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TITLE: "Ion Kinetics and Thermodynamics Pertinent to Mass Spectrometric
Organic Speciation".

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PROGRESS REPORT

I. Introduction

Essentially all of the completed/in progress studies during the last contract period have involved the NIST HPMS unit. Three distinct areas of in-house research are recognizable: (i) determinations of binding energies and entropies for association and cluster ions, which is accomplished by measuring the temperature dependence of the appropriate equilibrium, (ii) measurement of the temperature dependence unimolecular and bimolecular rate constants, and (iii) evaluation of PA's, HA's, and IP's via measurement of variable-temperature equilibria of the type $AH^+ + B \rightleftharpoons BH^+ + A$, $A^- + BH \rightleftharpoons AH + B^-$, and $A^+ + B \rightleftharpoons B^+ + A$. Key results from some representative projects are summarized below.

II. ION THERMOCHEMISTRY AND HIGH TEMPERATURE CHEMISTRY

A. Proton Affinity Scale

The major achievement of this past reporting period has been the completion of the experimental reevaluation of the upper proton affinity scale. An interlocking ladder of relative proton affinities for 43 molecules, over a range of 55 kcal/mol, was obtained from the temperature dependence of HPMS proton transfer equilibria. From C_3H_6 (PA = 179.5 kcal/mol) to $i-C_4H_8$ (PA = 195.9 kcal/mol) the results agree essentially quantitatively with tabulated values, but for the upper PA range our values are significantly increased. For example, the present vs. literature PA values are: NH_3 , 208.3 vs. 204.0; CH_3NH_2 , 219.6 vs. 214.1; $t-C_4H_9NH_2$, 229.2 vs. 220.8 kcal/mol (all relative to the reference standard $i-C_4H_8$, PA = 195.9 kcal/mol). The new value for $t-C_4H_9NH_2$ was also confirmed by the association thermochemistry of $t-C_4H_9^+$ with NH_3 ,

and our bridge between $i\text{-C}_4\text{H}_8$ and NH_3 was independently verified by T. McMahon's group at the University of Waterloo (Ontario). Entropies of protonation were generally found to be in reasonable agreement with expected rational symmetry changes.

However, for olefins and aromatics the entropies of protonation were found to be more positive by 3-5 cal/mol K, due to structural effects. These results will require a comprehensive reassessment of the recommended PA values for hundreds of molecules, and in many cases increases of 8-10 kcal/mol will be necessary. These data also impact seriously on the heats of formation of organic fragment cations, as well as a vast segment of neutral thermochemistry. We feel that this study represents one of the most significant breakthroughs in experimental gas phase ion thermochemistry reported in the last 10 years. See Attachment No. 1 to Progress Report.

B. Ionization Energies

1. Charge Transfer Ladders

In order to test the accuracy of ΔH ladders measured with our HPMS unit against independent standards, we constructed a ladder derived from variable-temperature charge transfer equilibria yielding relative ionization energies for aromatic molecules with IP's well-established by photoionization techniques. For the 14 compounds in the ladder, the average agreement of the equilibrium results with spectroscopic IP's was ± 0.6 kcal/mol. Over the entire range from naphthalene to C_6F_6 our experimental scale gave a ΔIP of 39.5 kcal/mol compared with the spectroscopic spread of 40.7 kcal/mol; i.e., a 3% difference. We also evaluated the sources of error in such measurements, and discussed some of the common pitfalls associated with HPMS which we have encountered over the years. These include steady states that appear as equilibria,

isomerization, pyrolysis of ions and neutrals, slow reactions and non-reactive systems, reactions outside the ion source, vapor pressure problems, and mass coincidences. Tests and solutions for these complications were also presented. The results of this analysis were published in a special issue of the Int. J. Mass Spec. Ion Proc. dedicated to Paul Kebarle on the occasion of his 65th birthday.

2. The SF_6 Problem

Recently there was an effort, in other laboratories, to substantially lower the accepted value for the $\text{SF}_5\text{-F}$ bond dissociation energy. Those measurements were based on ion-molecule chemistry using several different methods. Since the thermochemistry and mechanisms associated with bond rupture and ionization in fluorinated molecules are paramount in unraveling and modeling the reaction kinetics associated with decomposition in these systems, we reinvestigated the ion chemistry in order to verify and expand those results. Specifically, both Fourier Transform MS and HPMS were used at NIST to define the IP of SF_5 via electron exchange reactions. An IP of 9.60 ± 0.05 eV was derived from our data, in sharp disagreement with estimates from flowing afterglow measurements (IP = 10.15 eV). In addition, we found no evidence for a F^- transfer equilibrium involving CF_3^+ and SF_6 . This suggested equilibrium had been used by others to interrelate the heats of formation of CF_3^+ and SF_5^+ , and to lower the $\text{SF}_5\text{-F}$ bond dissociation energy. Our results support the recommended bond strength of ~ 4.0 eV, and suggest an energy threshold for SF_5^+ production from SF_6 of 13.6 eV. See Attachment No. 2 to Progress Report.

