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The objective of this grant is the generation and characterization of clusters of new materials of possible technological importance. Our work is currently focused on carbon based clusters and on metal/carbon composite clusters. The metals currently being investigated belong to the first and second row transition series. Progress has been made on both cluster types.

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PROGRESS REPORT

AFOSR Grant 49620-93-1-0134
Cluster Ions
February 15, 1993 to February 14, 1994

I. Abstract

The objective of this grant is the generation and characterization of clusters of new materials of possible technological importance. Our work is currently focused on carbon based clusters and on metal/carbon composite clusters. The metals currently being investigated belong to the first and second row transition series. Progress has been made on both cluster types.

II. Objectives

Characterization of the Structure and Growth Mechanisms of
A. Carbon Based Clusters
B. Metal/Carbon Composite Clusters

III. Progress

A. Carbon Based Clusters

Our work has focused on the growth pattern of carbon clusters. Using our recently developed ion chromatography methods, we've been able to show that carbon first forms linear chains. At about C_{10}, monocyclic rings become favored, and above C_{20}, these monocyclic rings cluster to form bicyclic and higher order planar ring systems. Finally, near C_{30}, the first fullerenes appear. The solution to the puzzling sudden appearance of fullerenes, when no obvious precursors are present at smaller carbon numbers, was answered by collisionally heating and annealing the carbon ring systems. When this was done, these species spontaneously convert to fullerenes, usually losing a small carbon particle to cool the nascent fullerene.

In the next grant year we intend to follow up on these experiments in two ways. We are puzzled by the complete absence of PAH type precursors for the fullerenes, even though theory predicts they are stable above C_{20}. Hence, we have initiated experiments where a small amount of H_2 is added to the He expansion gas in the cluster source. The hydrogen can react with the growing carbon clusters and perhaps induce PAH formation by stabilizing the five and six member ring network. In a second set of experiments, perchlorinated PAH's are subjected to electron impact. The relatively weak C–Cl bond makes Cl_2 an excellent leaving group, leaving behind carbon frameworks with varying amounts of Cl attached, as well as the bare C_n^+ nucleus. We are looking at the change in structure as Cl departs for initial sets in the range $C_{10}Cl_8$ to $C_{24}Cl_{14}$. In both types of experiments initial results look very promising.

B. Metal/Carbon Composites

The recent discovery of the stable M_8C_{12} "met-car" species has created a great amount of interest in metal carbon composite clusters. We are taking a two

pronged approach. In the first instance, we are attempting to follow the growth of small $M_nC_m^-$ clusters. Our initial work has focused on M=Fe for n=1,2,3 and m=3 to 8. Ion chromatography results indicate that for a single Fe atom both linear and planar monocyclic structures are obtained, for n=2 only planar cyclic structures with an Fe–Fe bond in the ring, and for n=3 a single family of 3-dimensional structures occurs. In order to both assign the IC spectra and to understand the bonding in detail, very high level electronic structure calculations are being pursued. One intriguing result is that Fe "charge transfers" to the C_m unit generating clusters with $Fe^+C_m^-$ or $Fe^+C_m^{2-}$ for neutral or negatively charged clusters respectively. Also, in both experiment and theory, the C_m moiety retains an unbroken carbon linkage up through $Fe_3C_8^-$. Eventually M–C_2 units will have to emerge if the current understanding of the structure of M_8C_{12} species as pentagonal iscosahedral species is correct. the tendency of metals to form M^+–C_2^- species may in fact provide the key driving force for such a transformation as clusters grow. This point remains to be proven.

A second thrust is the characterization of met-car species themselves. We have finally succeeded in making an intense beam of $Ti_8C_{12}^+$. Initial analysis of the single IC peak indicates it is indeed a hollow cage with approximately pentagonal icosahedral symmetry. It appears that $Ti_7C_{12}^+$, $Ti_7C_{13}^+$, $Ti_8C_{11}^+$ and $Ti_8C_{13}^+$ are also cages, and details of their structure need to be worked out. In the coming year we hope to push toward larger clusters as these have been proposed to switch to the cubic lattice structure at $Ti_{14}C_{13}$ and larger.

