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GAS-PHASE OXIDATION OF ALUMINUM ATOMS

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A. Summary

During the course of this grant we have accomplished the following tasks:

1) We have studied the chemiluminescent reaction $Al + O_3 \rightarrow AlO^* + O_2$ and based on an analysis of the observed AlO $B^2\Sigma - X^2\Sigma$ blue green band system we have placed a lower bound on $D_0^0(AlO)$ of 5.13 ± 0.05 eV and have suggested that the actual value of $D_0^0(AlO)$ will be only at most a few tenths of an eV higher.

2) We have developed a new technique for detecting reaction products using laser-induced fluorescence and we have applied this technique to study the ground state BaO molecules formed in the reaction

$$Ba + O_2 \rightarrow BaO + O$$

for which we have deduced an approximate vibrational temperature for the newly formed BaO products.

3) We have designed, constructed, assembled, and tested a new metal oven capable of producing beams of aluminum atoms so that the reaction

$$Al + O_2 \rightarrow AlO + O$$

can be studied under single-collision conditions using laser-induced fluorescence as an AlO detector.

B. Chemiluminescent reactions involving aluminum

In a molecular beam apparatus, a thermal beam of aluminum atoms (≈1700° K) traverses a scattering chamber containing ozone molecules (300° K), and the resultant visible chemiluminescence is recorded with a 1m scanning monochromator. The chemiluminescence spectrum consists of (a) the AlO $B^2\Sigma^+ - X^2\Sigma^+$ blue-green band system for which we have assigned bands to the strongly structured features in the 4200-4900Å spectral region, and (b) a more intense but weakly structured continuum in the region 4500-8500Å which appears to be emission from a polyatomic aluminum oxide, most likely, AlO_2. By identifying that up to the $v'=17$ level of the B state is populated in this reaction, we are able to place a minimum value of 5.13 ± 0.05 eV on the AlO bond energy i.e. the dissociation energy of the AlO ground state molecule. By accepting the upper limit of 5.20 eV deduced by MacDonald and Innes[1] from Tyte's[2] shock tube absorption data, we recommend the value $D_0^0(AlO) = 5.15 \pm 0.05$ eV. This work has been published in the Journal of Chemical Physics.[3]

C. Laser-Induced fluorescence as a molecular beam detector

Traditionally, molecular beam kinetic studies have relied on surface ionizers or electron-impact-ionizer-massfilters to detect the reaction products. However, both these techniques are "blind" to the internal state of excitation of the products. We have developed a new technique that overcomes this blindness by using light in the detection scheme. Here, a tunable dye laser is scanned in wavelength and the fluorescence of the reaction products are detected. Whenever the wavelength of the laser beam coincides with a molecular absorption line, corresponding to a specific (v,J) → (v',J') transition, those molecules in the (v,J) are excited and subsequently fluoresce. By measuring the intensity of the fluorescence signal as a function of laser wavelength, it is possible to deduce the relative (v,J) population distribution from a knowledge of Franck-Condon factors and photomultiplier wavelength response factors.

The first successful demonstration of this new molecular beam detector was the observation and analysis of the BaO ground state (v,J) distribution resulting from the reaction $Ba + O_2 \rightarrow BaO + O$. This work has been reported in the Journal of Chemical Physics.[4] Here it was shown that it was possible to resolve the rotational structure of the BaO bands in a slow scan using a not very narrow (0.5Å) laser bandwidth. The vibrational distribution was found to fit moderately well a Boltzmann distribution of 2500°K, but the rotational distribution seemed much cooler. Subsequent work (not published) has shown that the rotational distribution was collisionally relaxed at the high pressures used in the slow scan and that the rotational distribution is much hotter, approximately comparable to the vibrational temperature. The BaO A state lifetime was also measured. Using a swept narrow sampling window, our first lifetime measurements give a value of 350 ± 50 nsec, in reasonable agreement with Johnson.[5]

D. Unfinished Work and Future Plans

During the second half of this grant period, a major effort has been placed on generating in a reliable and controllable manner aluminum beams of useful fluxes. We have succeeded in accomplishing this by using a boron nitride crucible placed inside a resistance-heated tantalum tube surrounded by tantalum heat shields. This oven is very similar in design to that of Dagdigian, and Wharton.[6] Various crucible materials were tried. Carbon proved to be porous; molybdenum and tantalum form amalgrams. The chalky boron nitride container occasionally fractures but is not chemically attacked at the operating temperature of about 1350° C. The boron nitirde crucible normally lasts about 10 hours. A tapered stopper is used in order that the oven can be refileed between runs.

In addition, a new vacuum chamber has been fabricated for the forthcoming Al + O_2 reaction studies. This chamber has been designed with removable sides to enable easy access to the Al oven and to provide flexibility in the design of future experiments. The chamber is pumped by a 6" diffusion pump. This results in over a factor of ten increase in the differential pumping between the oven chamber and the reaction chamber over that previously obtained. Strong differential pumping ensures that the reaction does not occur within the oven chamber, such as on hot metal surfaces.

The immediate future plans are to investigate the reaction $Al + O_2 \rightarrow AlO + O$. Attention will be directed to 1) the highest v" level populated in the reaction (from which a new estimate of the AlO ground state dissociation energy can be obtained), 2) the vibrational-rotational distribution (which bears on the infrared emission from the species) and 3) the AlO $B^2\Sigma^+$ state radiative lifetime (which also bears on the importance of AlO as an infrared emitter).

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