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UMI
GAS-PHASE REACTIVITY OF NUCLEOPHILES WITH CARBONYL GROUPS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By
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*****

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ABSTRACT

A variable temperature flowing afterglow (VTFA) has been designed, constructed and implemented for the study of ion-molecule reactions. Benefits of this design are the ability to control the relative energy of the reactants and to accommodate a selected ion flow tube (SIFT) in a linear fashion. The rate coefficients of previously reported positive and negative ion-molecule reactions were determined for calibration purposes and are presented.

The reactions of carboxylic acid derivatives with a variety of anionic nucleophiles \( (\text{H}_2\text{N}^-, \text{HO}^-, \text{CH}_3\text{O}^-, \text{NCCH}_2^-, \text{F}^-, \text{CH}_3\text{C}(=\text{O})\text{CH}_2^-, \text{CH}_3\text{S}^- \text{ and } \text{O}_2\text{NCH}_2^-) \) have been extended beyond previous studies. For example, the reactions of anionic nucleophiles with formyl and acetyl esters have been studied extensively. The reactions that are observed in the gas phase are more varied than those seen in the condensed phase. Thus, the reactions seen in the gas phase show the intrinsic reactivity of these compounds instead of the reactions that are dominated by the solvent. The properties of the leaving group, the incoming nucleophile, and the importance of steric bulk of the carbonyl group have been investigated.
The product branching ratios and reaction rates have been determined for these and other reactions of carboxylic acid derivatives. For example, the reaction rate of NCCH$_2^-$ + HCO$_2$CH$_2$CH$_3$ has been found to be $(1.3 \pm 0.2) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ and the only product is HC(O$^-$)=CHCN which results from nucleophilic acyl substitution (BAC2) followed by a proton transfer within the ion-molecule complex. Other reaction mechanisms that have been observed include _-elimination (E2), bimolecular nucleophilic substitution at the alkyl group (BAL2), and the Riveros reaction (elimination of CO).

The observed experimental pathways have also been investigated computationally, via determination of the potential energy surface, for F$^-$ + HCO$_2$CH$_3$ at the B3LYP/6-31+G(d) level. Most notably, the two channels (BAL2 and Riveros) that were determined computationally are also observed experimentally. Furthermore, the Riveros pathway proceeds via nucleophilic attack on the carbonyl group (formally the BAC2 pathway) but leads to the decarbonylation products, F$^-$(CH$_3$OH) and CO. Reaction rates and product distributions for other reactions of carboxylic acid derivatives are reported as well.
To
my father, Norman,
my mother, Edith,
and my loving wife, Trishy
I would like to extend a sincere appreciation to my adviser, Dr. Christopher M. Hadad. He offered guidance and assistance with both my research and my coursework at The Ohio State University. More importantly, he and his family gave their friendships to me, a gift I will always cherish. I would also like to thank Dr. George McBane for his professional and personal guidance.

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# TABLE OF CONTENTS

ABSTRACT ......................................................................................................................... ii

DEDICATION ................................................................................................................... iv

ACKNOWLEDGMENTS ................................................................................................. v

VITA .................................................................................................................................. vii

LIST OF TABLES ............................................................................................................. xi

LIST OF FIGURES .......................................................................................................... xii

LIST OF SCHEMES ....................................................................................................... xiv

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. INTRODUCTION TO CARBONYL GROUPS</td>
<td>!</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Background on Experimental Techniques</td>
<td>5</td>
</tr>
<tr>
<td>Previous Work</td>
<td>6</td>
</tr>
<tr>
<td>Proposed Work</td>
<td>7</td>
</tr>
<tr>
<td>References</td>
<td>9</td>
</tr>
<tr>
<td>2. DESIGN OF OUR VARIABLE TEMPERATURE FLOWING AFTERGLOW</td>
<td>11</td>
</tr>
<tr>
<td>Introduction</td>
<td>11</td>
</tr>
<tr>
<td>Flowing Afterglow (FA) Design</td>
<td>12</td>
</tr>
<tr>
<td>FA Flow Tube</td>
<td>16</td>
</tr>
<tr>
<td>Electron Impact (El) Ionization Region</td>
<td>17</td>
</tr>
<tr>
<td>Ion Generation</td>
<td>19</td>
</tr>
<tr>
<td>Reaction Region</td>
<td>20</td>
</tr>
<tr>
<td>Temperature Control</td>
<td>24</td>
</tr>
<tr>
<td>Pumping</td>
<td>27</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Kinetic Determination</td>
<td>28</td>
</tr>
<tr>
<td>Determination of Rate Coefficients</td>
<td>31</td>
</tr>
<tr>
<td>Conclusions</td>
<td>43</td>
</tr>
<tr>
<td>Methods</td>
<td>45</td>
</tr>
<tr>
<td>Formation of Positive Ions</td>
<td>45</td>
</tr>
<tr>
<td>Formation of Negative Ions</td>
<td>45</td>
</tr>
<tr>
<td>Neutral Reagents Used</td>
<td>45</td>
</tr>
<tr>
<td>List of References</td>
<td>47</td>
</tr>
<tr>
<td>3. GAS PHASE NUCLEOPHILIC REACTIONS OF SOME ACYCLIC AND CYCLIC ESTERS</td>
<td>51</td>
</tr>
<tr>
<td>Introduction</td>
<td>51</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>55</td>
</tr>
<tr>
<td>Computational Methods</td>
<td>57</td>
</tr>
<tr>
<td>Results</td>
<td>58</td>
</tr>
<tr>
<td>General Trends</td>
<td>58</td>
</tr>
<tr>
<td>Reactions of Methyl Formate</td>
<td>65</td>
</tr>
<tr>
<td>Reactions of Ethyl Formate</td>
<td>73</td>
</tr>
<tr>
<td>Reactions with Methyl Acetate</td>
<td>75</td>
</tr>
<tr>
<td>Reactions of Ethyl Acetate</td>
<td>76</td>
</tr>
<tr>
<td>Reactions of β- and γ-lactones</td>
<td>77</td>
</tr>
<tr>
<td>Conclusions</td>
<td>80</td>
</tr>
<tr>
<td>List of References</td>
<td>82</td>
</tr>
<tr>
<td>4. COMPARISON OF NUCLEOPHILIC ACYL SUBSTITUTION (Bac₂) VERSUS REACTIONS AT THE ALKYL GROUP (Bal₂ AND/OR E₂) IN METHYL AND ETHYL ESTERS</td>
<td>87</td>
</tr>
<tr>
<td>Introduction</td>
<td>87</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>88</td>
</tr>
<tr>
<td>Results</td>
<td>90</td>
</tr>
<tr>
<td>Conclusions</td>
<td>95</td>
</tr>
<tr>
<td>List of References</td>
<td>96</td>
</tr>
<tr>
<td>5. REACTIONS OF OTHER CARBOXYLIC ACID DERIVATIVES</td>
<td>99</td>
</tr>
<tr>
<td>Introduction</td>
<td>99</td>
</tr>
<tr>
<td>Experimental Methods</td>
<td>100</td>
</tr>
<tr>
<td>Results</td>
<td>102</td>
</tr>
<tr>
<td>Reactions of N,N-Dimethylformamide</td>
<td>102</td>
</tr>
<tr>
<td>Reactions of Carboxylic Acid Chlorides</td>
<td>106</td>
</tr>
<tr>
<td>Reactions with (2',2',2'-Trifluoroethyl) 2,2,2-Trifluoroacetate</td>
<td>107</td>
</tr>
<tr>
<td>Reactions of Trifluoroacetyl Thioesters</td>
<td>108</td>
</tr>
<tr>
<td>Reactions of α-Chloro Acetyl Esters</td>
<td>109</td>
</tr>
</tbody>
</table>
LIST OF TABLES

2.1 Variable Temperature and Pressure Rate Coefficients for Positive Ion Reactions .............................................................................................................32

2.2 Variable Temperature and Pressure Rate Coefficients for Negative Ion Reactions .............................................................................................................37

2.3 Rate Coefficients of HO- with Diethyl Ether as a Function of Ionizer Conditions at 0.5 torr and 298K.................................................................41

2.4 Negative Ion Reactions with Methyl Formate and 2,2,2-Trifluoroacetyl Chloride at 0.5 torr ....................................................................................42

3.1 Rates and Ionic Product Distributions for Negative Ion Reactions with Methyl Formate............................................................................................59

3.2 Rates and Ionic Product Distributions for Negative Ion Reactions with Ethyl Formate.............................................................................................61

3.3 Rates and Ionic Product Distributions for Negative Ion Reactions with Methyl Acetate............................................................................................62

3.4 Rates and Ionic Product Distributions for Negative Ion Reactions with Ethyl acetate.............................................................................................63

3.5 Variable Temperature Studies at 0.5 torr .............................................................................................................69

3.6 Rates and Ionic Product Distributions for Negative Ion Reactions with lactones ....................................................................................................79

4.1 Use of H\textsuperscript{18}O\textsuperscript{-} and H\textsubscript{2}N\textsuperscript{-} as Probes into Reactivity of Esters at the Carbonyl Versus the Alkyl Substituent at 0.5 torr and 298K ........................................91

5.1 Reactions of Carboxylic Acid Derivatives with Various Nucleophiles ..........103
LIST OF FIGURES

1.1 Theoretical Potential Energy Surfaces in the Gas Phase and in Solution .............. 3

2.1 Schematic diagram of the Variable Temperature Flowing Afterglow-Selected Ion Flow Tube with a Neutral Flow Reactor ..................................................... 13

2.2 Assembly drawing of the Flowing Afterglow flow tube ........................................ 14

2.3 Assembly drawing of the five-way cross .................................................................. 15

2.4 Assembly view of our electron impact (El) source .................................................... 18

2.5 Assembly view of the kinetic inlets ........................................................................... 22

2.6 Solenoid system for flowing neutral reagents into the kinetic inlets ..................... 23

2.7 Flow tube with dimensions .................................................................................... 25

2.8 Ion intensity data for the reaction of N₂⁻ with O₂ at various temperatures for the addition of O₂ at different locations along the flow tube ...................... 33

2.9 A typical spectrum for the reaction of N₂⁻ with CH₃OH at 298K ......................... 35

2.10 Ion intensity data for the reaction of CH₃O⁻ with HC(=O)N(CH₃)₂ at various temperatures and multiple locations along the flow tube ..................... 38

2.11 Rate coefficients of the reaction of HO⁻ and (CH₃CH₂)₂O at various temperatures and pressures ................................................................. 39

3.1 Schematic diagram of the Variable Temperature Flowing Afterglow-Selected Ion Flow Tube with a Neutral Flow Reactor ..................................................... 56

3.2 A typical spectrum (0.5 torr and 298K) for the reaction of H₂N⁻ with methyl formate ................................................................................................................. 64
3.3 Correlation of the Riveros product yields for the formyl esters and the proton transfer yields for the acetyl esters for the different nucleophiles according to their gas phase acidity .................................................................66

3.4 A typical spectrum for the reaction of F⁻ with HCO₂CH₃ at 0.5 torr and 298 K........................................................................................................................................70

3.5 Potential energy surfaces for F⁻ and HCO₂CH₃ at B3LYP/6-31+G* .........................72

5.1 Products of HO⁻ + HC(=O)N(CH₃)₂ as a function of inlet ........................................105
LIST OF SCHEMES

3.1 Observed reaction pathways for esters in the gas phase ........................................54

4.1 The gas-phase reactions that have been observed and their possible mechanistic routes .................................................................................................................89
CHAPTER 1

INTRODUCTION TO CARBONYL GROUPS

Introduction

The carbonyl (C=O) group is a fundamental group in organic chemistry, and there have been many books written on its reactions. These studies were necessary because of the important role that carbonyl groups, particularly the carboxylic acid derivatives, play in biological systems. Therefore, carbonyl groups have been well examined in aqueous solution. The role of solvent is not well understood, and gas phase studies offer the ability to examine the intrinsic reactivity of carbonyl derivatives. With the recent advances in mass spectrometry, there has been an increase in the number of gas-phase studies of carbonyl compounds. Yet, despite the added interest there has been no exhaustive study of the reactivity of carboxylic acid derivatives.

The reactivity that is observed in solution, in most cases, can be described as addition-elimination chemistry, better known as nucleophilic acyl substitution or the $\text{Bac}_2$ mechanistic pathway. These reactions have a formal tetrahedral intermediate in the mechanism.

\[
\begin{align*}
R\backslash C\backslash Y & \xrightarrow{X^-} \quad X\backslash C\backslash Y \\
& \longrightarrow \quad R\backslash C\backslash X + Y^-
\end{align*}
\]
Also, the product distribution does change from the gas phase to the condensed (aqueous) phase. Previous workers\textsuperscript{3,4,5,6,7} have observed the following pathways: proton transfer/abstraction with or without fragmentation (PT, a), nucleophilic acyl substitution (B\textsubscript{Ac}2, b), SN2 displacements (B\textsubscript{Al}2, c), and decarbonylations (d).

\[
\begin{align*}
\text{CH}_3\text{C-X} + \text{Y}^- & \rightarrow \text{YH} + \text{CH}_2\text{C-X} \rightarrow \text{CH}_2\text{C}=\text{O} + \text{X}^- \quad \text{(a)} \\
& \rightarrow \text{CH}_3\text{C-Y} + \text{X}^- \quad \text{(b)} \\
& \rightarrow \text{X-Y} + \text{CH}_3\text{C}^- \quad \text{(c)} \\
& \rightarrow \text{CH}_3\text{Y} + \text{CO} + \text{X}^- \quad \text{(d)}
\end{align*}
\]

However, Brauman and coworkers have observed the reaction of \textsuperscript{37}\text{Cl}^\text{-} with CF\textsubscript{3}C(=O)\textsuperscript{35}\text{Cl} in the gas phase, and the authors have determined that this reaction has two equivalent ion-dipole complexes and that the tetrahedral intermediate may be, in fact, a transition state.\textsuperscript{5} This suggests that the gas-phase reaction proceeds via direct displacement at the carbonyl carbon, unlike its condensed-phase counterpart. In particular, the shape of potential energy surfaces for the gas-phase and the condensed-phase reactions are quite different. Further studies are needed to understand the differences.
Moreover, gas-phase reactions of carbonyl compounds have shown much more diversity. Reactions at the alkyl group of esters (BAL2) have been observed and are competitive with the reaction at the acyl carbon.\textsuperscript{6,7} Besides reactions at the alkyl group of esters, decarbonylation (loss of CO) reactions, commonly called the Riveros reaction, also occur during nucleophilic reactions with formyl esters.\textsuperscript{6} The increase in diversity of the observed gas-phase chemistry is not a function of the carbonyl group, but instead the aqueous studies are dominated by solvent interactions with the anion and the neutral reagent.

Figure 1.1. Theoretical Potential Energy Surfaces in the Gas Phase and in Solution
Nevertheless, the role of the solvent is not well understood. Therefore, a systematic study has been undertaken to study the role of the solvent in reactions involving carbonyl groups. The reactions of $X^-(\text{Solvent})_n$ with $RC(=O)Y$ will be studied. The place to start such a systematic study is to investigate the chemical system where $n = 0$. The reactions of the "naked" anion must be understood before adding even one solvent molecule. The focus of this dissertation is, therefore, the study of the non-solvated reactions.