C. High Temperature Chemistry

1. The $\text{NH}_3/\text{i-C}_4\text{H}_8$ System

Our project involving the PA ladder was actually prompted by our experimental observation in another study that the association thermochemistry in $\text{i-C}_4\text{H}_8/\text{NH}_3$ mixtures consistently indicated a PA for $\text{t-C}_4\text{H}_9\text{NH}_2$ of ~ 229 kcal/mol, approximately 8 kcal/mol above the recommended value. Kinetic analyses also revealed the addition/thermal decomposition reactions $\text{NH}_4^+ + \text{i-C}_4\text{H}_8 + \text{M} \longleftrightarrow \text{t-C}_4\text{H}_9\text{NH}_3^+ + \text{M}$, with an E_a for pyrolysis of $\text{t-C}_4\text{H}_9\text{NH}_3^+$ of 29.1 kcal/mol at the low pressure limit. The addition reaction exhibited a very strong negative temperature coefficient ($T^{-10.8}$). We found that our ΔH° values for association equilibria such as $\text{NH}_4^+ + \text{i-C}_4\text{H}_8 \longleftrightarrow \text{t-C}_4\text{H}_9\text{NH}_3^+$ (-46.5 kcal/mol) prove to be extremely useful for bridging large gaps in PA scales into regions where no absolute standards exist.

2. Structurally Hindered Reactants

The NIST HPMS unit permits evaluation of the temperature dependence of rate constants for simple particle transfer reactions over a very wide accessible range (100-700K). Accurate kinetic data of this type for selected reaction partners is essential for quantifying the various factors influencing the internal dynamics associated with ion-molecule collision complexes. Recent measurements here have detected substantial negative temperature coefficients and low overall reactivities in proton transfer reactions between 2,6-substituted pyridines having bulky alkyl groups adjacent to the basic site. Slow kinetics result in hindered systems because, in a large fraction of the collisions, steric effects prevent close approach of the reactive centers. The experimental observations were reproduced by a RRKM model that allowed several alternative

collision complexes to be rate-determining. These included a series of loose complexes, a locked rotor tight complex that occurs prior to the formation of a hydrogen-bonded complex, and a complex located at the central barrier. The analysis indicated that the rate-limiting transition state shifts from the loose to the tight and central-barrier complexes with increasing temperature, and suggests that at elevated temperatures, above 1000K, ion-molecule reactions will become slow even for unhindered, small reactants.

3. Entropy-Driven Reactions

An intriguing class of reactions are fast endothermic processes that proceed at near unity collision efficiency due to entropy effects. During the current reporting period we carried out an analysis of HPMS-derived data for such reactions for both anionic and cationic systems. The overall finding was that reactions that are endothermic (positive ΔH°) up to 7 kcal/mol can occur at the capture rate when positive entropy changes render ΔG° negative at elevated temperatures.

III. ASSOCIATION AND CLUSTER IONS

As discussed earlier, we have initiated a collaborative effort with staff members at the VCU beam expansion facility. Their capability complements that portion of our in-house program dealing with the thermochemistry of cluster ion formation since predictions concerning cluster stability, blocking in mixed clusters, etc., can be independently verified. Their measurements also provide a direct link between our data and condensed phase ion chemistry.

A. Joint HPMS/Beam Expansion Studies

1. Three-Component Clusters

One recent project probed ionic H-bonds in two or three component mixtures containing water (W), trimethylamine (T), and methanol (M). Cluster distributions in $H^+W_nT_m$ showed magic numbers for $(n,m) = (1,3), (2,4),$ and $(3,5)$ due to completion of solvent shells (by blocking methyl groups in trimethylamine) around a H_3O^+ core ion. Larger clusters showed deviations from the $(n+2)$ rule, suggesting structural changes. In these cases the H_2O core may start to form cyclic structures, making less hydrogens available for bonding to trimethylamine. For example, for clusters containing five or more water molecules, sharp decreases in ion intensities occurred when the cluster incorporated more than five trimethylamine molecules, suggesting the formation of a cyclic water pentamer with an extra labile proton. In the three component clusters, the predominate series was $H^+W_nM_mT_{n+2}$, indicating that the role of methanol is simply to form internal chains which are terminated by trimethylamine. The observed cluster distributions were completely consistent with predictions from thermochemical networks derived by HPMS, even though the differences in stabilities for various cluster combinations were found to be only on the order of a few kcal/mol.

