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Foreword

Thermochemistry and solvation of gas phase ions

As mass spectrometric techniques became more refined throughout the 1950 and 1960s an increasing number of physical chemistry experiments began to be performed on gas phase ions, which led to a more detailed and more sophisticated understanding of the intrinsic behaviour of these species. It very soon became quite clear that one of the key elements necessary for an in depth interpretation of gas phase ion chemistry was the thermochemistry of these fascinating entities, since the qualitative behaviour observed in the gas phase very frequently did not mimic solution phase behaviour. Among the first experiments to be performed, which gave rise to quantitative thermochemical data, were threshold ionization energy and fragmentation energy measurements. The early work on positive ions in this area using electron impact and, later, photionization methods could be used to derive quantities such as proton affinities, which were the direct gas phase analogues of solution phase basicities. The realization that such data could be obtained and then used subsequently to interpret gas phase ion behaviour led naturally to the desire to elucidate the role of solvent on the modification of this intrinsic ionic behaviour, giving rise frequently to a different solution phase behaviour. The rapidly increasing interest in gas phase ion chemistry was aided by the virtually simultaneous development of three dynamic mass spectrometric techniques capable of providing very precise data for relative thermochemical properties of ions. These techniques were: high pressure mass spectrometry, ion cyclotron resonance spectrometry and the flowing afterglow technique. Each of these techniques proved to be ideally suited to the determination of equilibrium constants for ion–molecule exchange reactions and the HPMS technique was particularly valuable in the examination of ion–molecule association reactions. The equilibrium data obtained permitted accurate enthalpy and, frequently, entropy changes to be determined for these processes and, in this way, very accurate values for a wide variety of thermochemical parameters could be determined. These techniques were later augmented by the very powerful, guided ion beam method for threshold determinations of endothermic processes and by the application of ab initio electronic structure methods to problems in gaseous ion thermochemistry.

The earliest gas phase ion thermochemistry experiments were associated with the determination of accurate relative gas phase acidities and basicities. In this way the apparently anomalous order of solution phase basicities of alkyl amines was resolved. A remarkable result was also the demonstration that in the gas phase *p*-hydroxy benzoic acid deprotonates preferentially from the phenolic site rather than the carboxylic acid site. Such experiments provided true insight into the intrinsic nature of inductive and resonance effects and the ability of solvent to mask intrinsic behaviour. Following the large number of determinations of relative basicities and acidities, efforts were made to obtain continuous scales of proton affinities of both neutral molecules and anions, ranging from the weakest to the strongest affinities and linking all important species of accurately established thermochemistry. The study of solvation of gas phase ions, pioneered by Paul Kebarle in his early high

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pressure mass spectrometric experiments, provided quantitative clues to the role that solvents can play in the modification of intrinsic gas phase character. As a result, solvation is now a fairly well understood phenomenon, at least as it relates to ionic species.

The articles contained in this special issue of the *International Journal of Mass Spectrometry* on Thermochemistry and Solvation of Gas Phase Ions represent a snapshot of the breadth and continued vigor of the ongoing activity in the field. A host of experimental techniques are represented with a diverse array of applications. In the review article contained in this volume on proton affinities, Michael Mautner has very nicely summarized the history of these efforts and the present state of affairs of the gas phase basicity scale. Similarly Peter Armentrout's review of guided ion beam studies of transition metal species contains a wealth of information on these complex and interesting species. The remaining current research articles all represent studies of particular systems and novel techniques for their investigation and interpretation. I would like to thank each of the authors for their contribution to this volume and I look forward to reading an update in ten years time.

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