MASTER

COO-1684-6

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

Technical Progress Report

February 1, 1968 to December 31, 1968

U.S. Atomic Energy Commission

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University of Toledo

TECHNICAL PROGRESS REPORT

February 1, 1968, through December 31, 1968
Jack G. Kay, Principal Investigator

I. Reports

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

COO-1684-3

"The Spectroscopic Observation of Gaseous TiF ", Jack G. Kay and Robert L. Diebner, Abstracts of Papers, PHYS. 80, 156th ACS National Meeting, Atlantic City, September, 1968.

COO-1684-4

"A Re-Investigation of the Catalytic Dehydration of Ethanol on Alumina", Jack G. Kay and W. Ronald Cares, Abstracts of Papers, PHYS. 142, 156th ACS National Meeting, Atlantic City, September, 1968.

COO-1684-5

"Electronic Absorption Spectrum of $^{55}\text{Mn}^{18}\text{O}$ and the Isotope Effect in MnO ", Michael B. Garrett and Jack G. Kay, submitted to Div. of Phys. Chem. for presentation at 157th ACS National Meeting, Minneapolis, April, 1969.

II. Effects of Flash Heating on Alumina

Mr. Cares has devoted another year to this problem. Some of the results were presented in September (COO-1684-4). Considerable time has been lost in getting the Perkin-Elmer, Model 820-IV, gas chromatograph to perform properly. The microcatalytic technique works very well when the equipment functions, however. The previous progress report (COO-1684-2) gives an adequate description of the method used. Mr. Cares is starting to write parts of his Ph.D. thesis and this will constitute a comprehensive report and evaluation of the work done.

At the time of writing this progress report, it has been found that the flash heating pretreatment of γ -alumina has no significant effect on the activation energy for catalytic diethyl ether or ethylene production from ethanol at temperatures below about 260°C. These activation energies now appear to be the same for ethylene as for ether. Above 260°C, the ether production seems less with flash heated catalyst than with normal catalyst. The effect is small. Flash heating pretreatment apparently has no effect on ethylene production.

The advantages of the pulse-injection microcatalytic technique for studying the dehydration of ethanol on alumina have been brought out in these experiments, however. We are able to control the number and type of surface sites by injection of water at low temperatures, heating above 410°C in flowing, dry helium for varying periods of time, and then cooling to the desired reaction temperature. The retention of moisture or surface hydroxyl groups is a function of the highest temperature of equilibration using these techniques. After alcohol injection, certain of the products are retained along with unreacted alcohol. The amounts retained are dependant

upon the reaction temperature and may be easily determined by subsequent displacement using water injections or by thermal desorption at increased temperatures.

Injection of diethyl ether onto the catalyst yields ethanol, water and ethylene and provides additional information regarding back reactions involved in the alcohol dehydration mechanism. Experiments using methylethyl ether have been suggested by W.K. Hall as a means of checking "alkyl group scrambling". These measurements scheduled for January, 1969, will show the possible production of dimethyl ether, diethyl ether, ethanol, methanol, ethylene, and other products from $\text{CH}_3\text{OC}_2\text{H}_5$ and should give additional clues regarding the mechanism.

Beyond observing that activation energies derived from the slopes of Arrhenius type kinetics plots are in the ranges reported for such reactions in the literature, it does not seem valid at this time to base any interpretations on the absolute values obtained. These are generally reproducible, but uncertainties in the duration of reaction times at various temperatures create doubts about the kinetic interpretations. Internal comparisons, such as ether rates with ethylene rates, for example, are considered more reliable, though.

III. Studies of KMnO_4 Crystals

Photoluminescence experiments have been carried out by Mr. Joaquin O. Uy in cooperation with Dr. E.C. Lim at Loyola University (Chicago) and, more recently, at Wayne State University in Detroit. Many measurements have been made using KMnO_4 crystals at liquid nitrogen temperatures. With available equipment, it is possible to observe a particular fluorescence wavelength while

scanning the UV and visible excitation spectrum or to excite monochromatically while scanning the fluorescence spectrum.

