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"Chemical Effects of Nuclear Transformations,
Flash Heating, or Flash Photolysis"

Final Report
January 1, 1969 through Septemb. 30, 1969

U. S. Atomic Energy Commission
Contract No. AT(11-1)-1684

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University of Toledo

Final Report

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I. Reports

The following reports have been prepared during the period covered and are forwarded separately:

COO-1684-7

"Participation of Alumina in Heterogeneous Catalysis",

W. Ronald Cares, Ph.D. Dissertation,
University of Illinois, Urbana, Illinois, April, 1969.

COO-1684-8

"The Production and Study of Titanium Monohalides by Flash Heating"

Robert L. Diebner, Ph.D. Dissertation,
University of Illinois, Urbana, Illinois, May, 1969.

COO-1684-9

"Absorption Spectrum of Vaporized Titanium Monofluoride", Robert L. Diebner
and Jack G. Kay, J. Chem. Phys. 51, 3547(1969).

COO-1684-10

"Flash Heating As a Technique for High Temperature Spectroscopy",

Michael B. Garrett, Ph.D. Dissertation,
University of Illinois, Urbana, Illinois, January, 1970

II. Effects of Flash Heating on Alumina

Dr. Cares completed work on this problem early in 1969 and received his Ph.D. in Inorganic Chemistry from the University of Illinois. The results of this work show that the reaction of ethanol on alumina occurs initially by forming surface ethoxide and -OH groups which subsequently react, releasing water, alcohol, ether or ethylene. The reactions of ethers and of other lower alcohols with the alumina are similar in the production of surface alkoxy- or hydroxy-alumina.

III. Studies of KMnO_4 Crystals

Photoluminescence experiments being carried out by Mr. Joaquin O. Uy in cooperation with Dr. E. C. Lim at Wayne State University have produced interesting, but not definitive results.

The previous observations of thermoluminescence of KMnO_4 in our laboratory showed emission in the spectral range from 500 to 600 nanometers. Using the Aminco-Bowman Spectrophotofluorometer, the photoluminescence showed an emission spectrum from 300 nm. excitation closely resembling the absorption band which occurs in the 500 to 600 nm. region. The excitation spectrum consists of a small peak at about 250 nm. and a strong, rather sharp band at about 300 to 320 nm. There appears to be no excitation or emission corresponding to the absorption spectrum of permanganate in the 350 to 400 nm. region.

The emission band observed in thermoluminescence of KMnO_4 is in the same region as the photoluminescence excited by 300 nm. light. Thermoluminescence may be attributed to reactions due to electrons excited from traps. For example, the neutral species, MnO_4 , representing an electronic vacancy could combine with an electron to produce the first excited singlet state of MnO_4^- , which would then fluoresce at 520 nm. while de-exciting to the ground state. The occurrence of a similar fluorescence with 300 nm. excitation is interesting because permanganates are known to undergo photodecomposition at 300 nm. and longer wavelengths. Photodecomposition might be expected to generate new species (impurities) which should produce additional fluorescence spectra, but these were not confirmed.

Attempts to study the permanganate ion isolated in a solvent matrix at low temperatures were unsuccessful because of the inability to obtain a suitable solvent which did not decompose the permanganate.

Because CrO_4^{2-} is isoelectronic with MnO_4^- and is not photodecomposed by exciting light at wavelengths as short as 240 nm., it was decided to examine the photoluminescence of K_2CrO_4 at 77°K and higher temperatures in ethylene glycol-water mixtures. The molecular orbitals of permanganate and chromate are considered to be alike, but at different energies, so that the same pattern of intramolecular transitions should be observable with one as with the other.

The photoluminescence spectrum of chromate shows emission bands at 275 nm. and at 385 nm., both due to excitation light peaking rather sharply at 240 nm. The absorption spectrum shows bands corresponding to the 385 nm. and 275 nm. luminescence peaks, although the absorptions are at slightly higher energies. The excitation peak at 240 nm. appears to correspond to a shoulder in the absorption spectrum.