IV. Papers Published or in Press (as of 2/14/94)

1. One- and Two-Dimensional Carbon Clusters: Isomers, Structures and Isomer Abundances, Gert von Helden, Ming-Teh Hsu, Paul R. Kemper and Michael T. Bowers, Materials Research Society, Symposium Proceedings, *Novel Forms of Carbon* **270**, 117 (1992).
2. Isomers of Small Carbon Cluster Anions: Linear Chains with up to 20 Atoms, G. von Helden, P.R. Kemper, N.G. Gotts and M.T. Bowers, *Science* **259**, 1300 (1993).
3. Do Small Fullerenes Exist Only on the Computer? Experimental Results on C20+/– and C24+/–, G. von Helden, M-T. Hsu, N.G. Gotts, P.R. Kemper and M.T. Bowers, *Chem. Phys. Lett.* **204**, 15 (1993).
4. Experimental Evidence for the Formation of Fullerenes by Collisional Heating of Carbon Rings in the Gas Phase, G. von Helden, N.G. Gotts and M.T. Bowers, *Nature* **363**, 60 (1993).
5. Annealing of Carbon Cluster Cations: Rings to Rings and Rings to Fullerenes, G. von Helden, N.G. Gotts and M.T. Bowers, *J. Am. Chem. Soc.* **115**, 4363 (1993).
6. Gas-Phase Ion Chromatography: Transition Metal State Selection and Carbon Cluster Formation, M.T. Bowers, P.R. Kemper, G. von Helden and P.A.M. van Koppen, *Science* **260**, 1446 (1993).
7. Carbon Cluster Cations with up to 84 Atoms: Structures, Formation Mechanism and Reactivity, G. von Helden, M-T. Hsu, N. Gotts and M.T. Bowers, *J. Phys. Chem.* **97**, 8182 (1993).

8. C_7^+ is Cyclic: Experimental Evidence, G. von Helden, N.G. Gotts and M.T. Bowers, *Chem. Phys. Lett.* **212**, 241 (1993).
9. The Lowest Energy Structures of C_7^+, C_7 and C_7^-: An Ab Initio Study, G. von Helden, W.E. Palke and M.T. Bowers, *Chem. Phys. Lett.* **212**, 247 (1993).

V. Personnel Associated with the Project

A. Senior:

Dr. Paul Kemper — Dr. W. E. Palke
Dr. Petra van Koppen
Dr. Nigel Gotts
Dr. Seung-Hoon Lee

B. Junior:

Mr. Gert von Helden
Mr. Ming-Teh Hsu

IV. Papers Presented at Meetings/Universities

A. Invited Lectures

1. Symposium on Fullerenes, National ACS Meeting, Denver, CO, March, 1993
2. Symposium on New Forms of Carbon, Materials Research Society Meeting, San Francisco, CA April, 1993
3. Symposium on Fullerenes, National Electrochemical Society Meeting, Honolulu, HI, May, 1993
4. Symposium on Fullerenes, National Electrochemical Society Meeting, New Orleans, LA, October, 1993

B. Contributed Papers

1. Presented two papers, West Coast Ion Chemistry Conference, Lake Arrowhead, CA, February 1993
2. Presented two posters, Gordon Conference on Structures, Energetics and Dynamics of Gas Phase Ions, Ventura, CA, March 1993
3. Presented three papers, American Society for Mass Spectrometry, San Francisco, CA, June 1993
4. Presented poster, AFOSR Contractors Meeting, Irvine, CA, November 1993

C. Seminars at Universities*

1. University of Wisconsin at Madison, November, 1992
2. University of California at Irvine, November, 1992
3. Westmont College, Montecito, CA, December, 1992
4. University of Warwick, Coventry, U.K., December, 1992
5. University of Sussex, Brighton, U.K., December, 1992
6. University of California at Davis, February, 1993
7. University of Colorado at Boulder, April, 1993
8. University of Nevada at Las Vegas, June, 1993
9. University of Georgia at Athens, October, 1993

* Since termination of prior grant November 15, 1992