The results for solid KMnO_4 have been interesting and have shown apparent fluorescence due to $3100\text{\AA}$ and $2300\text{\AA}$ excitation. G.A. Crosby (private communication) has indicated that he has been unable to observe fluorescence or phosphorescence from aqueous solutions of permanganate. It is too early to discuss our photoluminescence results in detail, but it appears that they may be helpful in sorting out some of the energy states in such crystals. Further interpretation must await measurements on other crystals, either pure or doped with known impurities.

The photoconductivity apparatus has been built and tested. The instrumentation works, but difficulties have arisen with the problem of getting good electrical contact with the small crystals available. Attention will be given to this problem while work continues on other aspects of the potassium permanganate problem.

IV. Flash Heating and Kinetic Spectroscopy

Mr. Robert L. Diebner has completed the first draft of his Ph.D. thesis and is completing the necessary revisions while beginning his active duty in the U.S. Army (Ordnance Branch). A report of this work was presented in September, 1968, (COO-1684-3) and a manuscript is being prepared for publication.

A significant part of this work is that the vibrational analysis for the electronic absorption spectrum of TlF has been completed. No other reports of the electronic spectra of this molecule have been found in the literature. We can report band head measurements with errors less than 0.1 cm^{-1} in the $25,000\text{ cm}^{-1}$ region. The observed multiplet splittings due to the $^4\Pi$ excited state are within the range predicted from the meager data available on other

transition metal diatomic halides. Further detailed studies should be made of the relationship between these splittings and the atomic spin-orbit coupling constants.

Estimates of fundamental vibration frequencies from these spectra are difficult because most of the observed transitions are $\Delta V=0$. Nevertheless, the spectra show a band tentatively identified as a (1,0) transition, and its location provides agreement with the predictions for TiF made in the JANAF Thermochemical Tables.

Mr. Michael B. Garrett has obtained the high resolution spectrum of vaporized MnO using oxygen-18 labeling. To our knowledge, this is the first spectrum to be obtained for this molecule. The vibrational isotope effect observed for light and heavy oxygen in MnO is in agreement with theoretical predictions. Interesting side effects involving rotational perturbation shifts with isotopic substitution are currently being examined.

Additional work has been done by Mr. Garrett in attempts to obtain a satisfactory rotational analysis of the MnO spectra. The excessive width of the rotational lines, probably due to unresolved nuclear hyperfine splitting by manganese, the large number of overlying rotational branches, and the abundance of perturbations have caused insurmountable difficulties thus far.

Mr. Garrett has also re-examined some of the earlier flash heating spectra of lead [Kay, Kuebler and Nelson, *Nature* 194, 671(1962)]. Additional information on energy levels and transitions of atomic lead has been obtained and will be described in Mr. Garrett's thesis.

V. Personnel

During the past year, four graduate students have received training and contributed to the work of this project. Mr. Garrett worked in the laboratories of Dr. Frank Tomkins and was supported by an AMU-ANL Fellowship at Argonne National Laboratories. His fellowship expired November 30, 1968, and he has subsequently received support from this project while continuing to pursue his work full time using Argonne facilities.

Mr. Diebner received support and contributed to the work of this project until November 15, 1968, when he was called to active duty by the Army.

Mr. Cares and Mr. Uy continue working on this project at Toledo.

In addition, two undergraduates, Mr. Michael Long and Mr. Charles Ritz, have received training and have worked as hourly technicians on this project at the University of Toledo. Mr. Long is now a graduate student in chemistry at Wayne State University and Mr. Ritz is making plans to attend graduate school in chemistry next fall, 1969.

Dr. Diefallah was employed for two weeks on this project for the purpose of re-examining some of the osmium hot atom chemistry data previously reported in his thesis. He completed a revision of manuscripts previously written and these are now being readied for publication.