of aquo-copper(II) complexes in acetone. The results of this study have been prepared for publication (preprints enclosed).

List of Publications:

- I. V. Nelson and R. T. Iwamoto, Anal. Chem., 33, 1795 (1961).
I. V. Nelson and R. T. Iwamoto, Anal. Chem., 35, 867 (1963).
I. V. Nelson and R. T. Iwamoto, J. Electroanal. Chem., 6, 234 (1963).
I. V. Nelson and R. T. Iwamoto, submitted for publication. (preprint)