1993
PROGRESS REPORT
INCLUDED

CONTRACT NO DE-AI02-93ER14314

DOE/ER/14314--T1

Application for Continuation
to

Division of Chemical Sciences
Office of Basic Energy Sciences

Department of Energy
Washington, DC 20545

INSTITUTION: National Institute of Standards and Technology
Gaithersburg, MD 20899

TITLE: "Competitive Ion Kinetics in Direct Mass Spectrometric Organic
Speciation"

PERIOD OF REQUESTED SUPPORT: December 15, 1993 through 14 December, 1994.

Principal Investigator:

L. Wayne Sieck

L. Wayne Sieck
Chemical Kinetics and Thermodynamics Division

Approved By:

Sharon G. Lias

Sharon G. Lias, Chief
Chemical Kinetics and Thermodynamics Division

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTRACT No. DE-AI02-93ER14314

PROGRESS REPORT

This contract period has been extremely rewarding, and volatile (see below), for DoE-supported projects. The collaborative efforts involving both theoretical and experimental studies with Universities and other facilities have been expanded in order to increase both the scientific input and scope of our in-house program, as well as to provide a more cost effective program. Specifically, the following joint projects are either in progress, or have been completed (off-campus sites as indicated).

(1) Southern Illinois University, Prof. S. Scheiner-Combined experimental-theoretical study of the thermochemistry of protonation, complexation, and hydration of di- and polyfunctional ethers. The theoretical treatments (Scheiner & co-workers) support the NIST experimental findings of size-specific intramolecular ionic bonding in these systems, and the combined results impact both on biological systems (proton wires) and evaporative mass spec analysis (Thermo/Electrospray) of polyfunctional analytes. Manuscript submitted to JACS.

(2) Eastern Illinois University, Prof. C. Deakyne- Essentially the same framework as above. The focus here was to determine whether C or N lone pair electrons were more effective in forming ionic hydrogen bonds. The experimental work was again carried out at NIST. Both cyanides (RCN) and isocyanides were investigated, and were chosen for comparison since little, if any, information exists concerning their respective cationic complexing properties. Various proton-bound association ions were investigated, and the stabilities analyzed both experimentally and theoretically. Manuscript submitted to JACS.

(3) Virginia Commonwealth University-Prof. S. El-Shall- We put the final wrap on a joint thermochemical (NIST) and beam expansion study (VCU) which probed structures and stabilities of methanol clusters incorporating either CH_3CN or $(\text{CH}_3)_3\text{N}$. MeCN and TMA were chosen because of their widely differing proton affinities (PA's) and the fact that they form single H-bonds (i.e., complex intraclusters involving multiple bonding are unlikely). So-called magic numbers corresponding to particularly stable (presumed cyclic) structures for $(\text{MeOH})_n^+$ were found at $n=5$ and $9-10$. Manuscript for JPC in preparation.

(4) University of Maryland-Baltimore County (Prof. J. Liebman) and the Phillips Laboratory Supercomputer Center, Kirtland Air Force Base, NM (A. Fant)- One of the perplexing problems among physical organic chemists has involved the site of protonation of a class of molecules referred to as quinones and, in particular, the symmetric member, para-benzoquinone, $\text{C}_6\text{H}_4(=\text{O})_2$, designated below as PBQ. Possible protonation sites either the 'ring' or carbonyl function. Literature information is absent, even for an estimated PA. We have used diagnostic kinetic techniques to confirm that the protonation of PBQ involves the carbonyl function, as well as determining via variable-temperature equilibria measurements the PA relative to reference bases and the thermochemistry associated with formation of the PBQH^+ monohydrate. The Supercomputer facility (Fant) is in the process of generating very high level calculations of the geometries and energetics of the various possible protonated forms in order to complement the NIST measurements. Unfortunately, the projected PA of PBQ lies within the disputed segment of the PA scale (see below). Final conclusions are therefore dependent upon our resolving this controversy.

(5) Other projects initiated during this reporting period, but put on hold because of higher priority items, include:

(i) Chain mechanism for conversion of ethylene glycol(EG) to acetaldehyde (AA) under high temperature acidic conditions. We have discovered a gas phase protonation-decomposition sequence occurring in EG-H₂O mixtures (essentially automotive antifreeze) which appears to 'catalytically' convert neutral EG to AA via consecutive proton transfer reactions. This effort resulted from an initial survey of the existing thermochemical ionic database for diols, which indicated no literature information concerning PA's, clustering energetics, etc. for this important class of compounds. Selectively-labeled deuterated analogs have been ordered to clarify kinetic schemes, and we expect to pursue the investigation of these high temperature (470-650K) reactions as soon as we clear out unfinished projects.

(ii) Comparison of the ion thermochemistry of trimethylsulfonium (CH₃)₃S⁺ and tert-butyl (CH₃)₃C⁺ cations. HPMS measurements involving the complexation thermochemistry of these two analogs have been completed. Again, final quantitative interpretation of the results awaits resolution of the PA scale problem involving i-C₄H₈, which dictates the heat of formation of (CH₃)₃C⁺. Both of these species are important intermediates in organic synthesis. Yet the thermochemical properties of (CH₃)₃S⁺ are basically unknown, except by inference.

