April 10, 1990

FG03-89ER14053

COMBUSTION-RELATED STUDIES USING WEAKLY-BONDED COMPLEXES

Submitted to : U. S. Department of Energy
Division of Basic Energy Sciences
19901 Germantown Rd.
Germantown, MD 20874
Attention: Dr. William Kirchhoff ER-141, G-236
(301) 353-5820

Submitted by: Department of Chemistry
University of Southern California
Los Angeles, CA 90089-0482

Attention: Contracts and Grants Department
(213) 743-7762

Principal Investigator:

Robert A. Beaudet

Robert A. Beaudet
Professor of Chemistry
(213) 743-2997

Approved for the Department:

Otto Schnepf

Otto Schnepf
Chairman
Department of Chemistry
(213) 732-2783

Approved for the University:

Cornelius J. Pings

Cornelius J. Pings
Provost/Vice President for
Academic Affairs
(213) 743-7762

Date: 4/25/90

MASTER

DISTRIBUTION OF THIS DOCUMENT

April 10, 1990

COMBUSTION-RELATED STUDIES USING WEAKLY-BONDED COMPLEXES

This program has two main objectives. The first involves the production and characterization of binary complexes involving molecular oxygen (e.g. O_2 -HCN, O_2 -HF, O_2 -HCl, O_2 -HBr, O_2 -HI and O_2 -hydrocarbons) and the corresponding photoinitiated reactions. While nearly all complexes studied to date have been formed from two or more molecules in $^1\Sigma$ states, these O_2 complexes involve triplet states. The spectra are complicated, since the O_2 moiety is presumed to remain in a triplet state, but the axial symmetry is broken by the other moiety if the cluster is not linear. The second thrust area is the study of a unique set of species involving oxygen atoms and small molecules such as HF, HCl, HBr, HI, HCN and simple hydrocarbons. We will encourage complex formation by producing O atoms close to the nozzle aperture, where numerous collisions occur and the adduct will consist of an $O(^3P)$ atom bound to a small molecule. Third, after some initial trial experiments, we have decided to build a new apparatus with a large 20 cm slit nozzle-high speed vacuum pumping and an order of magnitude higher sensitivity.

After these nine months we are at the following point. We have made initial attempts to make $O(^3P)$ in a jet by the photodissociation of NO_2 , and to cluster it with HCl, and we have decided to construct a new jet expansion apparatus with about 8-10 times more sensitivity than our present apparatus. We have been limited in the hydrogen halide species that we can study at this time by the availability of the tunable IR diodes that the company can fabricate, but the IR spectrum of O_2 -DCl has now been detected and recorded within the last few weeks. The new apparatus has been constructed and is being assembled in the laboratory as of this writing. We will discuss each of these in detail.

CONSTRUCTION OF A NEW PULSED JET VACUUM SYSTEM.

After some initial experiments, it was clear an order of magnitude increase in sensitivity would open up many new vistas for us. Also, there are heavy demands on our existing set-up. After examining what we could do within our space, financial support and time constraints, we decided to build a system with a 20 cm x 150 μ slit. This system requires ten times the pumping speed that we now have with a VHS 10 pump. Since the expansion is not CW but pulsed, the total buffer volume of the system is also important. We decided upon using a Ruvac Roots Pump, Model WA-251 as the roughing system for an Edwards oil vapor booster pump with 4000 liter/sec capacity. The chamber is a 24" x 20" x 20" SS cube with flanges on all sides. Because the booster pump is about 6' tall, the chamber is pumped via a 12" diameter U-tube connected to the

top of the chamber. The chamber arrived from the welder April 9, and is being assembled at this moment. The first design of the slit has been constructed and ready to try. A second tunable diode laser, a Nd-Yag laser, and an excimer laser are available for use on this system. Thus the two systems will be independently operable. This new system has been financed in large part by the University cost sharing funds (~\$33K) associated with this grant and should be in operation within 60 days.. It will be used for the oxygen atom work.

It is probably worth pointing out that a slit with 10 times the length is equivalent to using the smaller slit and time averaging the signal $10^2 = 100$ times as long. So, the larger slit provides a great saving in time. In fact, the thermal drifts of the IR laser, etalons, etc. would prohibit the accumulation of data over such a large time span. With the present laser detection system, we take a spectrum over $0.5\text{-}1.0\text{ cm}^{-1}$ of a single gas pulse in 0.8 milliseconds with S/N of 20-100!

THE IR SPECTRUM OF THE O₂-DCL COMPLEX.

At the present, we are limited in the hydrogen halides that we can use to obtain oxygen clusters by the upper frequency limit of the tunable IR diodes available: the vibrational frequency of HF and HCl are above the range. However, DCl, HBr, and DBr are accessible, but the smaller halides cluster more efficiently, so DCl provides the best probability of making the dimer. Our first attempts to find the complex used low concentrations of oxygen and DCl, similar to what we have used in the past to prepare the CO₂-HX clusters. If we did prepare the desired clusters, the spectra were hidden by the more intense spectra of Ar-DCl, (DCl)₂, etc. which appear to cluster preferentially. To push the equilibrium in the right direction, we have gone to high concentrations of molecular oxygen and replaced argon with helium as the carrier gas to eliminate argon clusters. An optimum mix contained 100 Torr of DCl, 100 psi of oxygen and 300 psi of helium. The 25% concentration of oxygen with the low concentration of DCl encouraged oxygen clusters while minimizing the DCl dimer. A small sample of the spectrum is included. To confirm that this spectrum is due to O₂-DCl, we have removed the DCl or the oxygen from the mixture, one at the time. The absence of any spectrum under these conditions confirms that this spectrum requires both O₂ and DCl. The spectrum does not resemble that of a linear molecule, so we presume it is an asymmetric top. Fine structure due to the spin-spin effects is also observable.

STUDY OF O(³P)-HX COMPLEXES.

Using a Nd-YAG laser with 200 millijoule per pulse we have dissociated NO₂ to form O(³P) in a jet. However, the NO₂ has been so reactive that it reacts with the hydrogen halide, so this reaction has not been very useful. We are also investigating the photolysis of SO₂ at 193 nm.

to produce $O(^3P)$. We also clearly need more sensitivity, thus the construction of a new apparatus described. It is also apparent that we should use LIF to provide the most sensitive early detection of the cluster prior to investigating the species with the tunable diode laser. So we have assembled a second apparatus for carrying out LIF from parts available in Wittig's laboratories. This setup is also now working.

END

DATE

FILMED

3/18/94