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Ion–Molecule Reactions: Introduction

Systematic studies of the reactions of positive ions and negative ions with molecules in the gas phase began in the early 1950s, although the occurrence of gas-phase ion reactions had been recognized at the beginning of this century with the detection of some ionic species (e.g., H_3^+, H_3O^+) using the first mass spectrometers. One of the first processes studied, the formation of the nonclassical ion CH_5^+, exemplifies some of the characteristics of this branch of gas-phase reaction kinetics. These are the frequent occurrence of nonclassical species (e.g., those with three-center and bridged bonds) and of open-shell species, attractive forces between reactants, the absence of significant energy barriers, and fast reaction rates, often collisional. Studies of the mechanisms, dynamics, and kinetics of ion–molecule reactions, both experimental and theoretical, run in parallel with similar studies of neutral–neutral reactions, and thus, they form an integral part of gas-phase chemistry.

From the beginning, a typical reaction vessel for studying gas-phase ion reactions was the low-pressure ion source of a mass spectrometer in which ion chemistry occurs under single collision conditions. Mass spectrometers remain the major tool for such studies, but now they are used in association with modern developments in the form of various ion traps, such as ion cyclotron resonance cells, fast-flow tubes, ion beams, and expanding jets, to produce clusters of atoms and molecules. These techniques are used to great effect to further the study of ion reactions, as is clearly demonstrated by the papers included in this thematic issue.

There are many review papers which describe both the various approaches to the study of ion–molecule reactions and the advances made in the understanding of this interesting topic. References to some recent monographs and special journal issues are given at the end of this editorial.

This thematic issue of *Chemical Reviews* concentrates on several topics in gas-phase ion chemistry which are currently receiving a great deal of attention: ion–molecule reactions related to interstellar chemistry, reactions of ion clusters, new topics in organic ion chemistry, and the kinetic energy dependence of the cross sections for some reactions studied using ion beams.

One of the most exciting areas of gas-phase ion chemistry is interstellar chemistry, and so it is properly represented in this thematic issue. As an overview of this field, the review by D. Smith serves as an introduction to the following two articles and describes how the many molecular species that have been detected in interstellar clouds are produced. The article by D. K. Bohme is a more detailed discussion of interstellar and circumstellar "organic" chemistry with an emphasis on the reactions which can lead to the production of polycyclic aromatic hydrocarbons (PAH) and fullerenes in these regions. Recent studies of the process of radiative association are thoroughly treated in the article by D. Gerlich and S. Horning; their experimental data on radiative association reactions, so very needed and yet so difficult to obtain, provide important insights into the processes occurring in the low-pressure, low-temperature environment of interstellar clouds.

During the last decade there has been a remarkable growth of interest in experimental and theoretical work on the properties and the reactivity of atomic and molecular clusters. This thematic issue addresses the subject of the reactions of ionized clusters and of van der Waals molecules in three reviews. A contribution on the preparation, properties and reactivity of metal cluster (B, Al, Ga, and In) and semimetal cluster (C and Si) ions, as investigated using a variety of techniques, is presented by S. L. Anderson and D. C. Parent. Ion–molecule reactions within clusters, studied by novel methods which combine laser spectroscopy, photoionization, and mass spectrometry, are discussed by B. Brutschy. E. Illenberger's article summarizes recent work on electron attachment to neutral clusters and on reactions in homogeneous and heterogeneous van der Waals clusters induced by the attachment of free electrons.

A comprehensive review of the reactions of the atomic oxygen radical anion $O^{\bullet-}$ is presented by J. Lee and J. Grabowski. It deals with the properties and the preparation of this radical, its reactions with a variety of neutral molecules, the identification of reactive intermediates involving $O^{\bullet-}$ in some reaction steps, and, briefly, the condensed-phase reactions of $O^{\bullet-}$. The present knowledge of the exciting topic of the reactions of gaseous distonic radical cations and the mechanisms of these reactions is summarized in the article by K. M. Stirk, L. K. M. Kiminkinen and H. I. Kenttämaa.

The dependence of the cross section on collision energy has been investigated since the very beginning of the studies of ion–molecule reactions. In fact, the cross sections for many ion–molecule reactions are known over the entire "chemical" energy range from thermal (<100 K and some as low as 2 K!) up to some tens of electronvolts, at which the collision energy

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greatly exceeds typical bond energies. Recently, new experimental developments of ion-beam techniques have made possible the study of ion–neutral reactions with high-energy resolution at and near to thermal energies, and some unexpected undulations in the cross sections have been observed. These are addressed by P. Tosi in his paper.

We are grateful to all the authors for their efforts in preparing the reviews and hope that this thematic issue will provide the reader with a useful view of some of the recent work in the field of gas-phase ion–molecule chemistry.

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