Why the reactions are so diverse in the gas phase is perhaps the first question. Does the strength of the nucleophile dictate the reactions that are observed, or is the reactivity controlled by the leaving group? Riveros\(^5\) has reported that $\beta$-elimination can occur with ethyl esters but not with methyl esters in the gas phase; therefore, the possible reactions may be dictated by the leaving group. But, does the leaving group ability play a role in the amount of the $\text{Bac}_2$ mechanism that the carboxylic acid derivative undergoes? The extent of reaction at the acyl group may probe the electrophilicity of the carbonyl carbon.

Probing the issue of nucleophile strength vs leaving group ability is best studied by systematically changing the nucleophile and also changing the leaving group. Nucleophiles that can easily be generated in the gas phase include, but are not limited to, $H_2N^-$, $HO^-$, $\text{CH}_3O^-$, $\text{NCCH}_2^-$, $F^-$, and $\text{O}_2\text{NCH}_2^-$. The leaving groups that can be studied are halides ($F^-$, $Cl^-$, and $Br^-$), alkoxide ions ($\text{CH}_3\text{O}^-$, $\text{CH}_3\text{CH}_2\text{O}^-$, $\text{CF}_3\text{O}^-$, $\text{CF}_3\text{CH}_2\text{O}^-$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$, $CH_3\text{CHO}^-$, etc.), alkyl thiolate ions ($\text{CH}_3\text{S}^-$, $\text{CH}_3\text{CH}_2\text{S}^-$, $\text{CF}_3\text{S}^-$, $\text{CF}_3\text{CH}_2\text{S}^-$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}^-$, $CH_3\text{CH}_2\text{CHO}^-$, etc.), amide ions ($(\text{CH}_3)_2N^-$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}^-$, $(\text{CH}_3)_2\text{CHS}^-$, etc.).
(CH₃CH₂)₂N⁻, (CH₃CH₂CH₂)₂N⁻, (CF₃)₂N⁻, etc.), and carboxylate ions. Mixed anhydrides may show the relative reactivity of the two different carbonyl groups.

**Background on Experimental Techniques**

Mass spectrometry lends itself readily to the study of gas-phase ion-neutral reactions. There are four main types of mass spectrometry that could be used: ion cyclotron resonance (ICR), sector mass spectrometry, high pressure mass spectrometry (HPMS), and the flowing afterglow (FA).

Modem ion cyclotron resonance or Fourier transform mass spectrometry (FTMS) is a method by which ions are detected based on their mass-to-charge ratio (m/z). Each unique m/z value produces a unique cyclotron orbiting frequency within a uniform magnetic field. This method allows for very high mass resolution. Thereby, CO⁺ and N₂⁺, which have the same nominal mass-to-charge ratio of 28, can be easily discerned in the ICR. However, to achieve such high resolution, the chamber must function under a high vacuum (10⁻⁶ to 10⁻⁸ torr), even when ion-neutral reactions are being studied. Therefore, excess energy in the ions are not quickly dissipated and may allow "hot" reactions to occur. Recent advances in this area have decreased the likelihood for this complication from "hot" ions. Furthermore, the ion density must also be finite and small as space-charge problems may occur.

In order to alleviate these concerns, mass spectrometers have been designed which allow reactions to be studied at higher pressures (10⁻³ to 10² torr). At higher pressures, the ion and neutral reagent can be equilibrated to the system's internal energy through collisions with a bath gas. Both the HPMS and FA techniques have this aspect in
common. However, the largest drawback to these techniques is that the instruments are not commercially available, as is the ICR. This may also be one of the greatest advantages to these techniques, as well. Each instrument can be fabricated with specific features for the reactions to be studied in mind. The advantages, design, fabrication, implementation and calibration of our home-built FA are discussed in detail in Chapter 2.

When studying a reaction using a mass spectrometer, only the ionic products are observed. However, besides knowing the mass-to-charge ratio of the ion, the structure of the ion can be investigated. The ion may undergo subsequent reactions further downstream so as to probe the structure. These ions can also be fragmented via collision induced dissociation (CID)\textsuperscript{11} which is also called collisionally activated dissociation (CAD). The daughter ions are then observed and the structure of the parent ion is further defined.

**Previous work**

Brauman has studied the reactions of carbonyl groups in an ICR.\textsuperscript{5b,c} The focus of the study was on the reaction of $X^- + RC(=O)Y$ where $X = F, \text{ Cl, CH}_3O, \text{ CN, and SH}$ with $Y = \text{ Br}^-$ and $\text{ Cl}^-$. For these systems $R = \text{ CH}_3, \text{ CH}_3\text{CH}_2, (\text{CH}_3)_2\text{CH}, (\text{CH}_3)_2\text{C}$, phenyl, and $\text{ CF}_3$ were examined. A general trend of the nucleophilicity was determined: $\text{CH}_3\text{O} > F > \text{ CN} \sim \text{ SH} > \text{ Cl}$. This trend follows the relative gas-phase basicity of the corresponding ions.

DePuy and coworkers have studied the reactions of formyl derivatives using both the FTMS and FA techniques.\textsuperscript{7} Riveros has probed the decarbonylation and proton transfer pathways of formyl and acetyl derivatives with $\text{ F}^-$ and $\text{ HO}^-$ ions.\textsuperscript{6}
Computationally, the reactivity of the carbonyl group has been investigated. Lee and coworkers have reported that the reactivity of the reaction can be inferred based on the exothermicity of the reaction. But, most of the computational studies to date have focused on the stabilizing factors of carbonyl groups and not on their reactivity. For instance, Hadad, Rablen and Wiberg have studied the factors which stabilize carbonyl (C=O) compounds and their thiono (C=S) analogs. Furthermore, most of the reactions involving nucleophiles and carboxylic acid derivatives exhibit single-well to multiple-well potential energy surfaces. Calculations by Jorgensen support the existence of a tetrahedral intermediate, unlike the experimental results of Brauman, but different carbonyl groups were investigated.

Proposed Work

Therefore, our goal is to design, fabricate, and implement a variable temperature flowing afterglow (VTFA) in order to study the reactions of carbonyl groups. First, the instrument will be tested against previously published results in order to determine if the instrument functions properly. This calibration will be followed by the use of the VTFA to probe the reactions of carbonyl groups at room temperature and also at elevated temperatures. Hopefully, new mechanisms will be seen or the yield of products obtained from one pathway versus another will change. Furthermore, the temperature dependence of these reactions can be determined, and Arrhenius plots can be examined.

The focus of these studies will involve the reactions of esters. Their simplicity and availability make them ideal candidates. The esters will be compared to lactones, their cyclic analogs, where appropriate. Work with other carboxylic acid derivatives will also be undertaken. This will help to further elucidate the role of the leaving group.
The design of the instrument will also contribute for the long-term goal to study the effect of micro-solvation. Therefore, the instrument will accommodate the addition of a selected ion flow tube (SIFT) which can be used for the "clean" generation of cluster ions in the FA, such as $F^-(H_2O)_2$. Furthermore, the instrument will attempt to adapt to the other interests of the research group, including the study of radical-neutral reactions via subsequent chemical ionization (CI) or single electron transfer (SET).

The design and fabrication of our VTFA and its applications to carbonyl reactions will now follow.
LIST OF REFERENCES


CHAPTER 2

DESIGN OF OUR VARIABLE TEMPERATURE FLOWING AFTERGLOW

Introduction

Gas phase ion chemistry has become important in the latter half of this century, and the use of mass spectrometry has been very important to the understanding of these reactions. The variety of mass spectrometric techniques include, but are not limited to, the Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICRMS or FTMS), the Time-of-Flight Mass Spectrometer (TOF-MS), the High Pressure Mass Spectrometer (HPMS), the Selected Ion Flow Tube (SIFT), and the Flowing Afterglow (FA). Flow techniques, like the FA, have been used to study a wide variety of chemical reactions. Atmospheric chemistry, inorganic and organic negative ion chemistry, and general positive ion chemistry have been surveyed. Each of these methods has grown in their versatility and popularity, especially due to the improvements in ionization sources, such as electrospray ionization and matrix assisted laser desorption ionization.

The FA was first described by Ferguson, Fehsenfeld, and Schmeltekopf in the 1960's. The reactions in a FA are carried out in a moderate pressure (~0.5 torr) of a bath gas, typically helium, nitrogen, or argon. The moderate pressure allows for the ions to be thermalized, preventing any 'hot' reactions. Another advantage is the ability to generate
Flowing Afterglow (FA) Design

During the design of our FA, the main considerations that were taken into account were the following:

(1) Generation of reactant ions that are thermally equilibrated with the bath gas;
(2) Construction of reagent inlets for product and kinetic studies;
(3) Ability to vary the temperature of the reactions;
(4) Efficient pumping of the reaction and detection regions; and
(5) Incorporation of a SIFT and a NFR.

A schematic of the VTFA-SIFT-NFR is shown in Figure 2.1.
Figure 2.1. Schematic diagram of the Variable Temperature Flowing Afterglow-Selected Ion Flow Tube with a Neutral Flow Reactor.
Figure 2.2. Assembly drawing of the Flowing Afterglow flow tube: (A) cut away of bottom view, and (B) side view of final assembly.
Figure 2.3. Assembly drawing of five-way cross: (A) the fit of the EDM and thermocouple attachment, and (B) the location of various ports at and near the five-way cross.
**FA Flow Tube** Special care was taken with the fabrication of the entire flow tube (Figure 2.2) and particularly with the five way cross (Figure 2.3), in order to ensure a smooth and consistent inner surface. The material for the flow tube and the five-way cross was a single stainless steel tube (3.25 in. o.d. x 0.25 in. wall). Prior to machining any of the final pieces, the entire tube was machined for a uniform outer surface and honed for a constant inner surface. The resulting inner diameter of the tube was 2.786 in., and the outer diameter was 3.25 in.

In order to facilitate the five-way cross for housing the electron impact (EI) source and the addition of neutral reagents, the stainless steel tube was cut by electric discharge machining (EDM), in order to create a tight fit for the cross and a smooth inner surface. The five-way cross, when assembled, appeared seamless on the inner and outer surfaces. The three ports on the five-way cross, when measured from the center of the cross, are 5.50 in. long, while the center of the cross is 38.50 in. from the detection end of the flow tube. Each of the three ports on the five-way cross terminate in NW80 flanges. The downstream end of the flow tube terminates with a plate that is welded to the flow tube and the outer vacuum jacket (see below); the upstream end terminates in a custom flange. The entire length of the flow tube is 41.325 in.

The flow tube has ports for the addition of neutral reagents 11.00 in. downstream of center of the five-way cross. These inlets are made from 0.25 in. stainless steel tubes that are directly welded to the flow tube. These ports are isolated from the flow tube by on/off valves (Parker: 4BW-DP4K-SS) and the flow of neutral reagents into these ports are regulated by metering valves (Parker: 2F-H4L-V-SS-KS and 4Z(A)-NSL-V-SS-KS). The port for the NFR is located 8.00 in. downstream of the center of the five-way cross. The NFR port was constructed from a stainless steel tube (2.00 in. x 0.125 in. wall). This port terminates in a NW50 flange and mates to a gate valve (MDC: KGV-2000V) which can be
used to isolate the NFR from the ion flow tube. The actual reaction region (for monitoring kinetics) of the flow tube has additional inlets and will be discussed in further detail below.

**Electron Impact (EI) Ionization Region** The electron impact (EI) ionization source, mounted on the flow tube at the five-way cross, has several advantages over other similar ionization sources. These advantages include, but are not limited to, the ability to produce a wide variety of ions steadily, efficiently and with great abundance. The reactions, described here, have been carried out using two similar EI sources. Our improved EI source is described.

To obtain useful kinetic information, the most important function of the EI source is to create and maintain a steady ion signal. For this purpose, the design of the EI ionization source (Figure 2.4) includes (a) three filament posts, (b) a sink post, (c) a sink plate, (d) an optional repeller plate, (e) an ionizer can, (f) the helium port, and (g) two filaments. All are mounted on a NW80 flange that attaches to the five-way cross.

We have used both thoriated iridium and rhenium filaments, and the latter is currently in use. The rhenium ribbon (H. Cross Company: 0.003 in. x 0.030 in.) is ~1 in. long and is bent in the middle to increase its effective surface area. The filaments are connected to the filament posts via compression between two nuts that are screwed onto each of the posts. The stainless steel filament posts make contact to feedthroughs (Ceramaseal: 9411020) via a tight-fit compression. There are three filament posts that connect two filaments in a V-shape design, where the central filament post attaches to both filaments and can function as the 'common wire'. Thus, either of the filaments (or both simultaneously) can be used.

The central filament post was also designed to hold an optional repeller plate. The addition of a repeller plate was intended to increase the ion signal from electron impact, but
Figure 2.4. Assembly view of our electron impact (EI) source.
it also increased the average energy of the generated ions. As we will discuss later, these ions could not be efficiently cooled prior to the kinetic region of the FA. The results of these calibrative studies will be discussed later. Currently, our EI source does not include the repeller plate.

The filaments and posts are housed inside the ionizer can, which is made of Teflon® to electrically isolate the sink plate (for current regulation) which is mounted on the top of the can. Another feedthrough, exterior to the ionizer can, is used as the sink post. This feedthrough is connected to the sink plate via a 12-gauge, multi-stranded, teflon-coated wire. The sink plate is made from perforated stainless steel (Small Parts: R-PMX-062-A, 41% open) which permits the helium bath gas and electrons to pass through and returns a voltage to the filament power supply (Spectrum Solutions: FPS-1) for effective emission current regulation. The FPS-1 regulates the EI source and has a 0.1 to 5.0 mA dynamic range for the emission current.

**Ion Generation** A flange, mounted on the five-way cross, has multiple connections for liquid and gaseous reagents. This NW80 flange has two inlets to the flow tube, and each line has an on/off valve (Parker: 4BW-DP4K-SS) from which three independent gas and/or liquid ports branch. All of the gas ports terminate in 0.25 in. VCO fittings, while all of the liquid ports have 0.25 in. Ultra-Torr® connections. (This is affectionately called the ‘tree’.) The flow rate of the liquids and gases are controlled by multiple metering valves (Parker: 2F-H#L-V-SS-KS; 2F-H1A-V-SS-KS); the smaller the number (#), the more restrictive the flow. Currently H1, H5, and H6 valves are currently in use, and the on/off valves can isolate the ‘tree’ from the flow tube. The neutral reagents, that enter at the ‘tree’, can react with the electron plasma that is generated at the EI source. Currently, the EI source is mounted in a perpendicular orientation relative to the ‘tree’.
The plasma is generated as the helium or other bath gas passes over the EI filament. Helium metastables (He\textsuperscript{m}) and ions (He\textsuperscript{+}) are formed.\textsuperscript{5} Electrons are also present in the ion plasma as they are ejected in the formation of He\textsuperscript{+}. As these species escape from the ionizer region, they can mix with the added neutral reagents and thereby create ions of interest. Some typical methods for the formation of common ions\textsuperscript{5} are:

\[
\begin{align*}
N_2O + e^- & \rightarrow N_2 + O^- + CH_4 \rightarrow CH_3^+ + HO^- \\
NF_3 + e^- & \rightarrow NF_2^+ + F^- \\
NH_3 + e^- & \rightarrow H^+ + NH_2^- 
\end{align*}
\]

These and other 'primary' ions can react with other reagents to produce 'secondary' ions. For instance, methanol will transfer a proton to hydroxide ion producing water and methoxide ion. Many ions can be produced via these secondary reactions. Therefore, the ion plasma includes neutral species as well as positive and negative ions.

