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Research has been done with pulsed-laser evaporated B, Be and Mg atoms and molecular hydrogen to explore the reactivities of these metals with H2 and to investigate infrared spectra of the product molecules in solid argon. The major products in the B/H2 system were BH, (H2(BH), Bh3, (H2) (BH3) and B2H6. It is clear that molecular hydrogen is complexed to BH and BH3 in these experiments. Pulsed laser ablated boron atoms have been reacted with NH3, CH3NH2 and NO to form novel boron insertion products which have been trapped in solid argon for infrared spectroscopic study. This work makes two important contributions. First, laser ablated boron atoms are shown to be highly reactive. Second, the importance of isotopic substitution for matching experimental observed and theoretical calculated frequencies for new molecules is clearly demonstrated.

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Final Technical Report to the AFOSR

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Boron Atom Matrix Chemistry

June 1, 1993 to October 31, 1996

ACCOMPLISHMENTS

Research has been done with pulsed-laser evaporated B, Be and Mg atoms and molecular hydrogen to explore the reactivities of these metals with H_2 and to investigate infrared spectra of the product molecules in solid argon. The major products in the B/H_2 system were BH, $(H_2)(BH)$, BH_3, $(H_2)(BH_3)$ and B_2H_6. It is clear that molecular hydrogen is complexed to BH and BH_3 in these experiments.

In the case of Be and Mg, the major products were the linear dihydride H-M-H and the monohydride M-H molecules. This work obtained the first experimental evidence for H-Be-H, which is the textbook example of sp hybridized bonding.

Pulsed laser ablated boron atoms have been reacted with NH_3, CH_3NH_2 and NO to form novel boron insertion products which have been trapped in solid argon for infrared spectroscopic study.

The major reaction products of laser-ablated B atoms with NH_3 are iminoborane, H-B≡N-H, formed by B insertion and H elimination, and BNBH, formed by a second B insertion and H elimination. These novel molecules were identified by isotopic substitution and comparison to *ab initio* calculated frequencies.

Reactions of B with CH_3NH_2 give the same HB≡NH and BNBH products and both methyliminoborane isomers $CH_3B{\equiv}NH$ and $HB{\equiv}NCH_3$. The methyliminoborane molecules are isoelectronic with methylacetylene. It appears that B inserts into the C-N and N-H bonds with comparable facility, but there is little evidence for insertion into C-H bonds in these experiments.

The major B atom reaction with NO is insertion to form triplet NBO which is identified from B-O stretching and NBO bending modes at 1996.8 and 493.5 cm^{-1}, respectively, through isotopic substitution and MP2 frequency calculations. Triplet NBO is a high energy density matter candidate. A second B atom adds to give BNBO also identified by 2068.2 and 500.9 cm^{-1} absorptions in the same regions.

Several of these products are highly reactive molecular species that might have possible applications as high energy density materials, in particular, iminoborane, the methyliminoboranes and NBO.

This work makes two important contributions. First, laser ablated boron atoms are shown to be highly reactive. Second, the importance of isotopic substitution for matching experimental observed and theoretical calculated frequencies for new molecules is clearly demonstrated.

PUBLICATIONS

1. T. J. Tague, Jr. and L. Andrews, "Reactions of Beryllium Atoms with Hydrogen. Matrix Infrared Spectra of Novel Product Molecules", *J. Am. Chem. Soc.* **1993**, *115*, 12111.
2. T. J. Tague, Jr. and L. Andrews, "Pulsed Laser Evaporated Magnesium Atom Reactions with Hydrogen: Infrared Spectra of Five Magnesium Hydride Molecules", *J. Phys. Chem.* **1994**, *98*, 8611.
3. T. J. Tague, Jr. and L. Andrews, "Reactions of Pulsed-Laser Evaporated Boron Atoms with Hydrogen. Infrared Spectra of Boron Hydride Intermediate Species in Solid Argon", *J. Am. Chem. Soc.* **1994**, *116*, 4970.
4. L. Andrews and T. J. Tague, Jr., "Reactions of Pulsed-Laser Evaporated Be Atoms with CO_2. Infrared Spectra of OCBeO and COBeO in Solid Argon", *J. Am. Chem. Soc.* **1994**, *116*, 6856.
5. C. A. Thompson, L. Andrews and R. D. Davy, "Reactions of Beryllium Species with N_2: Infrared Spectra and Quantum Chemical Calculations of Beryllium Dinitrogen Complexes in Solid Argon and Nitrogen", *J. Phys. Chem.* **1995**, *99*, 7913.
6. L. Andrews, T. J. Tague, Jr., G. P. Kushto, and R. D. Davy, "Infrared Spectra of Beryllium Carbonyls from Reactions of Beryllium Atoms with Carbon Monoxide in Solid Argon", *Inorg. Chem.* **1995**, *34*, 2952.
7. C. A. Thompson and L. Andrews, "Reactions of B Atoms with NH_3 to Produce HBNH, BNBH, and B_2N," *J. Am. Chem. Soc.* **1995**, *117*, 10125.
8. C. A. Thompson, L. Andrews, J. M. L. Martin, and J. El-Yazal, "Infrared Spectra of Boron Atom−Ammonia Reaction Products in Solid Argon," *J. Phys. Chem.* **1995**, *99*, 13839.

INTERACTIONS

AFOSR High Energy Density Matter Contractors Conference, June 4-7, 1995, Woods Hole.

Gordon Conference on Chemistry and Physics of Matrix Isolated Species, Plymouth, NH, July 30-August 4, 1995. Invited paper, "Reactions of Laser-Ablated Metal Atoms."

AFOSR High Energy Density Matter Contractors Conference, June 5-7, 1996, Boulder, CO. Presented talk "Reactions of Laser-Ablated Boron Atoms with NH_3, CH_3NH_2 and NO to Form Novel Boron Insertion Products."

Second International Conference on Low Temperature Chemistry August 4-9, 1996, Kansas City, MO. Presented invited plenary lecture "Reactions of Pulsed Laser Ablated Metal Atoms With Small Molecules. Matrix Infrared Spectra and Quantum Chemical Calculated Isotopic Frequencies of Novel Product Molecules."

Lester Andrews