

Chemical Reaction
Dynamics of the
Liquid/Vapor Interface
Studied by Mass
Spectrometry

Thesis by
Daniel A. Thomas

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Daniel A. Thomas
ORCID: 0000-0001-9415-5991

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ABSTRACT

This thesis presents investigations of chemical reactions occurring at the liquid/vapor interface studied using novel sampling methodologies coupled with detection by mass spectrometry. Chapters 2 and 3 utilize the recently developed technique of field-induced droplet ionization mass spectrometry (FIDI-MS), in which the application of a strong electric field to a pendant microliter droplet results in the ejection of highly charged progeny droplets from the liquid surface. In Chapter 2, this method is employed to study the base-catalyzed dissociation of a surfactant molecule at the liquid/vapor interface upon uptake of ammonia from the gas phase. This process is observed to occur without significant modulation of the bulk solution pH, suggesting a transient increase in surface pH following the uptake of gaseous NH_3 . Chapter 3 presents real-time studies of the oxidation of the model tropospheric organic compound glycolaldehyde by photodissociation of iron (III) oxalate complexes. The oxidation products of glycolaldehyde formed in this process are identified, and experiments in a deoxygenated environment identify the role of oxygen in the oxidation pathway and in the regeneration of iron (III) following photo-initiated reduction. Chapter 4 explores alternative methods for the study of heterogeneous reaction processes by mass spectrometric sampling from liquid surfaces. Bursting bubble ionization (BBI) and interfacial sampling with an acoustic transducer (ISAT) generate nanoliter droplets from a liquid surface that can be sampled via the atmospheric pressure interface of a mass spectrometer. Experiments on the oxidation of oleic acid by ozone using ISAT are also presented. Chapters 5 and 6 detail mechanistic studies and applications of free-radical-initiated peptide sequencing (FRIPS), a technique employing gas-phase free radical chemistry to the sequencing of peptides and proteins by mass spectrometry. Chapter 5 presents experimental and theoretical studies on the anomalous mechanism of dissociation observed in the presence of serine and threonine residues in peptides. Chapter 6 demonstrates the combination of FRIPS with ion mobility-mass spectrometry (IM-MS) for the separation of isomeric peptides.

PUBLISHED CONTENT AND CONTRIBUTIONS

Chapters 1 and 4 are based in large part on the publication:

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NOMENCLATURE

FIDI. Field-induced droplet ionization

MS. Mass spectrometry; typically combined with other nomenclature (e.g., FIDI-MS, ISAT-MS, BBI-MS, ROMIAC-MS, etc.)

HV. High voltage

HDB. Hexadecyl betaine (2-(hexadecyloxy)-N,N,N-trimethyl-2-oxoethan-1-aminium chloride)

ESI. Electrospray ionization

SSI. Sonic spray ionization

SOA. Secondary organic aerosol

BBI. Bursting bubble ionization

ISAT. Interfacial sampling with an acoustic transducer

PZT. Piezoelectric transducer

VSG. Vibrational sum frequency generation

HPLC. High-performance liquid chromatography

FRIPS. Free-radical-initiated peptide sequencing

TEMPO. 2,2,6,6-tetramethylpiperidine-1-oxyl free radical

BDE. Bond dissociation energy

IMS, IM-MS. Ion mobility spectrometry, ion mobility-mass spectrometry

ROMIAC. Radial opposed migration ion and aerosol classifier