After the reactant ions are generated in the EI source region, they collide with the helium bath gas and the ions are thermally equilibrated. Under typical operating conditions (0.5 torr and 230 SLPM helium flow rate resulting in a helium flow velocity of \sim 9500 cm/sec), the ions collide with helium approximately 1100 times per centimeter. Sufficient distance (time) has been allotted for the ions to be thermalized prior to entering the kinetic region of the flow tube as there are 38.1 cm (15 in.) between the center of the cross and the first kinetic inlet.

**Reaction Region** Some designs of an FA, with or without temperature variability, rely on a movable inlet for addition of reagents along the length of the flow tube. With the anticipated addition of a SIFT, we relied on a fixed inlet approach as pioneered by Bierbaum, DePuy, Grawbowski and coworkers.\textsuperscript{17,18} Therefore, the reaction
region of the flow tube consists of seven reagent inlets that are equally spaced (3.00 in. apart), and the closest inlet to the detection region is 5.00 in. away.

In order to determine absolute rate coefficients, it is critically important to establish and maintain laminar flow along the length of the flow tube. For this reason, these seven inlets were designed differently than the other reagent inlets of our FA. The kinetic inlets have channels (0.169 in. deep x 0.385 in. wide), as seen in Figure 2.5, which have been created by excavating some of the material from the ~0.23 in. wall thickness of the flow tube. The exterior surface of the flow tube was recreated by a stainless steel band (0.50 in. wide x 0.063 in. thick) which includes a stainless steel tube (0.25 in. o.d. x 0.049 in. wall) in order to allow the reagent into the channel. This band was welded into place to produce a smooth exterior surface and a 0.169 in. interior channel. The channel has 17 equally spaced (every 20°) points of entry into the flow tube. The 0.25 in. stainless steel tube on the band was placed in the middle of the 40° which does not have an entry point, so that the neutral reagent can enter the flow tube in a uniform manner through all 17 holes. The actual holes were made with a #79 drill bit (0.014 in. diameter). After fabrication, flowing water was used to verify that all 17 holes, for each of the seven inlets, were clear of obstructions.

The addition of neutral reagents to the gas flow is controlled via individual on/off solenoid valves (Snap-Tite: 203X-96) which are exterior to the flow tube (Figure 2.6). These solenoid valves are normally closed unless electrically activated, and they are controlled with a home-built actuator under either manual or computer control. Additional valves (Parker: 4Z(A)-PR4-VT-SS) are used to isolate inlets 1 and 2, from 3 and 4, and from 5, 6 and 7 (inlet 1 is the most upstream inlet). The flow rate of neutral reagents into the reaction region of the flow tube is controlled by various metering valves (Swagelok:
Figure 2.5. Assembly view of the kinetic inlets: (A) side view of the flow tube with the excavated wall, with and without the band, and (B) axial view of the 17 holes per inlet.
Figure 2.6. Solenoid system for flowing neutral reagents into the kinetic inlets.
SS-22RF4; Parker: 4A-NSL-V-SS-KS, 4A-NML-V-SS-KS, depending on the desired flow rate) upstream of the solenoid valves. The determination of the flow rate (i.e. the concentration of the neutral compound in the flow tube) will be discussed later in the calculation of absolute rate coefficients.

A pressure port was added in the middle of inlets 3 and 4. This port is made from a 0.25 in. stainless steel tube that is welded exterior to the tube. The hole that is generated is tapered down within the wall of the flow tube until a 0.125 in. hole penetrates the inner flow tube. The pressure is interpreted by a relative pressure capacitance manometer (MKS: 120AD00001, 1 torr limit).

**Temperature Control** The temperature of the buffer gas and the wall of the flow tube is controlled by flowing a heat transfer fluid that is pumped by a circulating bath. Some special considerations were made in the design of the flow tube in order to provide variable temperature control. Of particular concern, we did not want to affect the smooth inner surface of the flow tube while providing a means of heating or cooling the flow tube. In order to accommodate this goal, we chose to electroplate the exterior surface with a layer of copper and to insulate the flow tube with a vacuum jacket.

After construction of the reagent inlets and the five-way cross, the flow tube was electroplated with three metal layers (nickel, copper and tin). The electroplated surface covers the entire exterior of the flow tube and 0.25 in. of the side arms and ports (Figure 2.7). The flow tube was plated with a 0.0005 in. thick nickel layer first, due to nickel’s affinity for stainless steel. The nickel was then covered by a copper layer (0.003 in. thick), which provides excellent thermal conductivity. Finally, the copper layer was covered by a layer (0.0005 in. thick) of tin (60/40 lead/tin solder). An 80 ft. copper tube (0.25 in. o.d. x 0.035 wall) was wrapped around the flow tube (~0.25 in. spacing between concentric wraps) and then soldered to the underlying copper layer with the use of additional 60/40 lead/tin solder. This low-temperature soldering method guaranteed that the inner surface of
Figure 2.7. Flow tube with dimensions. The hatched area has been electroplated with 0.0005 in. of nickel, 0.003 in. of copper, and 0.0005 in. of tin/lead solder.
the flow tube would remain smooth and would not be warped. However as a result, our instrument has an upper temperature limit of about 260°C (the melting point of the solder), but there is no lower limit.

The copper tube is connected to a circulating bath (PolyScience: 9501) in order to flow a heat transfer fluid (DowTherm Q) for temperature control. The heat transfer fluid travels from the detection chamber end of the flow tube towards the ionization region. This counter-current flow, relative to the direction of the bath gas, should provide the most stable and well-defined temperature for the reaction region of the flow tube. The temperature of the flow tube's wall can be monitored via two thermocouples (Omega: Type T, copper-constantan) which were screwed to the exterior of the inner flow tube prior to the electroplating procedure. The thermocouples are located on the bottom face of the flow tube at the NFR port (8 in. from the center of the cross) and the pressure port (23.5 in. from the center of the cross). The bath gas passes through a 40 ft. copper coil (0.25 in. o.d. x 0.035 wall) submerged in the circulating bath prior to entering the EI source. The thermocouples on the flow tube are used to ensure that thermal equilibrium has been attained along the length of the flow tube, and the temperature of the circulating bath is used for the temperature of the buffer gas. The pre-equilibrated buffer gas should not possess a significant temperature gradient along the flow tube as the walls of the flow tube are heated or cooled by the heat transfer fluid from the same circulating bath. The copper tube, carrying the heat transfer fluid, has been designed to accommodate thermal expansion and contraction by including a stainless steel 'kink' (Figure 2.2).

As we anticipated the addition of a SIFT, the vacuum jacket was designed unlike previous designs. Currently, many vacuum jackets are designed to be a large all-encompassing box. Hence, the vacuum jacket for our VTFA was fabricated from a stainless steel pipe (6 in. schd. 10) that was welded to plates at the upstream and downstream ends of the flow tube. The space between the flow tube and the vacuum jacket
is pumped by a 1 in. diffusion pump (Edwards: E50/60). Typically, the pressure is lower
than $1 \times 10^{-3}$ torr, thereby preventing moisture from condensing on the copper coils during
low-temperature studies.

The wrapped inner flow tube was first insulated with Aluminized Mylar® and then
enclosed in a vacuum jacket. The vacuum jacket extends the length of the flow tube. All
ports penetrate from the inner flow tube and through the outer vacuum jacket. Because the
flow tube temperature will be variable but the vacuum jacket will remain near room
temperature, special precautions were made to allow for some differential thermal
expansion. The stainless steel vacuum jacket includes two bellows which are used to
compensate for differences in thermal expansion. For each of the 0.25 in. reagent inlets
further precautions were taken: extensions (1.00 in. long x 0.75 in. diameter) were
attached to the exterior of the vacuum jacket (Figure 2.2) and the 0.25 in. tubes for the
reagent inlets then protrude through these extensions; therefore, this detail lengthened the
distance between the inner and outer weld joints.

**Pumping** The pumping considerations are very important in a flow system. The
flow tube is kept at moderate pressures (typically 0.5 torr), while the quadrupole and
electron multiplier (EM) require lower pressures ($\leq 10^{-5}$ torr) for operation. Most of the
buffer gas is pumped away by a 1600 cfm roots pump (Stokes: 1721S) through a port
connected to the chamber made from a stainless steel tube (6 in. o.d. x 0.25 in. wall). This
port has a manual 6 in. to 8 in. gate valve (MDC: LGV-6000V-SP) mounted on it. The ion
lenses, quadrupole and EM are separated from the flow tube’s gas load by a nosecone
skimmer which holds a molybdenum plate with a 0.05 cm opening. The molybdenum
plate, nosecone skimmer and the detection chamber are all electrically isolated from one
another via Vespel™ insulators. The region behind the nosecone is pumped by two 6 in.
diffusion pumps (Edwards: Diffstak 160/700M), and they are backed by a single 20 cfm
rotary-vane pump (Stokes: V013-2). The chamber that holds the ion lenses, quadrupole and EM is very similar to that described by Grabowski,\textsuperscript{18} except that our chamber is pumped by two 6 in. diffusion pumps and is constructed from a single 10 in. stainless steel tube. The latter aspect allows our first 6 in. diffusion pump to reside directly under the lens region and thereby provides more efficient pumping.

The pumping line from the FA to the roots pump is made from aluminum pipe (8 in. schd. 40), and there are two 25 in. long, thick-wall, stainless steel bellows (HPS: 93-0260) attached to the gate valves (MDC: LGV-6000V-SP, LGV-8000V) on either end. The use of an 8 in. schd. 40 aluminum pipe allows for very efficient pumping during use.

The detection chamber houses a quadrupole with 0.625 in. rods from Extrel with a 750 amu mass range with unit mass resolution. All of the quadrupole hardware and optics are controlled by Merlin\textsuperscript{®} (Extrel). The Merlin\textsuperscript{®} system provides the voltages (±100 V) that are applied to the ion lenses of our home-built optics. The ions that pass through the quadrupole are collected by an electron multiplier (EM) (Detector Technology: 402A-H) and then amplified (Advanced Research: MTS-100). Finally, the signal intensity is recorded by Merlin\textsuperscript{®} as the quadrupole scans across the chosen mass range.

**Kinetic Determination** A detailed discussion of flow tube kinetics has been described elsewhere,\textsuperscript{18} and some specific information for our FA will now be presented. In determining the kinetics for reactions in our FA, the reactions are run under pseudo first-order conditions. In order to have pseudo-first order conditions, the concentration of the neutral reagent should be at least $10^2$ times greater than the ion concentration. The ion concentration and profile in the flow stream can be approximated.\textsuperscript{19}

The concentration of the ion is taken as the integrated peak area as recorded by Merlin\textsuperscript{®}. Because the quadrupole has unit mass resolution, the peak area is defined as the
position of the center of the peak ±0.5 amu. The concentration of the neutral reagent is calculated from the neutral flow rate ($v_{\text{neutral}}$), which is determined by equation 1, where the average time ($t_{\text{ave}}$, sec) is measured for changing the pressure ($\Delta P$, torr) of a calibrated volume ($V$, cc) by a known amount and at a known temperature ($T_{\text{room}}$, K).

$$v_{\text{neutral}} = \frac{[\Delta P \times V \times 0.3594]}{[t_{\text{ave}} \times (T_{\text{room}})]} \quad (1)$$

The neutral reagent flows through a metering valve, as mentioned earlier, into a vacuum rack. The volume of each side of our vacuum rack was determined with distilled water in triplicate measurements. The calibrated volumes of each side of our vacuum rack were then checked against the other via transfers of helium gas from one line into the other side where ideal gas behavior was assumed for the calculation. The pressure of the vacuum rack is measured by a capacitance pressure manometer (MKS: 120AD00010, 10 torr limit) during operation. The pressure in the vacuum rack is referenced to the pressure in the quadrupole chamber ($\leq 1 \times 10^{-5}$ torr). As these measurements are made, the temperature of the room is taken by a typical thermometer. The time required for filling the calibrated volume is measured using a stopwatch, and this aspect, as well as obtaining constant flow rates, are the major sources of our statistical error.

The concentration of the neutral reagent ($C_{\text{neutral}}$, particles/cc) in the flow tube depends upon the flow rate of the neutral reagent as well as the radius of the flow tube ($r_{FA}$, cm), the pressure in the flow tube ($P_{FA}$, torr), the temperature of the reaction ($T_{rxn}$, K) and the helium flow rate ($v_{He}$, SLPM). The calculation of the neutral reagent's concentration is shown in equation 2.
The helium flow rate \( (v_{He}, \text{ SLPM}) \) is calculated using the slope and intercept from the mass flow controller (MKS (Tylan General): FC261-4VCO), which was calibrated using a wet test meter (GCA Precision: 63126) and the pressure in the flow tube. The instantaneous rate of the reaction at a given inlet position is calculated using equation 3, where the concentration of the ion \( (C_{ion}, \text{ particles/cc}) \) is the integrated peak area for an ion at the inlet with a given distance \( (d_{inlet}, \text{ cm}) \). The rate coefficient is the linear least-squares regression of these instantaneous rates of reaction.

As previously mentioned, the reaction temperature is determined by the temperature of the pre-equilibrated buffer gas in the circulating bath. The average energy in the system is equal to the buffer gas' energy. This is ensured through collisions between the buffer gas and all of the other species. The number of collisions per centimeter \( (\text{coll/cm}) \) that the ion undergoes is calculated from the concentration of helium gas \( (C_{He}) \) and the velocity of the ion \( (v_{ion}) \), as seen in equation 4. The concentration of helium gas is calculated
Determination of rate coefficients

The absolute rates of some previously studied reactions have been determined using our system in order to detect any systematic errors. For example, variable temperature rate coefficients have been determined for some positive ion reactions (Table 2.1).

