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PREVIEW

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STUDIES IN HIGH PRESSURE MASS SPECTROMETRY

The University of Nebraska - Lincoln

Ph.D. 1982

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PREVIEW

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STUDIES IN HIGH PRESSURE

MASS SPECTROMETRY

by

Andreas J. Illies

A DISSERTATION

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Professor Gerhard G. Meisels

Lincoln, Nebraska

December 1982

TITLE

Studies in High Pressure

Mass Spectrometry

BY

Andreas J. Illies

APPROVED

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G. G. Meisels, A. J. Illies, R. S. Stradling and K. R. Jennings, "Time Resolved Measurements in High Pressure Mass Spectrometry: An Analysis of Assumptions," J. Chem. Phys. 68(3), 866 (1978).

A. J. Illies and G. G. Meisels, "High Pressure Chemical Ionization Source with Coaxial Electron Entrance and Ion Extraction Apertures," Anal. Chem. 52, 325 (1980).

C. W. Polley, Jr., A. J. Illies and G. G. Meisels, "Ion Mobilities and Residence Times under Chemical Ionization Conditions," Anal. Chem. 52, 1797 (1980).

A. J. Illies, M. T. Bowers and G. G. Meisels, "Sample Introduction and Pressure Measuring System for Chemical Ionization Mass Spectrometers," Anal. Chem. 53, 1551 (1981).

A. J. Illies, Shuying Liu and M. T. Bowers, "Formation and Structure of $C_2H_4N^+$. Effect of Pressure and Reaction Exothermicity on Collision-Induced Dissociation Spectra," J. Am. Chem. Soc. 103, 5674 (1981).

Publications (continued)

A. J. Illies and G. G. Meisels, "Collision-Induced Dissociation of Ion Association Complexes Outside Chemical Ionization Sources," In Press, J. Phys. Chem.

G. G. Meisels and A. J. Illies, "The Spatial Distribution of Ion Formation in Chemical Ionization Sources and the Ionization Ranges of 100 to 400 eV Electrons in Nitrogen and the Rare Gases," In Press, Anal. Chem.

Matrin F. Jarrold, A. J. Illies and M. T. Bowers, "Mechanism of the Metastable Reaction $H_2S^+ \rightarrow S^+ + H_2$; Product Energy Distributions and their Dependence on Temperature," In Press, Chem. Phys.

A. J. Illies and M. T. Bowers, "High Resolution Translational Energy Spectroscopy: Electronic Transitions in K^+ , I^+ and Vibronic Transitions in N_2^+ ," In Press, Chem. Phys.

A. J. Illies, M. F. Jarrold and M. T. Bowers, "The Fragmentation of Metastable CH_4^+ Ions and Isotopic Analogs: Kinetic Energy Release Distributions and Tunneling Through a Rotational Barrier; Experiment and Theory," In Press, J. Am. Chem. Soc.

Petra A. M. van Koppen, A. J. Illies and M. T. Bowers, "Internal Energy Effects in Collision-Induced Dissociation Spectra," Submitted to Org. Mass. Spectrom.

M. F. Jarrold, A. J. Illies and M. T. Bowers, "The Fragmentation of Metastable NH_3^+ Ions and Isotopic Analogs: An Example of Tunneling Through a Rotational Barrier," Submitted to Chem. Phys. Lett.

A. J. Illies, T. Fujii and G. G. Meisels, "Gas Phase Ionic Equilibria," Submitted to J. Am. Chem. Soc.

A. J. Illies, M. F. Jarrold and M. T. Bowers, "Structure of Gaseous COH^+ , COH_2^+ and COH_3^+ Ions," In Progress.

STUDIES IN HIGH PRESSURE

MASS SPECTROMETRY

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University of Nebraska, 1982

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High pressure mass spectrometry has been used to study various phenomena involving gaseous ions. A major portion of this work dealt with the design and development of a new hybrid drift tube-ion source. It employs coaxial geometry between the electron entrance aperture and the direction of ion drift and uses two field shaping rings to produce parallel equipotential lines throughout the ion drift region. Ion residence time distributions determined for this source are in good agreement with calculated residence time distributions; thus the source can be used to measure ion mobilities. The temperature of this ion source can be varied from 160-470 K. The well-defined electric fields in the ion source along with the temperature variability make this source particularly suitable for the study of ion-molecule equilibria and ion-molecule association reactions. The coaxial geometry also allows the determination of the initial spatial distribution of ion formation inside the ion source as a

function of the ionizing electron energy; it is obtained by correlating the residence times of the ions with their point of formation. Integrating the spatial distribution to the point within which a given fraction of the ionization has occurred yields the "ionization range" R_i which is similar to the range measured by electron penetration through absorbers.

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CHAPTER 1

INTRODUCTION

Mass spectrometry has been used since the early 1950's to study the kinetics and mechanisms of ion-molecule reactions occurring in the ion source.¹⁻⁴ In the mid-1960's mass spectrometers were modified by providing increased pumping speeds at the ion source housing as well as differential pumping between the ion source housing and the analyzer, thus permitting ion source pressures of ca. 1 torr.⁵⁻⁹ When ion source pressures are increased in this manner, the primary ions formed by electron impact undergo reactions with the neutral molecules in the ion source. Study of these reactions as a function of ion source residence times and neutral gas pressures yields ion mobilities, and ion-molecule reaction rate and equilibrium constants. Considerable effort has been expended by many research groups in the study of these fundamental aspects of ion chemistry in the gas phase.⁹⁻¹⁴

An outgrowth of high pressure mass spectrometry (HPMS) is chemical ionization mass spectrometry (CIMS) which was first described by Munson and Field in 1966⁶ and has since developed into a very powerful analytical technique.¹³⁻¹⁵ In CIMS, the sample molecules ($\leq 0.1\%$) are ionized by chemical reaction with reagent ions which are