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entitled

"STABLE ISOTOPE TRACER STUDIES"

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Submitted by

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I. Personnel

During the period from the inception of the research contract on 1 March 1968 through the period 28 February 1969, the following persons will have contributed to the program:

Research Assistants:

Robert Buchacek, 12 months, half-time

Eugene Grimley, 12 months, half-time

John Young, Summer, full-time

Research Associates:

Dr. Donald Hoppenjans, 6 months, full-time

Dr. Samir K. Mukherjee, 6 months, full-time

Research Supervisor:

Gilbert Gordon, 12 months, 1/5-time

II. Research Accomplished and in Progress

The year has been very productive in terms of initialization of research. A considerable amount of effort has been expended in the area of improvement and calibration of the rapid mixing and mass spectrophotometric equipment which was transferred from the University of Maryland to the University of Iowa. Since this corresponds to the first progress report on this grant, there are no publications. Progress has been good, however, and several manuscripts should be in publishable form within the next several months.

Specific reference should be made to two manuscripts (one published and one in press) initiated under contract AT(40-1)-2858 but completed and submitted for publication by the Principal Investigator under this contract [AT-(11-11)-1780].

Reprints will be submitted under separate cover and the titles and authors are listed below:

- (1) Bassam Z. Shakhashiri and Gilbert Gordon, "The Oxidation of Tris(1,10-Phenanthroline)Iron(II) Ion by Aqueous Chlorine", Inorg. Chem., 7, 2454 (1968).
- (2) Bassam Z. Shakhashiri and Gilbert Gordon, "The Oxidation of Tris(1,10-Phenanthroline)Iron(II) Ion by Chlorate and Chlorite Ions and Chlorine Dioxide in Aqueous Solution", J. Am. Chem. Soc., to be published (March 1969).

Research on projects initiated at the University of Iowa can be summarized most easily in terms of the two major projects which were described in the initial research proposal. The first project is concerned with the investigation of the mechanisms of inorganic reactions in aqueous solutions and three specific areas are under investigation.

The reactions between uranium(IV) or Fe(phen)_3^{+2} with sodium chlorite are being studied in an attempt to identify the kinetic role of the halogen-containing intermediate(s). The most fruitful results have been obtained from the various reactions of Fe(phen)_3^{+2} with chlorine, hypochlorous acid, chlorate and chlorite ions, and chlorine dioxide. It should be noted that this work was initiated at the University of Maryland under Atomic Energy Commission contract AT-(40-1)-2858 which was in effect terminated at the University of Maryland and reinitialized here at the University of Iowa. The completion of this work and its preparation for publication was carried out under the auspices of this research contract.

The oxidation of iron(II) species by chlorine may proceed through a two-electron step to form an iron(IV) intermediate:

or through a one-electron step to form a chlorine radical intermediate:

Our study of the oxidation of tris(1,10-phenanthroline)iron(II) ion, $[\text{Fe}(\text{phen})_3^{+2}]$, by aqueous chlorine was undertaken in an attempt to differentiate between these two possibilities.

Chlorine reacts much faster than HClO with $\text{Fe}(\text{phen})_3^{2+}$ as in the case when $\text{Fe}(\text{CN})_6^{-4}$ is the reducing agent, but HClO reacts more rapidly than Cl_2 with Fe^{2+} . Furthermore, Cl_2 reacts with $\text{Fe}(\text{phen})_3^{2+}$ via an outer-sphere path and involves a one-electron step. Formation of FeCl^{2+} as an initial product in the $\text{Fe}^{2+}\text{-Cl}_2$ and $\text{Fe}^{2+}\text{-HClO}$ reactions strongly suggests that an inner-sphere path is involved. The mode of reaction seems to change significantly as iron(II) is complexed with phenanthroline or cyanide ion but unfortunately, specific comparison of rates can be made only when all of the reactions proceed via the same path.

The reactions of chlorate and chlorite ions, and chlorine dioxide with $\text{Fe}(\text{phen})_3^{2+}$ have also been studied. The mode of reaction varies from one oxidant to another in that ClO_3^- was found not to react at all. In the case of ClO_2^- the rate of the reaction is controlled by the first dissociation step of $\text{Fe}(\text{phen})_3^{2+}$ and the iron(III) product is a dimeric species. Chlorine dioxide reacts via an outer-sphere path since the iron(III) product is the monomeric species $\text{Fe}(\text{phen})_3^{3+}$.