For instance, in the literature, the charge transfer reaction of \( \text{N}_2^+ + \text{O}_2 \) has been well studied due to its importance in ionospheric chemistry.\(^{13,20,21,22}\) The rate of this reaction has been determined many times and has ranged\(^{22,23}\) from \((0.50 \pm 0.08)\) to \(2.0 \times 10^{-10} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}\). Our value of \((0.96 \pm 0.04) \times 10^{-10} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}\) falls within this range but is higher than the 'accepted' value. Dunkin, et al.\(^{13}\) reported a temperature dependence of \(T^{(-0.6)}\), while McFarland, et al.\(^{21}\) reported a temperature dependence of \(T^{(-0.8 \pm 0.2)}\) for temperatures \(\leq 3560\text{K}\). Our temperature dependence for this reaction is \(T^{(-1.0 \pm 0.2)}\), and even though the absolute temperature dependence is not reproduced, our value is within the previously reported experimental values (Table 2.1). Our raw data for this reaction at the various temperatures are shown in Figure 2.8. We also note a small positive pressure dependence for this reaction.
Table 2.1. Variable Temperature and Pressure Rate Coefficients for Positive Ion Reactions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Neutral</th>
<th>P (torr)</th>
<th>T (K)</th>
<th>Rate*</th>
<th>Pub. Rate*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{i}\textsuperscript{+}</td>
<td>O\textsubscript{3}</td>
<td>0.4</td>
<td>298</td>
<td>1.0 ± 0.2</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>273</td>
<td>1.1 ± 0.1</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>298</td>
<td>0.96 ± 0.04</td>
<td>0.5 ± 0.08</td>
<td>20</td>
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<td></td>
<td></td>
<td>323</td>
<td>0.7 ± 0.07</td>
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<td></td>
<td></td>
<td>348</td>
<td>0.7 ± 0.04</td>
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<td></td>
<td>373</td>
<td>0.6 ± 0.1</td>
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<td></td>
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<td>423</td>
<td>0.56 ± 0.05</td>
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<tr>
<td>N\textsubscript{i}\textsuperscript{+}</td>
<td>O\textsubscript{3}</td>
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<td>1.5 ± 0.1</td>
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<td>CH\textsubscript{2}OH</td>
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<td>17. ± 4.</td>
<td>14. ± 4.</td>
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<td>16.3 ± 0.3</td>
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<td>17.7 ± 0.3</td>
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<tr>
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<td>7. ± 1.</td>
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<td>9. ± 1.</td>
<td>11. ± 2.</td>
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<td>9.4 ± 0.3</td>
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<tr>
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<td>CS\textsubscript{2}</td>
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<td>298</td>
<td>9. ± 2.</td>
<td>12. ± 2.</td>
<td>20</td>
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<td>14. ± 2.</td>
<td>21. ± 6.</td>
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<tr>
<td>N\textsubscript{i}\textsuperscript{+}</td>
<td>CO\textsubscript{2}</td>
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<td>298</td>
<td>8. ± 1.</td>
<td>8. ± 2.</td>
<td>20</td>
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<tr>
<td>CO\textsubscript{2}\textsuperscript{+}</td>
<td>O\textsubscript{3}</td>
<td>0.5</td>
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<td>0.57 ± 0.02</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>373</td>
<td>0.61 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>398</td>
<td>0.62 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>423</td>
<td>0.63 ± 0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Rates are given in units of \((10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})\) and the reported errors are one standard deviation of at least triplicate measurements.
Figure 2.8. Ion intensity data for the reaction of N$_2^+$ with O$_2$ at various temperatures for the addition of O$_2$ at different locations along the flow tube.
Furthermore, we have investigated other $N_2^+$ reactions for which rate coefficients have been studied at room temperature. Our rate coefficients at 298K for $N_2^+$ with a variety of neutral reagents are in reasonable agreement with previous studies (Table 2.1). We have also determined the temperature dependencies for $N_2^+ + CH_3OH$ and $N_2^+ + CH_4$.

The reaction of $N_2^+$ with methanol was found to be temperature independent \[(1.7 \pm 0.1) \times 10^{-9} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}\], while the reaction with methane has a positive temperature dependence \[T^{(2.0 \pm 0.2)}\] between the temperatures of 323 and 423K. We also studied the reaction of $N_2^+$ with methanol at 273K, but the intensity profile was indicative of possible condensation of methanol in our inlet system.

The rates of $N_2^+$ with $CS_2$ and $CO_2$ are in excellent agreement with literature values, but the rate of $N_2^+$ with $CH_3CN$ is slower than the reported value\[^{23}\] which has a large error bar. The products of all of these reactions agree with the reported data. These $N_2^+$ reactions proceed via charge transfer except for the reactions with carbon disulfide, methanol, acetonitrile and methane. These reactions cause fragmentation after the charge transfer and lead to the formation of $S^+$ and $CS_2^+$ (from carbon disulfide), $CH_3^+$, $CH_2OH^+$, $CH_3OH^+$ and the secondary ion $CH_3OH_2^+$ (from methanol), $CHCN^+$, $CH_2CN^+$ and $CH_3CN^+$ (from acetonitrile) and $CH_2^+$ and $CH_3^+$ (from methane). Typical spectra for the reaction of $N_2^+$ with $CH_3OH$ (before and after addition of $CH_3OH$) are shown in Figure 2.9.
Figure 2.9. A typical spectrum for the reaction of $\text{N}_2^+$ with $\text{CH}_3\text{OH}$ at 298K.
The charge transfer reaction of \( \text{CO}_2^+ + \text{O}_2 \) has also been studied.\(^{23,24,25}\) The rate coefficient at 298K is in good agreement with the accepted value,\(^{23}\) and the reaction was found to be temperature independent \([(6.0 \pm 0.2) \times 10^{-11} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}]\) from 298 to 423K. Miller, et al.\(^{25}\) report a negative temperature dependence over a wider temperature range (90 to 450K). A summary of the positive ion reactions is in Table 2.1.

The chemistry of some negative ions has also been studied. For instance, the reaction of methoxide ion (\( \text{CH}_3\text{O}^- \)) with N,N-dimethylformamide (DMF) has been studied as kinetic information is available from SIFT and FTMS experiments.\(^{26}\) Our rate coefficient \([(5.0 \pm 0.2) \times 10^{-10} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}]\) for this reaction at 298K is in good agreement with the literature value\(^{26}\) of \((3.8 \pm 0.8) \times 10^{-10} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}\) (Table 2.2). However, the products of this reaction do not match the reported products. DePuy, et al. reported the cluster ion \((\text{CH}_3\text{O}^- \cdot \text{HC}(=\text{O})\text{N}((\text{CH}_3)_2))\) using a FA–SIFT, while we see the cluster ion \((\text{CH}_3\text{O}^- \cdot \text{CH}_3\text{OH})\). In our FA experiment, excess methanol is present which leads to the displacement of DMF by methanol. We were able to determine that this reaction has an inverse temperature dependence \((T^{-1.0 \pm 0.2})\). The ion intensity data, leading to this conclusion, are shown in Figure 2.10.

The reaction of hydroxide ion (\( \text{HO}^- \)) with diethyl ether\(^{27}\) has been extensively studied. The reaction rate at 298K has been shown to have a positive pressure dependence, while having a negative temperature dependence at 0.36 torr. We are able to reproduce the pressure effect at 298K \([(4.71 \pm 0.03), (5.7 \pm 0.3), \text{ and } (6.5 \pm 0.6) \times 10^{-10} \text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1} \text{ at } 0.4, 0.5 \text{ and } 0.6 \text{ torr, respectively}]\), and we observe a negative
Table 2.2. Variable Temperature and Pressure Rate Coefficients for Negative Ion Reactions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Neutral</th>
<th>P (torr)</th>
<th>T (K)</th>
<th>Rate$^a$</th>
<th>Pub. Rate$^a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O$^-$ HC(O)N(CH$_3$)$_2$</td>
<td>0.5</td>
<td>273</td>
<td>6. ± 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>5. ± 0.5</td>
<td>3.8 ± 0.8</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>3.53 ± 0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>2.4 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO$^-$</td>
<td>(CH$_3$CH$_2$)$_2$O</td>
<td>0.4</td>
<td>298</td>
<td>4.71 ± 0.03</td>
<td>5.7$^a$ ± 0.4</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>4.4 ± 0.4</td>
<td>3.8$^a$ ± 0.4</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>448</td>
<td>3. ± 1.</td>
<td>2.80$^{ac}$ ± 0.04</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>HO$^-$</td>
<td>(CH$_3$CH$_2$)$_2$O</td>
<td>0.5</td>
<td>298</td>
<td>5.7 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>4.9 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>448</td>
<td>3.7 ± 0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO$^-$</td>
<td>(CH$_3$CH$_2$)$_2$O</td>
<td>0.6</td>
<td>298</td>
<td>6.5 ± 0.6</td>
<td>7.6 ± 0.2</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>6. ± 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>448</td>
<td>4.2 ± 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Rates are given in units of (10$^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$) and the reported errors are one standard deviation of at least triplicate measurements.

(b) Reaction pressure is 0.36 torr.

(c) Temperature for the reported value is actually 473K.
Figure 2.10. Ion intensity data for the reaction of \( \text{CH}_3\text{O}^- \) with \( \text{HC}(-\text{O})\text{N(CH}_3)_2 \) at various temperatures and multiple locations along the flow tube. An Arrhenius plot for the reaction is shown as an inset.
Figure 2.11. Rate coefficients of the reaction of HO⁻ and (CH₃CH₂)₂O at various temperatures and pressures.
temperature dependence at each pressure, as seen in Figure 2.11 and Table 2.2. However, our pressure dependence is not as great as the value reported in the literature. Furthermore, the products we observe for this reaction agree with the literature products (CH$_3$CH$_2$O$^-$, CH$_3$CH$_2$O$^-$•H$_2$O, and CH$_3$CH$_2$O$^-$•CH$_3$CH$_2$OH or HO$^-$•CH$_3$CH$_2$OCH$_2$CH$_3$); however, we do not see the ion at m/z=91 except when there is a great excess of diethyl ether present. We, therefore, attribute the m/z=91 ion to a secondary product with excess diethyl ether.

As mentioned earlier, in an attempt to generate a higher ion density, we included a repeller plate in the design of the our EI source. While the repeller plate creates many more ions, these ions appear to have more kinetic energy. Therefore, we used the reaction of HO$^-$ with diethyl ether to determine the origin of this problem. As seen in Table 2.3, the rates were faster [(23.7 ± 0.6) and (31.9 ± 0.5) x 10$^{-10}$ cm$^3$·molecule$^{-1}$·sec$^{-1}$] with the repeller plate in place regardless of the method of HO$^-$ formation. Only when the number of collisions with helium were increased (by decreasing the helium velocity), did the reaction rate return to the accepted value [(5.7 ± 0.3) x 10$^{-10}$ cm$^3$·molecule$^{-1}$·sec$^{-1}$]. If the helium flow velocity was reduced too much, then diffusional losses became important as well. These observations resulted in the removal of the repeller plate from the EI source, and after removal, the rate of reaction once again matched the accepted value.$^{27}$

Other negative ion reactions have also been compared to previous experiments. For instance, the reactions of various nucleophiles (H$_2$N$^-$, HO$^-$, CH$_3$O$^-$, CD$_3$O$^-$, NCCH$_2$-$^-$, F$^-$ and O$_2$NCH$_2$-$^-$) with methyl formate were studied. The reaction rates and products were compared to known data$^{26}$ (when available) and are in good agreement (Table 2.4). The
Table 2.3. Rate Coefficients of HO\textsuperscript{-} with Diethyl Ether as a Function of Ionizer Conditions at 0.5 torr and 298K.

<table>
<thead>
<tr>
<th>Method of Ion Generation</th>
<th>Use of a Repeller Plate</th>
<th>Flow Rate (SLPM)</th>
<th>Collisions per cm</th>
<th>Rate\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}O + e\textsuperscript{-} + CH\textsubscript{4}</td>
<td>No</td>
<td>231</td>
<td>970</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>231</td>
<td>1060</td>
<td>31.9 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>163</td>
<td>1470</td>
<td>5.48 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>108</td>
<td>2250</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>NH\textsubscript{3} + e\textsuperscript{-} + H\textsubscript{2}O</td>
<td>Yes</td>
<td>231</td>
<td>1070</td>
<td>23.7 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>163</td>
<td>1390</td>
<td>5.5 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>108</td>
<td>2250</td>
<td>4.68 ± 0.09</td>
</tr>
</tbody>
</table>

(a) Rates are given in units of (10\textsuperscript{-19} cm\textsuperscript{3} molecule\textsuperscript{-1} sec\textsuperscript{-1}) and the reported errors are one standard deviation of at least triplicate measurements.
Table 2.4. Negative Ion Reactions with Methyl Formate and 2,2,2-Trifluoroacetyl Chloride at 0.5 torr.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Neutral</th>
<th>T (K)</th>
<th>Rate$^a$</th>
<th>Pub. Rate$^a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>17.8 ± 0.2</td>
<td>25. ± 5.</td>
<td>26</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>18. ± 3.</td>
<td>18. ± 4.</td>
<td>26</td>
</tr>
<tr>
<td>CH$_3$O$^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>8.1 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$O$^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>10. ± 3.</td>
<td>13. ± 1.</td>
<td>26</td>
</tr>
<tr>
<td>O$_2$NCH$_3^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>0.07 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>21. ± 2.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>27.2 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>398</td>
<td>25.8 ± 1.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>448</td>
<td>21.4 ± 3.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCH$_3^-$</td>
<td>HCO$_2$CH$_3$</td>
<td>298</td>
<td>0.48 ± 0.01</td>
<td>0.3 ± 0.06</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>0.38 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>398</td>
<td>0.23 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>CF$_3$C(O)Cl</td>
<td>298</td>
<td>11.2 ± 0.5</td>
<td>4.2. ± 0.9</td>
<td>28</td>
</tr>
<tr>
<td>CH$_3$O$^-$</td>
<td>CF$_3$C(O)Cl</td>
<td>298</td>
<td>11. ± 1.</td>
<td>3.2 ± 0.7</td>
<td>28</td>
</tr>
<tr>
<td>CH$_3$S$^-$</td>
<td>CF$_3$C(O)Cl</td>
<td>298</td>
<td>15. ± 1.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCH$_3^-$</td>
<td>CF$_3$C(O)Cl</td>
<td>298</td>
<td>14. ± 1.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$NCH$_3^-$</td>
<td>CF$_3$C(O)Cl</td>
<td>298</td>
<td>13. ± 1.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Rates are given in units of \((10^{-10} \text{ cm}^3\text{-molecule}^{-1}\text{-sec}^{-1})\) and the reported errors are one standard deviation of at least triplicate measurements.
reactions of $F^-$ and $NCCH_2^-$ with methyl formate were studied as a function of temperature as well. The reaction of $F^-$ is near the collision rate and is temperature independent \[ (2.4 \pm 0.3) \times 10^{-9} \text{ cm}^3\text{-molecule}^{-1}\text{-sec}^{-1} \]; however, the reaction with $NCCH_2^-$ with methyl formate shows a small, inverse temperature dependence.

Many nucleophiles ($F^-$, $CH_3O^-$, $CH_3S^-$, $NCCH_2^-$, and $O_2NCH_2^-$) were also examined with 2,2,2-trifluoroacetyl chloride ($CF_3C(=O)Cl$) at 298K and 0.5 torr, as seen in Table 2.4. The product of all of these reactions is the rapid formation of $Cl^-$, except in the case of $NCCH_2^-$ where a minor product from nucleophilic acyl substitution \[ [(CF_3C(=O)CHCN)^-] \] is also formed. These reactions ($F^-$ and $CH_3O^-$) have been compared to the literature values by Brauman,$^{28}$ and our results are in poor agreement with the ICR results. In particular our reaction rates are faster than the ICR results. Since we have been able to match literature values in so many other instances, we believe that the ICR experiments from the 1960's may not have had an accurate measure of the neutral concentration. Small inaccuracies in pressure measurements for the ICR experiments can easily cause the differences seen in the rate coefficients.