The observation of two emission bands suggests that both the first and second excited states of chromate may be fluorescing, which would be a rather unique phenomenon. Furthermore, the relative intensities of the 275 and 385 nm. emission bands are reversed at 77°K from their intensities at room temperature, the 385 nm. band being the more intense band at room temperature. Using the phosphoroscope, it was shown that delayed fluorescence occurs in the 385 nm. band at room temperature, and at 77°K in this and a new band at 500 nm..

The 500 nm. component might correspond to the first excited triplet state in the chromate ion. The lack of delayed fluorescence at 275 nm. may indicate that charge radical recombination leading to population of 385 nm. emitting level does not populate the 275 nm. level.

The observed temperature dependance might result from competition between vibrational deactivation processes and radiant transitions. On the other hand, the participation of some impurity species has not been ruled out by the experiments. In particular, the possible formation of dimeric species, such as dichromate, needs to be investigated by concentration dependance studies. Thus, while our observations suggest a possible charge-transfer absorption at 240 nm. leading to formation of chromate which fluoresces from both the first and second excited states, it is possible that one of the emitting bands could be due to formation of dichromate or some similar species. The observation of delayed fluorescence suggests that dichromate or impurity emission could account for the longer wavelength bands. The 500 nm. delayed fluorescence might then be attributed to a triplet state of the emitting impurity.

Further work is needed before these observations for permanganate or chromate may be satisfactorily explained.

IV. Flash Heating and Kinetic Spectroscopy

Dr. Robert L. Diebner completed his requirements for the Ph. D. degree in Inorganic Chemistry at the University of Illinois and a report of his analysis of the TiF spectrum has been published in Journal of Chemical Physics.

Further studies of the spin-orbit coupling constant, as observed for the $^4\Pi$ excited state of TiF, should be carried out. In particular, the apparent variation of the vibrational constants between different branches of the multiplet should be examined in more detail. Also, the variations in the spin-orbit coupling constant appear to correlate with variations in the vibrational force constant for a number of diatomic molecules. Further studies of this correlation should be done in order to obtain a better understanding of the molecular electronic structures and interactions involved.

Michael B. Garrett has completed his Ph. D. dissertation for a degree in Inorganic Chemistry to be awarded in 1970 at the University of Illinois. His work on the electronic spectrum of MnO and of atomic lead has been described in previous work.

V. Personnel

During the past year, three graduate students received training and contributed to the work of this project. Mr. Garrett completed his work in the laboratories of Dr. Frank Tompkins at Argonne National Laboratories where he was supported by an AMU-ANL Fellowship. Mr. Garrett received support from this project until his appointment as an Instructor-Postdoctoral Associate at Drexel Institute of Technology in April, 1969.

Dr. Cares received support from this project until his appointment in April, 1969, as a Postdoctoral Associate with Professor J. W. Hightower in the Department of Chemical Engineering at Rice University.

Mr. Joaquin O. Uy continues as a Ph. D. candidate in chemistry at the University of Toledo where he is completing his thesis research begun under the auspices of this contract. It is expected that he will complete his Ph.D. requirements in 1970. Mr. Uy has been supported by a Doctoral Candidate Assistantship at the University of Toledo. This assistantship amounts to over \$4,000. plus fees contributed by the University to the work of this project.

VI. Termination

The termination of this project at the University of Toledo occurs because of the decision of the Principal Investigator to accept a new position as Professor and Head of Chemistry at Drexel Institute of Technology in Philadelphia, Pa. This research, which began under Atomic Energy Commission sponsorship at the University of Illinois and was continued at the University of Toledo, will be continued again at Drexel Institute of Technology. The primary emphasis at Drexel will be on the use of high resolution spectroscopy to extend the studies of diatomic molecules described in this and previous reports.

The Principal Investigator, in behalf of Mr. Uy, Dr. Garrett, Dr. Cares, Dr. Diebner, Dr. Diefallah, and others associated with the work of this project at the University of Toledo, wishes to express appreciation to the U. S. Atomic Energy Commission for its continued interest and support.