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INSTITUTION: National Institute of Standards and Technology
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TITLE: "Competitive Ion Kinetics in Direct Mass Spectrometric Organic
Speciation"

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This contract period has again been extremely rewarding 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 more cost effectiveness.

Proton Affinity Problem

The experimental work on the gas phase proton affinity (PA) scale, discussed in some detail in last year's Progress Report, will be completed within the next few weeks. Basically this effort involves the development of a precise and accurate interlocking ladder of relative PA's derived from the temperature dependence of proton transfer equilibria incorporating a variety of reactant pairs using the technique of pulsed high pressure mass spectrometry (NIST has the only U.S. facility). The PA subset under investigation was expanded from our original list to cover the region between CH_3CHO and $(\text{CH}_3)_2\text{CO}$, which spans a PA range of approximately 12 kcal/mol. More than 300 separate equilibrium measurements have been carried out to date over the temperature range 240-395°C. The thermochemical region under study creates a bridge between the so-called 'upper and lower' PA scales, and includes two primary reference standards, CH_3CHO and $i\text{-C}_4\text{H}_8$, with PA's independently defined elsewhere via photoionization techniques. The impact of this very methodical and time-consuming project is as follows:

(i) It is clear that the entropies of protonation of various classes of simple organic molecules (nitriles, ketones, esters, etc) derived from the experimental data of the group at Waterloo (see attached FY '93 Progress Report, appropriate text highlighted) are in substantial error. This is extremely important because our ΔS° data casts doubt on the validity of their ΔH° (PA) measurements as well, all of which were reported in a widely advertised article (JACS 115, 7839 (1993)) and, if taken at face value, would seriously muddy the water during the current attempt within our Division (ION Energetics Data Center) to completely reevaluate and fine-tune the gas phase PA scale. Their results also disagreed with an earlier major DoE-sponsored study from this laboratory. Our present data defines only a slight compression of our earlier data within the disputed subset, which lies in the critical region of the current PA reassessment, but not nearly at the level suggested by the Waterloo group.

(ii) Our current ΔS and $\Delta G_{600\text{K}}$ data have been used as a reference anchor to assign effective temperatures for the ICR measurements pertinent to the PA evaluation, all of which were taken at a single but undefined temperature and incorporated assumed ΔS values for various reaction pairs in order to generate relative PA's. The ICR values derived in other laboratories comprise the vast majority (thousands of measurements) of the existing database on gas phase basicities.

(iii) In our effort to extend and clarify the existing published data, it is obvious that we will step on a few toes. This will be done as softly as possible within the peer-reviewed literature in order to resolve this controversy. Reliable PA values are the essential ingredient in the assignment of heats of formation of organic cations, which find widespread use by analytical chemists in the interpretation of CI spectra as well as theoreticians while defining structures and stabilities, functional influences, etc.

An in-depth study of the cationic polymerization of isobutene was initiated and completed. The dual nature of the initial and subsequent reactions of the molecular cation with neutral isobutene has remained a mystery to ion chemists, in spite of its industrial importance, since this unusual behavior was first uncovered within our group over twenty years ago. The new NIST results on the temperature dependence of rate constants, branching ratios, parent-daughter relationships, ion structures, etc. are currently being combined with beam expansion and condensed phase results from VCU (ElShall) to provide a comprehensive picture of the polymerization intermediates and mechanisms.

We have also completed the experimental phase of a project involving the thermochemistry of internal bonding in association ions incorporating NH_4^+ and other core ions with diethers and ketones. High-level theoretical treatments of these systems are still in progress (S. Scheiner, SIU). This study addresses multiple hydrogen bonding of ligands surrounding 'small' core ions.

The experimental investigation of the protonation and hydration thermochemistry of parabenzoquinone, discussed in last year's Progress Report, has also been completed. Again, we are awaiting final results of a theoretical analysis by A. Fant (NCI, Frederick, MD, coordinated by J. Liebman, UMBC).

Wrap-up work on the cationic intracluster reactions in CH_3OH , $(\text{CH}_3)_3\text{N}$, and CH_3CN mixtures, as well as isoprene polymerization diagnostics, will also be completed. These are both joint projects in collaboration with S. El-Shall, VCU, who carries out complementary beam expansion/ionization measurements. The focus is on structural stabilities within protonated clusters of hydrogen-bonded systems, and cyclic, non-reactive intermediates generated during ionic chain polymerization in olefins.

The following manuscripts were accepted/published during this reporting period:

"Filling of Solvent Shells about Ions. 3. Isomeric Clusters of $(\text{HCN})_n(\text{NH}_3)_m\text{H}^+$ ", Journal of Molecular Structure, 307, 217 (1994), Deakyne, C.A., Knuth, Dawn M., Speller, C.V., Meot-Ner, M., and Sieck, L.W..

"The Carbon Lone Pair as an Electron Donor. Ionic Hydrogen Bonds in Isocyanides", Meot-Ner, M., Sieck, L.W., Koretke, K.K., and Deakyne, C. A., J. Phys. Chem., November, 1994.

"The Ionic Hydrogen Bond. 5. Polydentate and Solvent-Bridged Structures. Complexing of the Proton and the Hydronium Ion by Polyethers", Meot-Ner, M., Sieck, L.W., Scheiner, S., and Duan, X., JACS, scheduled for August 24, 1994 Issue.

(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.

~~4~~(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

Preliminary diagnostic studies of proton transfer between appropriate donor bases and HFC's indicate that protonation leads to HF elimination from HFCH^+ in most cases under conditions where ΔH and ΔS values for the various reaction pairs should be measured ($T > 200^\circ\text{C}$). Consequently it will not be possible to experimentally generate any quantitative PA's for this class of molecules, which are among the leading candidates for future alternative refrigerants. However, recent measurements here indicate that partially fluorinated ethers (HFOC's), which are also viable industrial candidates for replacement coolants due to similar thermophysical properties, are chemically stable in the protonated form under our measurement conditions in terms of the temperature ranges required for reliable proton transfer data. The opportunity in this case is fairly unique since this is the first class of acyclic molecules for which one can systematically investigate the substitution of F atoms for H atoms on a step-by-step basis; i.e., $\text{CF}_3\text{OCH}_3 \rightarrow \text{CF}_2\text{HOCH}_3 \rightarrow \text{CH}_2\text{FOCH}_3$, or $\text{CF}_3\text{OCF}_3 \rightarrow \text{CF}_2\text{HOCHF}_3$, etc. Most of these are in the synthesis process as of this writing (external suppliers under contract to our Division) since they are not yet commercially available. Stepwise substitution of F for H is expected to affect the overall dipole moment via reduction of the effective electron density at the oxygen site, simultaneously influencing both the anionic and cationic clustering and particle transfer thermochemistry (acidities and PA's).

As we had planned for the HFC's, the following program is anticipated:

- (1) Define PA's of highest priority HFOC's versus reference bases already in the appropriate region of the PA scale.
- (2) Determine binding energies of HFOC's in symmetric proton-bound dimers, hydrates, and other cluster ions via variable-temperature equilibrium studies. Correlate same with dipole moments, PA's, etc. as they become available to generate predictive schemes.
- (3) Investigate anionic chemistry of same class of compounds, focussing on the thermochemistry of association ions of the type $\text{Cl}^- \cdot \text{HFOC}$ and $\text{RCO}_2^- \cdot \text{HFOC}$.

We also intend to 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 SIU (Scheiner).