Conclusions

Our design approaches have resulted in a fully functional flowing afterglow. A plethora of rates coefficients have been determined and are reported here. Some of these rates have been for calibration purposes, while many new rates have been determined. Because there is no systematic problem with the determination of reaction rates for positive or negative ions and at a multitude of temperatures and pressures, the design of the variable
temperature flowing afterglow has been a success. Some advantages of this design include:

1) Generation of reactant ions of known thermal energies;
2) The construction of fixed inlets for kinetic and product studies from the walls of the flow tube to allow for better flow properties;
3) The ability to vary the temperature of the system;
4) The future addition of a SIFT in a linear fashion; and
5) The incorporation of a NFR for increased versatility in the chemistry.

Our FA is now being used to determine previously unknown rate coefficients for ion-molecule reactions. The addition of our SIFT and NFR have begun, and the results of these endeavors will be reported in due course.

The chemistry that has been studied is varied. Rate coefficients from $10^{-9}$ to $10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ have been reproduced. Positive ion reactions with direct ($N_2^+$ + CH$_4$), inverse ($N_2^+$ + O$_2$), and no temperature dependence ($N_2^+$ + CH$_3$OH as well as CO$_2^+$ + O$_2$) have been observed. In negative ion mode, reactions with inverse (OH$^-$ + (CH$_3$CH$_2$)$_2$O as well as CH$_3$O$^-$ + DMF) and no temperature dependence (F$^-$ + HCO$_2$CH$_3$) have been observed. The temperature dependencies have also been confirmed at various pressures for the reaction of OH$^-$ + (CH$_3$CH$_2$)$_2$O where the reaction shows an inverse temperature dependence and a direct pressure dependence.

We are continuing to explore reactivity at carbonyl groups, and these studies with our FA will be reported in due course.
Methods

The helium (Praxair, ≥99.995%) bath gas is further purified by passing the gas through a copper coil that contains 4Å molecular sieves that is submersed in liquid nitrogen. The purified helium is then passed over the filament of the EI source.

Formation of Positive Ions  The $\text{N}_2^+$ and $\text{CO}_2^+$ ions are formed by adding $\text{N}_2$ (Praxair, 99.998%) and $\text{CO}_2$ (Praxair, 99.99%) at the 'tree' to the ion stream. Neither the $\text{N}_2$ nor the $\text{CO}_2$ were further purified.

Formation of Negative Ions  $\text{H}_2\text{N}^-$ is formed from electron impact ionization of $\text{NH}_3$ (AGA, 99.99%). For some experiments, $\text{H}_2\text{N}^-$ was used to deprotonate $\text{H}_2\text{O}$ for generating $\text{HO}^-$, but on most occasions, $\text{HO}^-$ was generated by dissociative electron attachment on $\text{N}_2\text{O}$ (AGA, 99.5%) followed by hydrogen atom abstraction from $\text{CH}_4$ (AGA, 99.99%). $\text{HO}^-$ was subsequently used to deprotonate $\text{CH}_3\text{OH}$ (Fisher, 99.9%), $\text{CD}_3\text{OD}$ (Cambridge Isotopes, 99.8%), $\text{CH}_3\text{CN}$ (Malinckrodt, 99.9%), and $\text{CH}_3\text{NO}_2$ (Aldrich, 96%) to form $\text{CH}_3\text{O}^-$, $\text{CD}_3\text{O}^-$, $\text{NCCH}_2^-$, and $\text{O}_2\text{NCH}_2^-$, respectively. The reaction of $\text{HO}^-$ with $(\text{CH}_3)_2\text{S}_2$ (Aldrich, 98%) generated $\text{CH}_3\text{S}^-$. Finally, $\text{F}^-$ is formed by electron impact upon $\text{NF}_3$ (Air Products, 99.5%). None of these compounds have undergone further purification.

Neutral Reagents Used  The neutral reagents that were used in these experiments were all available from commercial sources and were not purified any further. The gaseous reagents are $\text{O}_2$ (AGA, 99.98%), $\text{CH}_4$ (AGA, 99.99%) and $\text{CF}_3\text{C}(=\text{O})\text{Cl}$ (Aldrich, 97%).
and the liquids are $\text{CS}_2$ (Baker, 100%), $\text{HC}(=\text{O})\text{N}((\text{CH}_3)_2$ (Baker, 99.5%), $(\text{CH}_3\text{CH}_2)_2\text{O}$ (Baker, 100%), and $\text{HCO}_2\text{CH}_3$ (Aldrich, 97%).
LIST OF REFERENCES


CHAPTER 3

GAS PHASE NUCLEOPHILIC REACTIONS OF SOME ACYCLIC AND CYCLIC ESTERS

Introduction

The carbonyl moiety (C=O) is fundamentally important in organic chemistry as well as in biological systems. For instance, carbonyl groups are involved in a variety of enzymatic processes in aqueous conditions. The reaction pathways that occur in solution have been well examined,¹ and stabilization effects of the carbonyl group in the gas phase are reasonably well understood.² However, what makes carbonyl groups reactive is less well understood, and the effect of solvent (typically water) can be quite dramatic.³ Brauman⁴ and Riveros⁵ have noted that many mechanistic pathways are available in the gas phase, some of which are not typically observed in aqueous solution. By investigating reactions with carbonyl groups in the gas phase, the intrinsic reactivity of the carbonyl group can be systematically examined, and the importance of the leaving group, the nucleophilic strength as well as the electronic and steric properties of the carbonyl group can be explored.

Previous gas-phase experiments on carbonyl compounds have utilized both ion cyclotron resonance⁴-⁶ (ICR) and flowing afterglow⁶c,⁷ (FA) techniques. The FA has been
shown to be particularly reliable in determining rate coefficients for gas-phase reactions due
to the presence of a bath gas (typically helium) and the moderately high pressure (typically
0.5 torr) in the reaction region. Recent advancements to the FA technique include the
selected ion flow tube (SIFT),\(^8\) collision induced dissociation (CID),\(^9\) drift capability\(^{10}\) and
temperature variability,\(^{11}\) and these techniques have increased the role of the FA method for
studying gas-phase reactions. These advancements allow for product determination (via
the mass-to-charge ratio) as well as the molecular structure via subsequent ion-neutral
reactions or CID experiments. Many advantages of the flow discharge method have been
elegantly reviewed by Graul and Squires.\(^{12}\)

Many groups have investigated the reactivity of esters in the gas phase. Brauman\(^4\)
and Riveros\(^5\) utilized an ICR to study the reactions of various methyl esters. DePuy,
Nibbering and coworkers\(^6c\) have used both ICR and FA methods to study a number of
nucleophiles for their reactions with methyl formate. Riveros and coworkers\(^5,13\) have
focussed on F\(^-\) and HO\(^-\) reactions with formyl and acetyl derivatives. Bartmess and
coworkers have examined some reactions of carbanions with a variety of esters in an ICR
spectrometer.\(^14\) Brauman\(^4\) has probed the potential energy surface of \(^{37}\)Cl\(^-\) +
CF\(_3\)C(=O)\(^{35}\)Cl experimentally and determined that the surface contains two wells which
correspond to ion-dipole complexes. Furthermore, they determined that the tetrahedral
intermediate, as characterized in aqueous solution, may be a transition state or energetically
inaccessible for some carbonyl reactions in the gas phase. RRKM transition-state theory
and \textit{ab initio} calculations provide support for the different potential energy surfaces in the
gas and condensed phases.\(^4\)
Other *ab initio* calculations have probed the factors that stabilize the carbonyl group but not the driving force for their reactivity. Reactions between nucleophiles with carbonyl derivatives have been studied computationally. Jorgensen and coworkers have examined nucleophilic attack at carbonyl groups (aldehydes and acid chlorides) and explored the stability of the tetrahedral intermediates. Of particular interest is the reduction of carbonyl compounds, particularly the reaction of hydride ions with carbonyl compounds (typically aldehydes and ketones), and acyl transfer reactions that have recently been reported by Lee and coworkers. They noted that the calculated potential energy surfaces can be as simple as a single well and as complex as a triple well. They also noted that the BAC2 mechanism is affected by the electronic preferences of the incoming nucleophile and the leaving group as well as the overall exothermicity of the reaction. These effects have also been noted experimentally.

Some possible reactions of an anionic nucleophile with ethyl acetate are shown in Scheme 3.1. The pathways that are available for ethyl acetate are (a) nucleophilic acyl substitution (BAC2), (b) proton transfer (PT) which may also be followed by fragmentation, (c) SN2 displacement (BAL2) which can occur on either alkyl group, and (d) E2 eliminations. Decarbonylation (loss of CO) is also possible for some systems and is a predominant product for formyl esters. This pathway has been termed the Riveros reaction, and solvated, anionic clusters are usually generated.

We have completed an exhaustive study of a variety of anionic nucleophiles with formyl and acetyl esters. In addition, we present some computational results for F− attack.
Scheme 3.1. Observed reaction pathways for esters in the gas phase.
on methyl formate so as to understand the experimental product distribution and the mechanisms for their formation.

**Experimental Methods**

These reactions were studied using a home-built variable temperature flowing afterglow (Figure 3.1) which has been previously described. Briefly, ions are generated via electron impact ionization and traverse the length (~1 m) of a stainless steel flow tube via a constant flow of a helium buffer gas. Neutral reagents are added downstream in order for reactions to occur, and the charged species from these reactions are subsequently monitored using quadrupolar mass spectrometry. By adding these reagents at different locations along the length of the flow tube, ion-neutral reactions can be monitored as a function of distance/time, and rate coefficients can be determined.

Rate coefficients are determined under conditions of pseudo-first order kinetics, and the reported rates are averages of at least three measurements. Most of the rates reported here were obtained at 298 K and 0.5 torr, but some have been determined as a function of temperature and/or pressure.

Upon reaction with a neutral reagent, product ions can be observed. The yield of each product ion was determined by extrapolating the normalized ion percentage to the zero flow limit of the neutral reagent. This method allows for the determination of primary and secondary ions and has been well employed in the literature. Even with this extrapolation, the accuracy of the product determination should be considered as ±10%. These percent yields are taken as the average of three different initial flow rates of the neutral reagent where each is extrapolated to the zero flow limit of the neutral compound.

In this work, the helium (Praxair, ≥99.995%) bath gas is further purified by passing the gas through a copper coil, packed with 4Å molecular sieves, that is submerged
Figure 3.1. Schematic diagram of the Variable Temperature Flowing Afterglow-Selected Ion Flow Tube with a Neutral Flow Reactor.
in liquid nitrogen. The purified helium is then passed over the filament of the EI source. 
H$_2$N$^-$ is then formed from electron impact ionization of NH$_3$ (AGA, 99.99%). For some experiments, H$_2$N$^-$ was used to deprotonate H$_2$O for generating HO$^-$, but on most occasions, HO$^-$ was generated by dissociative electron attachment on N$_2$O (AGA, 99.5%) followed by hydrogen atom abstraction from CH$_4$ (AGA, 99.99%). HO$^-$ or H$_2$N$^-$ was subsequently used to deprotonate CH$_3$OH (Fisher, 99.9%), CD$_3$OD (Cambridge Isotopes, 99.8%), CH$_3$CN (Mallinckrodt, 99.9%), CH$_3$C(O)CH$_3$ (Mallinckrodt, 99.8%), and CH$_3$NO$_2$ (Aldrich, 96%) to form CH$_3$O$^-$, CD$_3$O$^-$, NCCH$_2$$^-$, CH$_3$C(O)CH$_2$$^-$, and O$_2$NCH$_2$$^-$, respectively. The reaction of HO$^-$ with CH$_3$SSCH$_3$ (Aldrich, 98%) generated CH$_3$S$^-$. Finally, F$^-$ was formed by electron impact upon NF$_3$ (Air Products, 99.5%). 
These compounds were used as provided by the manufacturer. The neutral reagents, HCO$_2$CH$_3$ (Aldrich, 97%), HCO$_2$CH$_2$CH$_3$ (Baker, 98.1%), CH$_3$CO$_2$CH$_3$ (Aldrich, 99+%), CH$_3$CO$_2$CH$_2$CH$_3$ (Mallinckrodt, 99.9%), β-propiolactone (Acros, 98%), and γ-butyrolactone (Acros, 99+%), were used as provided by the commercial sources.

**Computational Methods**

All calculations were performed with the Gaussian 94 suite of programs. All stationary points were fully optimized at the B3LYP/6-31+G* level of theory and confirmed as minima or transition states via vibrational frequency analysis calculations. All transition states were confirmed to have only one imaginary vibrational frequency. The
reactant and product which connected each transition state was confirmed by an intrinsic reaction coordinate (IRC) search or by incremental (typically 10%) displacement along the vibrational mode for the imaginary frequency and then a careful optimization in either direction. All energies reported here include (unscaled) zero point vibrational energy and thermal corrections to 298 K (1 atm pressure).

**Results**

Rate coefficients have been determined for the reactions of H$_2$N$^-$, HO$^-$, CD$_3$O$^-$, NCCH$_2^-$, F$^-$, CH$_3$C(=O)CH$_2^-$, and O$_2$NCH$_2^-$ with methyl formate and methyl acetate. For reactions with ethyl formate and ethyl acetate, only H$_2$N$^-$, HO$^-$, CH$_3$O$^-$, NCCH$_2^-$, F$^-$, and O$_2$NCH$_2^-$ were used. The reactivity of these esters are compared to β-propiolactone and γ-butyrolactone in order to examine acyclic vs cyclic esters.

**General Trends** The rate coefficients for the reactions of H$_2$N$^-$, HO$^-$, CH$_3$O$^-$ or CD$_3$O$^-$, and F$^-$ with all of the esters have been found to be near the theoretical (ADO) rate limit (1.5 to 2.5 x 10$^{-9}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$ for these systems). However, the rate coefficients with NCCH$_2^-$, CH$_3$C(=O)CH$_2^-$, and O$_2$NCH$_2^-$ are much less efficient with rates between 10$^{-10}$ to 10$^{-12}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$, as seen in Table 3.1.

For example, the reaction rates for H$_2$N$^-$ with methyl formate, ethyl formate, methyl acetate, and ethyl acetate are (19.2 ± 0.8), (28 ± 1), (26 ± 2), and (33 ± 5) x 10$^{-10}$.
Table 3.1. Rates and Ionic Product Distributions for Negative Ion Reactions with Methyl Formate ($\Delta H^{\text{calc}} = 391$ kcal-mol$^{-1}$).