2. Blocking in $CH_3CN/MeOH$ Mixtures

Another study of blocked H-bonding involved binary mixtures of CH_3CN and MeOH. This is a special case in that the hydrogen-bonded network incorporating MeOH only allows the formation of the chain, rather than a three-dimensional network. Furthermore, the components have similar PA's ($\Delta PA = 6$ kcal/mol), providing a particularly sensitive model for the effects of small energy differences on cluster

composition and structure. Some of the HPMS data to be included in an expanded analysis of this system has been presented in an earlier section, and a preliminary assessment has been published (see Attachment No. 3 to Progress Report). The major findings were (i) the cluster distributions showed a predominate sequence with the composition $\text{H}^+(\text{MeOH})_n(\text{CH}_3\text{CN})_2$, corresponding to completion of solvent shells through incorporation of terminal CH_3CN blocking groups, and (ii) even though the ionization processes in the beam studies involved substantial excess energies, the observed cluster distributions were apparently sensitive to thermochemical differences derived from HPMS as low as 1-3 kcal/mol.

3. Methanol

Electron impact ionization of neutral MeOH clusters was found to yield $\text{H}^+(\text{MeOH})_n$, with n in the range 1-17. Formation of $\text{H}^+(\text{H}_2\text{O})(\text{MeOH})_n$ was observed to occur only for $n \geq 6$. In CD_3OH , both $\text{H}^+(\text{CD}_3\text{OH})_n$ and $\text{D}^+(\text{CD}_3\text{OH})_n$ were produced, and the D^+/H^+ ratio showed a strong dependence on cluster size, which is apparently related to neutral boil-off sequences influenced by intracluster ion-molecule reactions. Reduced data for production of $\text{H}^+(\text{H}_2\text{O})(\text{MeOH})_n$ also revealed two distinct size-specific manifolds, confirming earlier MPI results. The profiles also suggest that the ion $\text{H}^+(\text{MeOH})_n$ is particularly stable and corresponds to filling of the first solvent shell around a protonated MeOH molecule. New HPMS thermochemical data were generated for the $\text{H}^+(\text{MeOH})_n$ series. These data show that the limiting attachment energy of MeOH to the large clusters (9 kcal/mol) is very close to the condensation energy of liquid methanol, suggesting that the complex intermolecular forces

characteristic of the bulk liquid phase are also operative in these relatively small aggregates.

B. Miscellaneous Studies

1. Polydentate Hydrogen Bonding

The complexing thermochemistry of the proton and hydronium ions with acrylic and crown ethers was investigated by HPMS. The binding energies were found to increase with decreasing restraints in the ligands, with open (floppy) ethers binding much more effectively than rigid crown ethers having the same number of polar groups due to better optimization of the geometries of the $\text{OH}^+ \cdots \text{O}$ bonds. The results significantly extend the existing database on polydentate hydrogen bonding in structurally complex ions.

2. Intermolecular Forces in Organic Clusters

Another HPMS project involved the thermochemistry of protonated alcohol clusters in the series $(\text{MeOH})_n\text{H}^+$, $n = 2-14$; $(n\text{-PrOH})_n\text{H}^+$, $n = 2-9$; $(n\text{-PeOH})_n\text{H}^+$, $n = 3-6$; as well as $(\text{MeCOOH})_n\text{H}^+$, $n = 2-6$. In small clusters ($n < 5$), the bonding energies, $-\Delta H_{n-1,n}^\circ$, were found to be independent of the alkyl substituents. However, in larger aggregates the limiting attachment energies associated with increasing n varied from 9 to 12 kcal/mol, mirroring the macroscopic condensation energies for the respective neutrals ($-\Delta H_{\text{vap}}^\circ$). The results suggest that small clusters are purely hydrogen bonded, but that a combination of intermolecular forces, including hydrophobic interactions, are significant in the outer shells and are similar to those operative in the condensed phase.

IV. RECENT PUBLICATIONS DESCRIBING DOE-SPONSORED RESEARCH

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El-Shall, M. S., Marks, C., Sieck, L. W., and Meot-Ner, M., "Reactions and thermochemistry of Protonated Methanol Clusters Produced by Electron Impact Ionization", J. Phys. Chem., 96, 2045 (1992).

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Deakyne, C., Meot-Ner, M., Sieck, L. W., and Speller, C. V., "Multicomponent Cluster Ions. 3. The Proton in Ammonia and Hydrogen Cyanide", manuscript in preparation.

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V. ATTACHMENTS TO PROGRESS REPORT

1. Example of a variable-temperature equilibria study yielding relative proton affinities. J. Am. Chem. Soc., 113, 4448 (1991).
2. Example of a project utilizing ion-molecule reaction kinetics to generate thermochemical information. J. Chem. Phys., 93, 8374 (1990).
3. Example of a joint HPMS/beam expansion study. Chem. Phys. Lett., 185, 193 (1991).