It should be noted that most reactions between $\text{Fe}(\text{phen})_3^{2+}$ and many oxidants can be classified into one of two groups based on whether or not $\text{Fe}(\text{phen})_3^{3+}$ is formed as a product. Thus, reactions of $\text{Fe}(\text{phen})_3^{2+}$ with Ce(IV) ,¹ Co(III) ,¹ Mn(III) ,¹ Cl_2 ² and ClO_2 fall into the first group since they yield $\text{Fe}(\text{phen})_3^{3+}$ rapidly. Reactions of $\text{Fe}(\text{phen})_3^{2+}$ with peroxydiphosphate ion³ and chlorite ion fall into the second group since they are slow and do not yield $\text{Fe}(\text{phen})_3^{3+}$ as a product.

Reactions of the first group are first-order in each reactant and usually take place in acidic solutions. These reactions, which involve one-equivalent oxidizing agents, proceed via an outer-sphere path since electron transfer takes place rapidly and the first coordination sphere of the iron complex retains the same ligands throughout the process.

Reactions of the second group take place in the 1.0 to 9.0 pH range; their rates are controlled by the first dissociation step:

and are usually independent of oxidant concentration. These reactions involve multi-equivalent oxidants. Electron transfer from Fe(phen)_2^{2+} to the oxidizing agent may take place via an outer-sphere path only if the rate of exchange between solvent and the water molecules in the first coordination sphere of Fe(phen)_2^{2+} is slower than the rate of oxidation.

Several multi-equivalent oxidants such as Cr(VI), peroxydisulfate ion and lead dioxide react with Fe(phen)_3^{2+} rapidly to form Fe(phen)_3^{3+} . These reactions belong in the first group, but their mechanism must involve a one-equivalent process. For example, Cr(V) has been postulated⁴ as an intermediate in the Fe(phen)_3^{2+} -Cr(VI) reaction. Sulfate radical is proposed⁵ also as an intermediate in the Fe(phen)_3^{2+} -peroxydisulfate ion reaction. Although no kinetic studies have been reported on the Fe(phen)_3^{2+} - PbO_2 reaction, formation of Pb(III) as an intermediate could be postulated since Fe(phen)_3^{3+} is the product.

Preliminary experiments have revealed that the Fe(phen)_3^{2+} - MnO_2 reaction yields Fe(phen)_3^{3+} as a product. Thus, reduction of Mn(IV) to Mn(II) involves two one-electron steps in this reaction. Another preliminary experiment revealed that the Fe(phen)_3^{2+} - H_2O_2 reaction belongs in the second group. Formation of Fe(phen)_3^{3+} could not be detected even when the oxidant concentration was 100-fold in excess and the acidity was sufficiently high to stabilize Fe(phen)_3^{3+} if it were formed. The major product formed was the iron(III)-phenanthroline dimer.

Therefore, it is suggested that reduction of H_2O_2 by $\text{Fe}(\text{phen})_3^{2+}$ does not involve an outer-sphere, one-electron process.

In conclusion, it should be noted that coordination of ligand to metal ions can either facilitate or retard the rates of oxidation of these ions. It appears that complexed iron(II) species such as $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{CN})_6^{4-}$ react slower than Fe^{2+} .

Mr. Robert Buchacek is working in the second area of interest and has continued his study of the kinetics of the reaction between uranium(IV) and sodium chlorite in the presence of phenol and various chlorophenols by means of a rapid-mixing technique.⁶ At this point, we are quite convinced that the results can be expressed in terms of the following mechanistic equations:

The mechanism can be summarized in terms of the following stoichiometric equation:

In the presence of the phenol scavenger, the reaction is indeed first order in both reactants for more than 80% of the reaction but small deviations from the second order process are observed. Presently, we are investigating the possibility that chlorite ion (or more properly HClO_2) is disproportionating to form chlorine dioxide and chloride ions or that phenol or the chlorinated phenols are in some way interacting with uranium(IV) and causing deviations from a simple second order process.

We have sufficient evidence on the interactions between sodium chlorite and hypochlorous acid to be able to predict the rates of these reactions to form chlorine dioxide and sodium chlorite under the conditions of the uranium(IV) - chlorite reaction.

Most probably, the species Cl_2O_2 is responsible for the formation of chlorate $[\text{Cl(V)}]$ ion during the course of these reactions:

The intermediate can decompose by one of two paths. In concentrated solutions

and in diluted solutions, corresponding to our reaction conditions,

We propose that Cl_2O_2 more rapidly oxidizes phenol than does Cl_2 or HOCl . Thus, the intermediate can be removed by phenol and the reaction between U(IV) and Cl(III) corresponds to a single two-electron transfer reaction accompanied by oxygen transfer from Cl(III) [chlorite ion] to the product UO_2^{++} . Our present plans include a detailed study of these reactions as a function of concentration, hydrogen ion, temperature and ionic strength. These studies will be followed by more detailed tracer experiments in order to elucidate the details of the electron transfer process itself.