<table>
<thead>
<tr>
<th>Ion (A$^-$)</th>
<th>$\Delta H^{\text{calc}}$ (HA$^-$)</th>
<th>Ionic Products</th>
<th>Rate Path</th>
<th>$\Delta H^{\text{exp}}$</th>
<th>Rate$^d$</th>
<th>ADO Rate$^d$</th>
<th>Eff.$^f$</th>
<th>Pub. Rate$^d$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$N$^-$</td>
<td>404 HCl=O (NH$_3$) (36%)</td>
<td>Bac2</td>
<td>-38.7</td>
<td>$19.2 \pm 0.8$</td>
<td>23.6</td>
<td>0.814</td>
<td>25. $\pm$ 5.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$O (29%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$O(NH$_3$) (42%)</td>
<td>Riveros</td>
<td>10.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCO$_3^-$ (10%)</td>
<td>Riveros</td>
<td>10.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$O(CH$_2$OH) (Secondary Ion)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO$^-$</td>
<td>391 HCO$_3^-$ (42%)</td>
<td>BAL2 or Bac2</td>
<td>-38.1 or -38.1</td>
<td>$17.9 \pm 0.2$</td>
<td>23.0</td>
<td>0.778</td>
<td>18. $\pm$ 4.</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$O (39%)</td>
<td>Bal2</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$O(H$_2$O) (20%)</td>
<td>Riveros</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$O$^-$</td>
<td>380 CH$_2$O(CH$_2$OH) (97%)</td>
<td>Riveros</td>
<td>20.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCO$_3^-$ (7%)</td>
<td>Riveros</td>
<td>20.5</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CD$_2$O$^-$</td>
<td>380* CH$_2$O(CD$_2$OD) (64%)</td>
<td>Riveros</td>
<td>35.7</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$O(CD$_2$OD) (29%)</td>
<td>Riveros</td>
<td>35.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCO$_3^-$ (7%)</td>
<td>Riveros</td>
<td>35.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCH$_2^-$</td>
<td>373 HCO$_3^-$=CHCN (100%)</td>
<td>Bac2</td>
<td>0.48 $\pm$ 0.01</td>
<td>$17.1 \pm 0.028$</td>
<td>30. $\pm$ 0.06</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>371 F=O(CH$_2$OH) (57%)</td>
<td>Riveros</td>
<td>21. $\pm$ 2.</td>
<td>$22.1 \pm 0.950$</td>
<td>22.1 $\pm 0.950$</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCO$_3^-$ (43%)</td>
<td>Riveros</td>
<td>19.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$C=O</td>
<td>CH$_2$O (60%)</td>
<td>Riveros</td>
<td>0.09 $\pm$ 0.01</td>
<td>$15.5 \pm 0.006$</td>
<td>15.5 $\pm 0.006$</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCO$_3^-$ (40%)</td>
<td>Riveros</td>
<td>19.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$S$^-$</td>
<td>377 CH$_2$S(OH) (95%)</td>
<td>Bal2</td>
<td>19.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_2$S(OH) (5%)</td>
<td>Riveros</td>
<td>19.4</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>O$_2$NCH$_3^-$</td>
<td>HCO$_3^-$ (66%)</td>
<td>Bal2</td>
<td>0.07 $\pm$ 0.01</td>
<td>$15.3 \pm 0.005$</td>
<td>15.3 $\pm 0.005$</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2$NCH$_3^-$=CH$_2$OH (34%)</td>
<td>Riveros</td>
<td>0.07 $\pm$ 0.01</td>
<td>$15.3 \pm 0.005$</td>
<td>15.3 $\pm 0.005$</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Values from the NIST website (http://webbook.nist.gov).
(b) % Yields are extrapolated for a zero flow rate of neutral reagent in STP cm$^{-1}$-sec$^{-1}$.
(c) $\Delta H^{\text{calc}}$ in kcal-mol$^{-1}$calculated from values reported by NIST (http://webbook.nist.gov).
(d) Rates in units of (10$^{-16}$ cm$^{-1}$-molecule$^{-1}$-sec$^{-1}$) and the reported errors are one standard deviation of at least triplicate measurements.
(e) Rates in units of (10$^{-16}$ cm$^{-1}$-molecule$^{-1}$-sec$^{-1}$) and the polarizability for HCO$_3$CH$_3$ is approximated using group additivity.
(f) Efficiency = (experimental rate/ADO rate).
(g) Reference 6.
cm$^3$-molecule$^{-1}$-sec$^{-1}$, while the efficiencies$^{23} (k_{\text{obs}}/k_{\text{ADO}})$ of these reactions are 0.81, 1.03, 1.06, and 1.21, respectively (Tables 3.1-3.4). When comparing the rates and efficiencies for the formate and acetate esters, the ethyl esters seem to react faster and more efficiently. This trend appears to be independent of the chosen nucleophile (except $\text{O}_2\text{NCH}_2^-$ which does not react with the ethyl esters). Thus, the alkyl group of the ester has an important role in the rate of reaction. This is most likely due to the different reaction pathways that are available to the various esters (see below).

However, $\text{NCCH}_2^-$ reacts exclusively with formate esters via a $\text{BAc2}$ mechanism to yield $\text{HC(O)}=\text{CHCN}$ and the corresponding alcohol (Tables 3.1 and 3.2) and undergoes $\text{BAc2}$ or proton transfer reactions with acetate esters (Tables 3.3 and 3.4). This is the one example where the products of the reaction seem to be driven entirely by the nucleophile. (We should also note that Bartmess and coworkers did investigate reactions of $\text{NCCH}_2^-$ with methyl formate, but they report that a trace product was observed only for unquenched conditions.$^{14}$) Plots of the Riveros product yields for the formyl esters and the proton transfer yields for the acetyl esters for the different nucleophiles are shown in Figure 3.2, and these will be discussed further below.

Not only are the ethyl esters more reactive, based on the rate coefficients, but they also yield a larger percentage of products from the reaction at the alkyl group than at the carbonyl group. If the ethyl esters were undergoing $\text{BA}L2$ reactions, like the methyl esters, the reactions should be slower due to increased steric congestion. In addition, the methylene carbon should be less electrophilic as the methyl group is generally considered to be electron donating as compared to a hydrogen atom. Both of these would cause the reaction to slow down, yet the reaction rate increases. Therefore, the formation of the
Table 3.2. Rates and Ionic Product Distributions for Negative Ion Reactions with Ethyl Formate.

<table>
<thead>
<tr>
<th>Ion (A⁻)</th>
<th>ΔH°&lt;sub&gt;rea&lt;/sub&gt; (kcal/mol)</th>
<th>Ionic Products¹</th>
<th>Rxn Path</th>
<th>ΔH&lt;sub&gt;th&lt;/sub&gt; (kcal/mol)</th>
<th>Rate (10⁻¹⁰ sec⁻¹)</th>
<th>Eff.¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂N⁻</td>
<td>404</td>
<td>HCO₃⁻ (or CH₃CH₂O⁻) (72%)</td>
<td>E2 or BAI2 (or Riveros)</td>
<td>-41.1 or ___ (or -13.1)</td>
<td>28. ± 1.</td>
<td>27.2 1.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCN⁻ (or CH₃CH₂O⁻) (26%)</td>
<td>Bac2</td>
<td></td>
<td>-38.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CH₂O⁻(NH₃) (3%)</td>
<td>Riveros</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO⁻</td>
<td>391</td>
<td>HCO₃⁻ (95%)</td>
<td>E2 or BAI2 or BAC2</td>
<td>-26.7 or -37.7 or -37.7</td>
<td>27. ± 1.</td>
<td>26.5 1.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CH₂O⁻(H₂O) (5%)</td>
<td>Riveros</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CH₂O⁻(CH₃OH) (47%)</td>
<td>Riveros</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td>380</td>
<td>HCO₃⁻ (or CH₃CH₂O⁻) (53%)</td>
<td>E2 or BAI2 (or BAC2)</td>
<td>-18.6 or -34.8 (or -2.7)</td>
<td>19. ± 2.</td>
<td>21.1 0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CH₂O⁻(CH₃OH) (47%)</td>
<td>Riveros</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCH₂⁻</td>
<td>373</td>
<td>H₃O⁺=CHCN (100%)</td>
<td>BAC2</td>
<td></td>
<td>1.3 ± 0.2</td>
<td>19.3 0.07</td>
</tr>
<tr>
<td>F⁻</td>
<td>371</td>
<td>HCO₃⁻ (or CH₃CH₂O⁻) (79%)</td>
<td>E2 or BAI2 (or BAC2)</td>
<td>-7.5 or -29.7 (or +22.2)</td>
<td>36. ± 6.</td>
<td>25.4 1.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F⁻(CH₃CH₂OH) (21%)</td>
<td>Riveros</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂NCH₂⁻</td>
<td>356</td>
<td>HCO₃⁻ (100%)</td>
<td>E2 or BAI2</td>
<td>+4.4 or ___</td>
<td>0.06 ± 0.01</td>
<td>17.1 0.004</td>
</tr>
</tbody>
</table>

(a) Values from the NIST website (http://webbook.nist.gov).

(b) % Yields are extrapolated for a zero flow rate of neutral reagent in STP cm⁻³·sec⁻¹.

(c) ΔH<sub>th</sub> in kcal-mol⁻¹ calculated from values reported by NIST (http://webbook.nist.gov).

(d) Rates in units of (10⁻¹⁰ cm⁻³·molecule⁻¹·sec⁻¹) and the reported errors are one standard deviation of at least triplicate measurements.

(e) Rates in units of (10⁻¹⁰ cm⁻³·molecule⁻¹·sec⁻¹).

(f) Efficiency = (experimental rate/ADO rate).
Table 3.3. Rates and Ionic Product Distributions for Negative Ion Reactions of Methyl Acetate ($\Delta H_{\text{ind}} = 372$ kcal-mol$^{-1}$).

<table>
<thead>
<tr>
<th>Ion (A$^-$)</th>
<th>$\Delta H_{\text{ind}}$ (KA$^-$)</th>
<th>Ionic Products$^a$</th>
<th>Rxn Path</th>
<th>$\Delta H_{\text{ex}}$</th>
<th>Rate$^d$</th>
<th>ADO Rate$^e$</th>
<th>Eff.</th>
<th>Pub. Rate$^e$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$N$^-$</td>
<td>404 (M-H)$^-$ (299%)</td>
<td>CH$_3$C(=O)NH$^+$ (61%)</td>
<td>PT</td>
<td>-32.0</td>
<td>26. ± 2. 24.5</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO$^-$</td>
<td>391 CH$_3$CO$_2^-$ (78%)</td>
<td>(M-H)$^-$ (22%)</td>
<td>BAc2 or BAc2</td>
<td>-36.7</td>
<td>28. ± 2. 23.9</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$O$^-$</td>
<td>380 (M-H)$^-$ (100%)</td>
<td>PT</td>
<td>-19.0</td>
<td>15.1</td>
<td>0.7</td>
<td>18.4</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCH$_2^+$</td>
<td>373 (M-H)$^-$ (57%)</td>
<td>CH$_3$C(=O)CH$_2$CN (43%)</td>
<td>BAc2</td>
<td>-1.0</td>
<td>0.37</td>
<td>0.02</td>
<td>17.5</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>371 F(=O)CH$_3$ (36%)</td>
<td>CH$_3$CO$_2^-$ (21%)</td>
<td>BAc2+PT</td>
<td>28. ± 1. 22.9</td>
<td>1.00</td>
<td>54.</td>
<td>g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$NCH$_2^+$</td>
<td>369 No Observed Reaction</td>
<td>No Observed Reaction</td>
<td>Adduct</td>
<td>15.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Values from the NIST website (http://webbook.nist.gov).
(b) % Yields are extrapolated for a zero flow rate of neutral reagent in STP cm$^3$-sec$^{-1}$.
(c) $\Delta H_{\text{ind}}$ in kcal-mol$^{-1}$ calculated from values reported by NIST (http://webbook.nist.gov).
(d) Rates in units of (10$^{-6}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$) and the reported errors are one standard deviation of at least triplicate measurements.
(e) Rates in units of (10$^{-6}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$).
(f) Efficiency = (experimental rate/ADO rate).
(g) Reference 5a.
Table 3.4. Rates and Ionic Product Distributions for Negative Ion Reactions with Ethyl Acetate.

<table>
<thead>
<tr>
<th>Ion (A⁻)</th>
<th>ΔH_{m}^{\circ} (kJ/mol)</th>
<th>Ionic Products</th>
<th>Rxn Path</th>
<th>ΔH_{rxn}^{\circ} (kJ/mol)</th>
<th>Rate (^{a}) (10(^{-13}) cm(^3) molecule(^{-1}) sec(^{-1}))</th>
<th>ADO Rate (^{b}) (10(^{-13}) cm(^3) molecule(^{-1}) sec(^{-1}))</th>
<th>Pub. (^{c}) Rate (^{d}) (10(^{-13}) cm(^3) molecule(^{-1}) sec(^{-1}))</th>
<th>Eff. (^{e})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)N(^{-})</td>
<td>404</td>
<td>(M-H(^{-})) (64%)</td>
<td>CH(_3)CO(^{-}) (31%)</td>
<td>CH(_3)C≡N(^{-}) (5%)</td>
<td>PT</td>
<td>-40.0 or ____</td>
<td>33. ± 5</td>
<td>27.2</td>
<td>1.21</td>
</tr>
<tr>
<td>HO(^{-})</td>
<td>391</td>
<td>CH(_3)CO(^{-}) (68%)</td>
<td>(M-H(^{-})) (32%)</td>
<td>CH(_3)C≡N(^{-})</td>
<td>BAC2 or E2 or BAC2</td>
<td>-36.6 or -25.6 or -36.6</td>
<td>24. ± 1</td>
<td>26.5</td>
<td>0.91</td>
</tr>
<tr>
<td>CH(_3)O(^{-})</td>
<td>380</td>
<td>(M-H(^{-})) (83%)</td>
<td>CH(_3)CO(^{-}) (17%)</td>
<td>CH(_3)C≡N(^{-})</td>
<td>BAC2 or E2 or BAC2</td>
<td>-17.5 or -33.7</td>
<td>19.1 ± 0.1</td>
<td>20.9</td>
<td>0.91</td>
</tr>
<tr>
<td>NCCH(_2)(^{-})</td>
<td>373</td>
<td>CH(_3)C=O=CHC(_2) (53%)</td>
<td>(M-H(^{-})) (47%)</td>
<td>CH(_3)C≡N(^{-})</td>
<td>BAC2</td>
<td>0.41 ± 0.1</td>
<td>19.1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>F(^{-})</td>
<td>371</td>
<td>F(_2)C=O=CH(_2) (54%)</td>
<td>CH(_3)CO(^{-}) (46%)</td>
<td>CH(_3)C≡N(^{-})</td>
<td>E2 or BAC2</td>
<td>-6.5 or ____</td>
<td>35. ± 8</td>
<td>25.3</td>
<td>1.38</td>
</tr>
<tr>
<td>O(_2)NCH(_2)(^{-})</td>
<td>356</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Values from the NIST website (http://webbook.nist.gov).
(b) % Yields are extrapolated for a zero flow rate of neutral reagent in STP cm\(^{-1}\) sec\(^{-1}\).
(c) ΔH_{m} in kcal/mol calculated from values reported by NIST (http://webbook.nist.gov).
(d) Rates in units of (10\(^{-13}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\)) and the reported errors are one standard deviation of at least triplicate measurements.
(e) Rates in units of (10\(^{-13}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\)).
(f) Efficiency = (experimental rate/ADO rate).
(g) Reference 5a.
Figure 3.2 A typical spectrum (0.5 torr and 298 K) for the reaction of H$_2$N$^-$ with methyl formate (HCO$_2$CH$_3$) at the longest reaction time (top), an extrapolation to zero flow of methyl formate for determining the primary products of this reaction (bottom).
carboxylate ion in the alkyl esters occurs via an elimination (E2) rather than a nucleophilic substitution (Bac2) pathway (Scheme 1).