(6) Proton Affinity Problem- A major controversy surfaced in the spring of this year involving the upper gas phase proton affinity scale. Based on their experimental measurements, a highly-regarded group at the University of Waterloo in Ontario, Canada (Prof. T. B. McMahon), which also possesses the only other pulsed HPMS in the world, reported that the PA of i-C₄H₈ should be lowered by approximately 4 kcal/mol. This is the only facility which can "duplicate" the NIST capability at high temperature. On the surface, this report may seem trivial, but the entire upper PA scale, which includes all of the di- and polyfunctional molecules, N, O, and S-containing heterocyclic and acyclic molecules, would be seriously affected if the 'benchmark' value for i-C₄H₈ on which the upper scale is based would be substantially revised. The impact of the suggested change on ion thermochemistry and physical organic chemistry, as well as on in progress and published high level theoretical attempts to account for specific effects associated with ion fragmentation and stabilities would be very confusing, at the least. Several years ago (JACS 113, 4448 (1991)), the DoE-sponsored program generated an interlocking experimental PA ladder extending from C₃H₆ to (CH₃)₃N, a span of 54 kcal/mol, which included the PA of i-C₄H₈ as a standard reference value (independently determined elsewhere by photoionization techniques). An essential subset of this scale has been challenged (JACS, apparently in press) by the group at Waterloo and is, in fact, the basis for their revision. As a result our lab has devoted several months during this reporting period exclusively to the extension and clarification of the thermochemical bridges associated with that section of the scale which is in question. Our results to date support our earlier data within a fraction of a kcal/mol in the disputed region. How we will eventually pursue this in the open literature is still under debate. The timing of this effort is particularly important because the Office of Standard Reference Data (NIST) and our Division (Ion Energetics Data Center) have initiated a major effort to provide an upgraded version of the gas phase PA scale. The original evaluation (J. Phys. Chem. Ref. Data, 13, 695 (1984)) is one of the most widely-cited publications in the physical sciences, and is the basis for a large fraction of the entries in the so-called GIANT Tables (J. Phys. Chem. Ref. Data, 17, Supplement No. 1, 1988), which is widely used by analytical mass spectrometrists to interpret CI and other spectra.

PLANS FOR COMING YEAR

Our immediate primary goal is to complete the experimental measurements required to solidify the upper PA scale. The time frame for this effort is uncertain. Fortunately, most of the laboratory documentation has already been accumulated. No off-campus sites are involved-this is strictly our game. As indicated above, several current projects are on hold until this problem is resolved. We anticipate approximately 1-2 months of instrument time to wrap up this issue.

Particularly important in this context is the fact that we want to begin in-depth investigations of the ion thermochemistry associated with alternative refrigerants (HFC's). These efforts would include experimental evaluation of PA's, acidities, anionic and cationic clustering and association reactions, as well as simulated stratospheric and tropospheric studies focussing on possible destructive mechanisms involving anionic cluster ions typical of these regions. No information exists in any of these areas as of this writing. The same techniques used in standard analytical negative chemical ionization measurements can be used to investigate possible reactive kinetics including dissociative electron attachment, fluoride transfer, etc. The latter projects (destructive modes) are not deviations from our overall DOE-sponsored program. Our feeling is that we have the capability to inspect time-resolved gas phase ion chemistry under essentially any conditions. Why not pursue it? In any event, studies of that particular type would be initiated only after all of the requisite fundamental ionic properties of representative target 'emergent' compounds have been evaluated. We anticipate that a great deal of attention will be directed towards the detection and quantification of HFC's during the coming decade using various MS techniques. We plan to give the investigation of the ionic properties of this class of molecules our highest priority during the coming contract period.

Specifically, we propose the following:

- (1) Complete experimental definition of the subset of interlocking PA's in the disputed region. Clear out unfinished manuscripts dependent upon well-defined PA scale.
- (2) Measure PA's of highest priority HFC's versus reference bases already in the middle PA scale.
- (3) Determine binding energies of HFC's in symmetric proton-bound dimers, hydrates, and other cluster ions via variable-temperature equilibrium studies. Correlate same with dipole moments, PA's, etc, in order to generate predictive schemes.
- (4) Investigate anionic chemistry of same class of compounds, emphasizing destructive ion-molecule reaction kinetics (if any) and clustering thermochemistry.
- (5) Pursue the high temperature studies involving protonated diols and simple carboxylic acids such as acetic acid. Partially deuterium-labeled analogs will be used as diagnostic aids to unravel the complex chemistry associated with these systems.
- (6) Continue the extramural collaborative efforts with other labs. We expect to be particularly involved with the beam expansion group at VCU and the theoretical unit at EIU (Deakne).

Budget removed