The third area is being studied by the Principal Investigator and is concerned with additional tracer studies on the chromium(II)-chlorine oxidant reactions. The role of the proton in the activated complex is not clear. The corresponding iron(II)-chlorate ion reaction has a relatively simple rate law but the chromium-chlorate reaction appears to include a proton in the principle activation process. The rates of the oxygen transfer reaction have been suggested by Edwards to involve the equilibrium

The role of the proton is to weaken the strong bond between the negative oxygen atom and the positive central chlorine atom. We are attempting to carry out detailed oxygen-18 tracer studies to determine if any chlorate oxygen is transferred to the $[\text{Cr(OH}_2)_6]^{+3}$ product in the $\text{Cr(II)}-\text{ClO}_3^-$ reaction. Thusfar, we have been

successful in separating the various chromium species formed during the reaction on a Dowex-50 ion exchange column and preliminary tracer experiments suggest that oxygen is indeed transferred from chlorate ions to chromium(II) in the net activation process. A variety of blank experiments have been carried out and although some difficulties in precipitation of the $(\text{H}_2\text{O})_5\text{CrCl}^{++}$ and the $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ species do occur, it appears that maintaining the ion exchange column at 0° followed by immediate precipitation after separation will result in excellent tracer experiments. This information in conjunction with the stoichiometric data published by Gordon and Thompson^{7,8} should provide two somewhat independent approaches to the understanding of the details of the halogenate oxidation of chromium(II).

The last project is primarily concerned with oxygen transfer reactions and oxygen exchange reactions in the gas phase and the effect of a variety of catalysts on these reactions. We have successfully looked at the homomolecular isotopic exchange reaction⁹ between oxygen-16 and oxygen-18 and the homomolecular exchange reaction between oxygen-16 and oxygen-18 as catalyzed by silver metal.¹⁰

Preliminary experiments at the University of Iowa have been concerned with updating and improving both the precision and accuracy of the Nuclide Double-Beam Isotope Ratio Mass Spectrometer. We have devised two techniques for improving the ease and accuracy with which isotope ratios can be determined. Although the specific details of the techniques are only important with respect to our instrument, the results are particularly noteworthy. The isotope ratio $[\text{mass } 46 / (\text{mass } 44 + \text{mass } 45)]$ for a series of "identical" samples are given below.

The imprecision reflected in the average value (less than one part per thousand) is very probably a measure of the difficulty in sample preparation techniques rather than precision of the mass spectrometer. Thus, we are quite certain that it should be possible to carry out the detailed tracer experiments with somewhat less

<u>Sample Code</u>	<u>Enrichment Ratio</u>
140	27.694
141	27.650
142	27.732
143	27.732
144	27.680
145	27.650
	<hr/>
	27.690 ± 0.023

highly enriched samples than those previously suggested. Necessarily, this will result in lower cost per experiment and provide the possibility of doing more experiments.

The other area in which some progress has been made during this past year has been in an understanding of the way in which uranium peroxide dihydrate decomposes thermally. For these experiments, we are using double-tagged (oxygen 18-18, oxygen 16-16) hydrogen peroxide to prepare the $\text{UO}_2\text{O}_2 \cdot \text{H}_2\text{O}$. Thermal decomposition of the peroxide samples results in the formation of oxygen and water as given by the equation¹¹ below:

The question arises as to the source of the oxygen. Since only one oxygen molecule is formed for every two uranium peroxides which decompose it can be envisioned that the O_2 arises either by means of a homomolecular or heteromolecular reaction. It is also possible that the molecular oxygen is formed as a result of recombination of oxygen atoms. We have sufficient experimental evidence from the double-tagged tracer experiments to suggest that oxygen atoms indeed cannot be the source of the molecular oxygen which is formed in that complete mixing of oxygen isotopes does not occur.

We have carried out preliminary experiments with eight-fold enriched hydrogen peroxide which has been mixed with normal hydrogen peroxide and followed the decomposition as a function of time. The techniques for preparation of the hydrogen peroxide, isotopic and chemical analysis of the peroxide and isotopic and chemical analysis of the resulting uranium peroxide have been successful. Presently, we are attempting to prepare 50% enriched oxygen-18 containing hydrogen peroxide such that the final experiments can be carried out on the decomposition of uranium peroxide in an attempt to obtain information about the exact mechanism of decomposition and the role of intermediate oxygen-containing species in the decomposition.

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III. Incident Reports

In compliance with the AEC regulation that reports be submitted on accidents, fires, and unusual operational incidents which occur in conjunction with work being performed under AEC contract, the following are reported:

1. Serious accidents - none
2. Fires, explosions, etc. - none
3. Other property damage - none
4. Personal injuries - none