Reactions of Methyl Formate  The product ions observed from nucleophilic attack on methyl formate can be used to infer the mechanistic pathways that generated these product ions. For the $\text{H}_2\text{N}^- + \text{HCO}_2\text{CH}_2$ reaction in our FA, four primary products, $\text{HC(=O)NH}^- (36\%)$, $\text{CH}_3\text{O}^- (29\%)$, $\text{CH}_3\text{O}^-(\text{NH}_3) (24\%)$ and $\text{HCO}_2^- (10\%)$, and one secondary product $\text{CH}_3\text{O}^-\text{(CH}_3\text{OH)}$ are generated (Table 3.1). These products and their approximate yields are in good agreement with results by DePuy and coworkers.$^{6c}$ A typical spectrum of $\text{H}_2\text{N}^- + \text{HCO}_2\text{CH}_3$ as well as the extrapolation to zero methyl formate flow (so as to obtain the product yields) are shown in Figure 3.3. As stated above, the extrapolation procedure should provide reasonable information about the primary products of these reactions, but the accuracy of such measurements should be considered as $\pm 10\%$. As seen in Figure 3.3, the presence of the $\text{HC(=O)NH}^-$ product demonstrates that there is sufficient time and energy for proton transfer to occur between $\text{CH}_3\text{O}^-$ and $\text{HC(=O)NH}_2$ in the ion-molecule complex during the Bac2 pathway. Therefore, a tetrahedral species is accessible for this reaction.

$$
\text{H}_2\text{N}^- \rightarrow \text{HCO}_2\text{CH}_3 \rightarrow \text{HCO}_2\text{NH}_2 \rightarrow \text{HCO}_2\text{NH}^- + \text{CH}_3\text{O}^- + \text{CH}_3\text{OH}
$$
Figure 3.3. Correlation of the Riveros product yields for the formyl esters and the proton transfer yields for the acetyl esters for the different nucleophiles according to their gas phase acidity ($\Delta H_{\text{acid}}$).
The methoxide ion product is most likely generated via a Riveros (decarbonylation) reaction since the HC(=O)NH\textsuperscript{−} ion is also observed (see below). The CH\textsubscript{3}O(=NH\textsubscript{3}) complex is definitely formed via a Riveros (decarbonylation) reaction. The formate ion is generated via a BAL2 mechanism, and attack on the methyl group of the ester results in formation of methylamine as a neutral (and undetected) product.

The reaction of HO\textsuperscript{−} ion with methyl formate produces HCO\textsubscript{2}\textsuperscript{−} (42%), CH\textsubscript{3}O\textsuperscript{−} (39%), and CH\textsubscript{3}O\textsuperscript{−}(H\textsubscript{2}O) (20%). Again, the reaction agrees well with results by DePuy and coworkers.\textsuperscript{6c} Both the methoxide ion and the methoxide ion-water complex products are formed from the Riveros reaction. The methoxide ion could be generated via a BAL2 reaction, but the formic acid product would transfer a proton (like formamide, above) to the methoxide ion to produce the more stable methanol and formate ion. The formate ion can be formed via a BAL2 pathway (after a proton transfer in the ion-molecule complex) or from BAL2 attack upon the methyl group of methyl formate. The efficiency of the HO\textsuperscript{−} reaction with methyl formate reaction was 79%, while the reaction with amide ion was 81%.

The reaction of CH\textsubscript{3}O\textsuperscript{−} and CD\textsubscript{3}O\textsuperscript{−} with methyl formate yields HCO\textsubscript{2}\textsuperscript{−} resulting from the BAL2 pathway in small percentages (3 and 7%, respectively). The other products observed are complexes of methoxide ion with methanol (protiated or deuterated) which result from a Riveros reaction. We observed two different complexes as the original deuterated methoxide was generated from the reaction of HO\textsuperscript{−} (or H\textsubscript{2}N\textsuperscript{−}) with CD\textsubscript{3}OD, and some H/D exchange could have occurred. In previous ICR experiments by Riveros and coworkers,\textsuperscript{5} the naked methoxide ion was also observed as a product. However, we do
not observe this ionic product, and this is in agreement with previous FA results by DePuy and coworkers.\textsuperscript{6c} Therefore, the formation of the methoxide ion may be due to the low pressures in which the ICR experiments were conducted.

The remainder of the ions, excluding NCCH$_2^-$ which was mentioned previously, follow the same pattern as methoxide ion. A Riveros product is formed as a complex between methanol and the reactant ion, and HCO$_2^-$ is formed as another product via a BAL2 reaction. The Riveros products are dominant for both F$^-$ and CH$_3$C(=O)CH$_2^-$, while the Riveros pathway is the minor channel for CH$_3$S$^-$ and O$_2$NCH$_2^-$. In fact, the Riveros reaction is the favored pathway for the less basic ions (A$^-$) with a $\Delta H_{\text{acid}}$ (HA) $\geq$ 369 kcal-mol$^{-1}$ (Table 3.1) -- neglecting NCCH$_2^-$ where only the BAL2 pathway is observed as noted earlier.

We also examined the Riveros reaction of NCCH$_2^-$ with methyl formate as a function of temperature from 298 to 448 K, in 50 K increments (Table 3.5). The reaction shows a negative temperature dependence, and the only product observed at all temperatures is HC(O$^-$)=CHCN (via a BAL2 mechanism followed by a proton transfer).

Experimentally, the reaction of F$^-$ with HCO$_2$CH$_3$ occurs with 95% efficiency and yields F'(CH$_3$OH) (Riveros) and HCO$_2^-$ (BAL2) products. A representative spectrum is shown in Figure 3.4. The reaction occurs upon almost every collision, and the Riveros product is slightly favored at 298 K. Therefore, despite the larger exothermicity (calculated
Table 3.5. Variable temperature studies at 0.5 torr.

<table>
<thead>
<tr>
<th>Mechanistic Pathway</th>
<th>Temperature (K)</th>
<th>298</th>
<th>348</th>
<th>398</th>
<th>448</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate*</td>
<td>21. ± 2.</td>
<td>27.2 ± 0.4</td>
<td>26. ± 1.</td>
<td>21. ± 3.</td>
<td></td>
</tr>
<tr>
<td>HCO₂⁻</td>
<td>BAL2</td>
<td>43</td>
<td>18</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>F⁺(CH₃OH)</td>
<td>Riveros</td>
<td>57</td>
<td>82</td>
<td>85</td>
<td>94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate*</th>
<th>28. ± 1.</th>
<th>29. ± 4.</th>
<th>31. ± 2.</th>
<th>29. ± 5.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁺(CH₃OH)</td>
<td>BAC2+E2</td>
<td>14</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>CH₃CO₂⁻</td>
<td>BAL2</td>
<td>21</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>F⁻(=O)CH₃⁻</td>
<td>BAC2+PT</td>
<td>36</td>
<td>70</td>
<td>65</td>
</tr>
<tr>
<td>(M-H)⁻</td>
<td>PT</td>
<td>14</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>F⁺(CH₃CO₂CH₃) Adduct</td>
<td></td>
<td>14</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rate*</th>
<th>0.48 ± 0.01</th>
<th>0.38 ± 0.01</th>
<th>0.23 ± 0.01</th>
<th>0.15 ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC(O⁻)=CHCN</td>
<td>BAC2</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

(a) Product distributions are given in % for each temperature.

(b) Rates in units of (10⁻¹⁰ cm³-molecule⁻¹-sec⁻¹) and the reported errors are one standard deviation of at least triplicate measurements.
Figure 3.4. A typical spectrum for the reaction of $F^-$ with $\text{HCO}_2\text{CH}_3$ at 0.5 torr and 298 K.
at the B3LYP/6-31+G(d) level) of the BAL2 reaction ($\Delta H_{\text{rxn}} = -24.1 \text{ kcal-mol}^{-1}$), the Riveros pathway ($\Delta H_{\text{rxn}} = -12.9 \text{ kcal-mol}^{-1}$) dominates.

The origin of this preference is of interest. We, therefore, calculated the entire potential energy surface for F$^-$ + HCO$_2$CH$_3$ at the B3LYP/6-31+G(d) level. These enthalpy results (in kcal-mol$^{-1}$ at 298 K) are presented in Figure 3.5. The Riveros reaction could possibly occur via direct attack of F$^-$ on the formyl hydrogen. This pathway for the Riveros reaction was exhaustively searched for without success. This is no surprise based on a comparison of the acidities of HF ($\Delta H_{\text{acid}} = 371 \text{ kcal-mol}^{-1}$) and methyl formate ($\Delta H_{\text{acid}} = 391 \text{ kcal-mol}^{-1}$).

The calculated potential energy surface does predict the formation of F$^-(\text{CH}_3\text{OH})$, and HCO$_2^-$ as the only products, in complete agreement with our experimental results; furthermore, the Riveros reaction is formed via F$^-$ attack on the carbonyl carbon. Thus, a tetrahedral intermediate is generated, and the transition state for the C–OCH$_3$ bond cleavage leads directly to deprotonation of the formyl hydrogen by CH$_3$O$^-$ upon departure. Subsequent fragmentation of FCO$^-$ within the FCO$^-(\text{CH}_3\text{OH})$ complex then leads to the F$^-(\text{CH}_3\text{OH})$ complex.

The transition state for the cleavage of the C–OCH$_3$ bond has a barrier that is larger than the energy of the initial F$^-$ and HCO$_2$CH$_3$. Therefore, an increase in internal energy
Figure 3.5. Potential energy surface for $\text{F}^- + \text{HCO}_2\text{CH}_3$ at B3LYP/6-31+G*. Relative enthalpies are given in kcal-mol$^{-1}$ with unscaled zero point energy corrections.
(temperature) should be able to favor the Riveros reaction. Experimentally, the reaction of $\text{F}^-$ with methyl formate at room temperature (Table 3.5) produces $\text{F}^-(\text{CH}_3\text{OH})$, the Riveros product, in 57% yield and $\text{HCO}_2^-$, the $\text{B}2\text{L}2$ product, in 43% yield. The percent yield (57, 82, 85, and 94%) of the Riveros reaction increases with increasing temperature (298, 348, 398, and 448 K, respectively) as predicted by the barrier seen in the calculated potential energy surface (Figure 3.5).

Reactions of Ethyl Formate As with methyl formate, the reaction of $\text{NCCH}_2^-$ with ethyl formate is unique and generates only a $\text{B}2\text{C}2$ product ($\text{HC}(=\text{O})\text{CHCN}^-$). For most of the anionic reactions with ethyl formate, the Riveros reaction is the minor pathway for reaction. As stated earlier, the reaction at the alkyl group is most likely to occur via an E2 elimination, but the possibility of $\text{B}2\text{L}2$ has not been conclusively eliminated. However, the fast reaction rates and the high efficiencies of the ethyl formate reactions suggest that a new pathway is dominant. We believe that this new pathway is an E2 elimination and is in agreement with previous results by Riveros and coworkers. For the reaction with ethyl formate, the formate and ethoxide ions cannot be distinguished in our system as our instrument only has unit mass resolution. However, in analogy to the acetyl ester reactions (see below) where this isobaric situation may not occur for acetate vs ethoxide ions, we are confident that $\text{HCO}_2^-$ is the dominant ion for the reactions with ethyl formate.

For $\text{H}_2\text{N}^-$ with ethyl formate, the products are very similar to those in the case of methyl formate. The products are $\text{HCO}_2^-$ and/or $\text{CH}_3\text{CH}_2\text{O}^-$ (72%), $\text{HC}(=\text{O})\text{NH}^-$ (26%),
and \( \text{CH}_3\text{CH}_2\text{O}^-\text{(NH}_3\text{)} \) (3%). The mechanisms that would lead to the formation of these product ions are E2 and/or Riveros, BAc2, and the Riveros pathways, respectively.

Similar reactivity is seen for HO\(^-\). The products, as in the reaction with methyl formate, are HCO\(_2^-\) and/or CH\(_3\)CH\(_2\)O\(^-\) (95%) and CH\(_3\)CH\(_2\)O\(^-\)(H\(_2\)O) (5%). The pathways involved are E2 and/or BAc2 for the formation of HCO\(_2^-\), and the Riveros reaction would form CH\(_3\)CH\(_2\)O\(^-\) and the CH\(_3\)CH\(_2\)O\(^-\)(H\(_2\)O) complex.

For the reaction of methoxide ion with ethyl formate, the products are HCO\(_2^-\) and/or CH\(_3\)CH\(_2\)O\(^-\) (53%) and CH\(_3\)CH\(_2\)O\(^-\)(CH\(_3\)OH) (47%). Since CH\(_3\)O\(^-\) was not generated in the reaction with CD\(_3\)O\(^-\) with methyl formate, the amount of CH\(_3\)CH\(_2\)O\(^-\) generated from the reaction with ethyl formate is likely to be negligible. Also, the true yield of the Riveros reaction can be assigned to the CH\(_3\)CH\(_2\)O\(^-\)(CH\(_3\)OH) complex. In this case, the Riveros pathway only accounts for 47% of the reaction, while the E2 reaction accounts for about 53%.

The reaction of F\(^-\) with ethyl formate yields HCO\(_2^-\) (79%) and F\(^-\)(CH\(_3\)CH\(_2\)OH) (21%). Here, we have once again reasoned by analogy and discounted the possibility of CH\(_3\)CH\(_2\)O\(^-\) as a possible product ion because this F\(^-\) reaction seems to compare very well to the methyl formate case. The ethyl formate reaction favors E2 (79%) over decarbonylation (21%).
With $O_2NCH_2^-$ and ethyl formate, the Riveros product is not seen. The reaction is very slow \[ ((6 \pm 1) \times 10^{-12}\, \text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}) \] and yields $HCO_2^-$ as the only product. It appears that the reaction proceeds exclusively via a BAL2 reaction at the alkyl group.

**Reactions with Methyl Acetate** In the reactions with methyl acetate ($\Delta H_{\text{acid}} = 372 \, \text{kcal-mol}^{-1}$), the noticeable trend is that proton transfer is the favored pathway for this ester with all nucleophiles/bases considered here except $HO^-$ and $F^-$ ions. Furthermore, $\text{CH}_3\text{C}(=\text{O})\text{CH}_2^-$ and $O_2NCH_2^-$ were unreactive on the time scale of our experiments. Table 3.3 lists all of the products and rate coefficients for the reactions with methyl acetate.

The reaction of $H_2N^-$ proceeds at a rate of \[ (26 \pm 2) \times 10^{-10}\, \text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1} \] and produces $\leq 1\%$ of $\text{CH}_3\text{C}(=\text{O})\text{NH}^-$ (proton transfer comprises the rest of the products), while $HO^-$ reacts with a rate coefficient of \[ (28 \pm 2) \times 10^{-10}\, \text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1} \] and produces the acetate ion in 78% yield. The acetate ion can be formed via BAC2 or BAL2 mechanisms, but the major pathway is more likely to be BAC2 since this product channel is seen for $H_2N^-$. The most interesting reaction with methyl acetate occurs with $F^-$ as the nucleophile. In this reaction, five primary products are formed. Two of these products, $\text{FC}(=\text{O})\text{CH}_2^-$ (36%) and $F^-(\text{CH}_3\text{OH})$ (14%), occur from addition to the carbonyl carbon followed by subsequent fragmentation to form $\text{FC}(=\text{O})\text{CH}_3$ and $\text{CH}_3\text{O}^-$. The $\text{FC}(=\text{O})\text{CH}_2^-$ ion is
generated when a proton transfer occurs within the ion-molecule complex, while the F\(^-\)(CH\(_3\)OH) cluster ion is formed when the proton transfer leads to an elimination reaction to form neutral ketene. Two other products are acetate ion (21%), formed via B\(_2\)A, and the deprotonation product (14%). This reaction is also the only case of the acyclic esters studied here to yield an adduct (14% yield), and this product may be a tetrahedral intermediate or a loose ion-molecule complex between F\(^-\) and the alkyl groups of the ester. Previous ICR experiments by Riveros and coworkers have seen only two major products (FC(=O)CH\(_2\)\(^-\) and CH\(_3\)CO\(^-\)).\(^{5a,24}\)

The ionic products, FC(=O)CH\(_2\)\(^-\) and F\(^-\)(CH\(_3\)OH), which are produced by the B\(_2\)Ac pathway, are generated even more efficiently at higher temperatures (Table 3.5), but the overall reaction rate is essentially constant across the temperature regime. This demonstrates that the B\(_2\)Ac pathway becomes more accessible with increasing temperature and suggests that a small barrier exists for traversing the B\(_2\)Ac mechanism.

**Reactions of Ethyl Acetate** As in the reactions with methyl acetate, the dominant products with ethyl acetate are derived from proton transfer, but the products derived from reaction at the alkyl group also increase. The acetate ion, formed in 31% yield, is now produced for the reaction with H\(_2\)N\(^-\), unlike with methyl acetate. The alkyl reaction pathway available to the methyl acetate is via B\(_2\)Al only, but ethyl acetate may also undergo an E2 elimination to yield acetate ion as a product. The increased yield must be due to an E2 pathway. Overall, the reaction rates are quite fast and are very efficient for most of the nucleophiles, except for NCCH\(_2\)\(^-\).
Another difference between the reactions of methyl and ethyl acetate is that the reaction with methoxide as a nucleophile yields exclusively the (M-H)^- product with methyl acetate, but the (M-H)^- and acetate ions are formed as products with ethyl acetate. The acetate ion product is obviously formed from an E2 reaction at the alkyl group with ethyl acetate.

Finally, the reaction of F^- with ethyl acetate produces only FC(=O)CH_2^- (54%) and CH_3CO^- (46%). The former is generated from a BAC2 mechanism followed by proton transfer, while the latter is produced from an E2 or a BAL2 pathway. The increased reaction rate and efficiency for F^- with ethyl acetate (as compared to methyl acetate) also suggests that the E2 pathway is dominating.

Reactions of β- and γ-lactones The reactions of β-propiolactone with all of the ions considered here are much faster than the acyclic counterparts; however, the chemistry is not very interesting (Table 3.6). The observed reactions are dominated by proton transfer to yield the (M-H)^- ion. Moreover, the reactions with γ-butyrolactone also produce the corresponding (M-H)^- ion. The acidity of β-propiolactone appears to be lower than 370 kcal-mol^{-1}, but we have not resolved that value any further at this point.

The only exception is CH_3S^- with β-propiolactone which produces an adduct of some kind. Experiments to determine the nature of the adduct have been attempted. In order to understand if a simple ion-molecule complex was being formed, the reaction was carried out at three different pressures in hopes that the higher pressure would favor
complex formation and the reaction rates would increase. However, if there is a pressure
dependence, it is within our experimental error (Table 3.6).

Attempts were made to observe hydrogen-deuterium exchange between the adduct and \( \text{CD}_3\text{OD} \) or \( \text{CD}_3\text{CO}_2\text{D} \), but these studies were not successful. The attempt to determine the acidity of the adduct also met with little success. The adduct would not undergo proton transfer under the timescale of the experiment. The small amount of \( \text{H/CD} \) exchange that was observed was not convincing, but a small amount (~10%) occurs with acetic acid. This signal decrease may actually be the protonation of a reactant and thereby decreases the amount of product seen. The major limitation for these experiments is simply the length of the reaction region (~0.5 m) of our FA as we have to make the reactants, then the adduct ion and finally study its subsequent chemistry. The product of this reaction may also be the ring-opened species formed via the \( \text{Bal2} \) pathway, which is commonly seen in solution.\textsuperscript{25}

Another limitation of our FA is seen in attempts to gain reaction rates with \( \gamma \)-butyrolactone and larger lactones, such as \( \delta \)-valerolactone and \( \epsilon \)-caprilactone. These lactones do not have sufficient vapor pressures at room temperature in order to obtain consistent flow rates of the neutral reagent that is needed to generate accurate kinetic measurements. However, since proton transfer was the only significant channel observed with \( \beta \)-propiolactone and \( \gamma \)-butyrolactone, we did not investigate these reactions any further.
Table 3.6. Rates and Ionic Product Distributions for Negative Ion Reactions with Lactones.

<table>
<thead>
<tr>
<th>Ion (A⁻)</th>
<th>ΔH$_{calc}$ (HA)</th>
<th>P (torr)</th>
<th>Neutral Reagent</th>
<th>Ionic Products</th>
<th>Rxn Path</th>
<th>Rate</th>
<th>ADO Rate</th>
<th>Eff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>391</td>
<td>0.5</td>
<td>β-propiolactone</td>
<td>(M-H)$^-$</td>
<td>PT</td>
<td>45.</td>
<td>± 3.</td>
<td>41.5</td>
</tr>
<tr>
<td>CH$_3$O⁻</td>
<td>380</td>
<td>0.5</td>
<td>β-propiolactone</td>
<td>(M-H)$^-$</td>
<td>PT</td>
<td>30.</td>
<td>± 2.</td>
<td>33.1</td>
</tr>
<tr>
<td>F⁻</td>
<td>371</td>
<td>0.5</td>
<td>β-propiolactone</td>
<td>(M-H)$^-$</td>
<td>PT</td>
<td>39.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$S⁻</td>
<td>357</td>
<td>0.5</td>
<td>β-propiolactone</td>
<td>CH$_3$S(β-lactone) Adduct</td>
<td>7.9 ± 0.6</td>
<td>28.9</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8</td>
<td></td>
<td>CH$_3$S(β-lactone) Adduct</td>
<td>8.2 ± 0.4</td>
<td>28.9</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td>CH$_3$S(β-lactone) Adduct</td>
<td>8.2 ± 0.6</td>
<td>28.9</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>OH⁻</td>
<td>391</td>
<td>0.5</td>
<td>γ-butyrolactone</td>
<td>(M-H)$^-$</td>
<td>PT</td>
<td>12.3</td>
<td>± 0.3</td>
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</tr>
<tr>
<td>CH$_3$O⁻</td>
<td>380</td>
<td>0.5</td>
<td>γ-butyrolactone</td>
<td>(M-H)$^-$</td>
<td>PT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCH$_2$⁻</td>
<td>373</td>
<td>0.5</td>
<td>γ-butyrolactone</td>
<td>(M-H)$^-$</td>
<td>PT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$NCH$_3$⁻</td>
<td>356</td>
<td>0.5</td>
<td>γ-butyrolactone</td>
<td>No Observed Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Rates for the reactions with γ-butyrolactone, δ-valerolactone and ε-caprolactone were tried with little or no success due to vapor pressure problems (see text).
(b) Values from the Bartmess Tables.
(c) % Yields are 100%, extrapolated for a zero flow rate of neutral reagent in STP cm$^2$-sec$^{-1}$.
(d) Rates in units of (10$^{-10}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$) and the reported errors are one standard deviation of at least triplicate measurements.
(e) Rates in units of (10$^{-10}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$) and the polarizability for β-propiolactone is approximated using group additivity.
(f) Efficiency = (experimental rate/ADO rate).
Conclusions

Some interesting trends have been observed. For example, NCCH$_2^-$ controls the reactivity with all of the esters considered here, and the reaction pathways are dominated by the $\text{Bac}_2$ mechanism. For nucleophilic reactions, the ethyl esters typically react faster than the methyl esters, and the reactivity with the ethyl esters are dominated by chemistry at the alkyl group. This change is due to the availability of the E2 pathway for alkyl reactions with the ethyl esters.

A comparison of formyl and acetyl esters demonstrates that the formyl esters react more readily with less basic ions, but the rate of reaction of formyl esters with more basic ions are slower than the acetyl esters. The main reason for the increased reaction rate of basic nucleophiles with the acetyl esters is the availability of the proton transfer pathway. The acidity ($\Delta H_{\text{acid}}$) of the formyl esters is approximately 391 kcal-mol$^{-1}$, while the acidity of the $\alpha$-hydrogen in the acetyl esters is approximately 374 kcal-mol$^{-1}$. Other reaction pathways do not compete effectively when proton transfer is favorable (i.e. exothermic).

The Riveros pathway dominates the reactivity of methyl formate. The $\text{Bac}_2$ pathway is observed to only a very small extent with methyl formate as a substrate. $F^-$ ion demonstrates some interesting reactivity with the esters considered here. Experimental and computational (B3LYP/6-31+G(d)) results are in excellent agreement for the potential energy surface of $F^-$ with methyl formate. The Riveros pathway for $F^- + \text{HCO}_2\text{CH}_3$ is calculated to have a small activation barrier (as compared to $\text{Bac}_2$), and variable temperature studies demonstrate an increase in the Riveros product as the temperature is increased from 298 to 448 K.
Moreover, from a mechanistic sense, the Riveros pathway proceeds through nucleophilic attack at the carbonyl carbon, and the only difference between the Riveros and Bac2 pathways is whether the alkoxide leaving group abstract a proton from the formyl or acetyl group or simply departs from the complex, respectively.

Further examples of nucleophilic reactivity with carbonyl groups will be presented in due course from both experimental and computational approaches.
LIST OF REFERENCES


CHAPTER 4

COMPARISON OF NUCLEOPHILIC ACYL SUBSTITUTION (Bac2) VERSUS REACTIONS AT THE ALKYL GROUP (BαL2 AND/OR E2) IN METHYL AND ETHYL ESTERS

Introduction

The carbonyl moiety (C=O) is fundamentally important in organic chemistry as well as in biological systems. For instance, carbonyl groups are involved in a variety of enzyme functions under aqueous conditions. The reaction pathways that occur in solution are fairly well understood, and the stabilization effects of the carbonyl group have also been well studied. However, the requirements for reactivity for carbonyl groups is less clear. The solvent effect (typically water) may be quite dramatic. Solvent effects on other important reactions, such as the Sn2 mechanism, have recently been investigated. By investigating reactions with carbonyl groups in the gas phase, the intrinsic reactivity of the carbonyl group can be systematically examined and the importance of the leaving group as well as the electronic and steric properties on the reaction path can be explored.

Gas-phase studies with carbonyl compounds have utilized both ion cyclotron resonance (ICR) and flowing afterglow (FA) methods. The FA has been shown to be particularly reliable in determining rate coefficients for gas-phase reactions due to the
presence of a bath gas (typically helium) and the moderately high pressure in the reaction region. Recent advancements to the FA technique, as reviewed by Graul and Squires, include the selected ion flow tube (SIFT), collision induced dissociation (CID), drift capability and temperature variability. These techniques have extended the role of the FA method for studying gas-phase reactions. These advancements allow for product determination (via the mass-to-charge ratio) as well as for probing the molecular structure via subsequent ion-molecule reactions or CID experiments.

A number of researchers have examined the reactivity of esters in the gas phase. The reactions shown in Scheme 4.1 have been observed in FA experiments with ethyl esters and either H$_2$N$^-$ or H$^{18}$O$^-$. The pathways shown in Scheme 4.1 are (a) nucleophilic acyl substitution (Bac2), (b) Sn2 displacement (Bal2) which can occur on either alkyl group, (c) E2 elimination, (d) decarbonylation (loss of CO) pathways which occurs for formyl esters, and (e) proton transfer (PT) which may also be followed by fragmentation.

In this study, we have examined the reactions of methyl and ethyl esters with H$_2$N$^-$ or H$^{18}$O$^-$ in order to determine the product yields of Bac2 versus Bal2 or E2. The reactions of H$_2$N$^-$ readily reveals if the Bac2 pathway has occurred; however, isotopically labelled experiments with H$^{18}$O$^-$ are required to distinguish Bac2 from Bal2/E2 pathways.

**Experimental Methods**

These reactions were studied using our home-built flowing afterglow which has been previously described. Briefly, ions are generated via electron impact ionization and traverse the length of the flow tube (~1 m) by the constant flow of a helium buffer gas. Neutral reagents are added downstream for reactions to occur in situ. The charged species
Scheme 4.1. The gas-phase reactions that have been observed and their possible mechanistic routes.

where X = $^{18}$O or NH
from these reactions are subsequently monitored using quadrupolar mass spectrometry. These reagents can be added at different locations along the length of the flow tube; therefore, ion-neutral reactions can take place with various amounts of time which allows for kinetics of these reactions to be determined.

In this work, the helium (Praxair, ≥99.995%) bath gas is further purified by passing the gas through a copper coil, packed with 4Å molecular sieves, that is submerged in liquid nitrogen. The purified helium is then passed over the filament of the EI source. Electron impact on NH$_3$ (AGA, 99.99%) generates NH$_2^-$ which can subsequently be reacted with H$_2^{18}$O (Cambridge Isotopes, 97%) in order to form H$_2$O$^{18}$O$^-$ via a facile proton transfer reaction.

The neutral reagents, HCO$_2$CH$_3$ (Aldrich, 97%), HCO$_2$CH$_2$CH$_3$ (Baker, 98.1%), CH$_3$CO$_2$CH$_3$ (Aldrich, 99+%), CH$_3$CO$_2$CH$_2$CH$_3$ (Mallinckrodt, 99.9%), (CH$_3$)$_3$CCO$_2$CH$_3$ (Acros, 99%), (CH$_3$)$_3$CCO$_2$CH$_2$CH$_3$ (Acros, 98%), CF$_3$CO$_2$CH$_3$ (Acros, 99%), CF$_3$CO$_2$CH$_2$CH$_3$ (Acros, 99%), and CF$_3$CO$_2$CH$_2$CF$_3$ (Aldrich 99%), were available from commercial sources and were not purified any further.

Upon reaction with a neutral reagent, product ions can be observed. The yield of each product ion was determined by taking the average ratio of the respective integrated peak areas. The more accurate measure measurement was not done for all of these compounds as the rates of these reactions were not determined.

**Results**

The reactions of NH$_2^-$ and H$^{18}$O$^-$ with methyl and ethyl formate and methyl and ethyl acetate have been studied and the results are presented in Table 4.1. Also, methyl and
Table 4.1. Use of H\textsuperscript{14}O\textsuperscript{-} and H\textsubscript{2}N\textsuperscript{+} as probes into the reactivity of esters at the carbonyl carbon versus the alkyl substituent at 0.5 torr and 298K.

<table>
<thead>
<tr>
<th>Esters</th>
<th>Reactions with H\textsubscript{2}N\textsuperscript{+}</th>
<th>Reactions with H\textsuperscript{14}O\textsuperscript{-}</th>
<th>Published Results* for Reactions with H\textsuperscript{14}O\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BAC2</td>
<td>BAC2 (or E2)</td>
<td>BAL2 (or E2)</td>
</tr>
<tr>
<td>HCO\textsubscript{2}CH\textsubscript{3}</td>
<td>81%</td>
<td>19%</td>
<td>79%</td>
</tr>
<tr>
<td>CH\textsubscript{3}CO\textsubscript{2}CH\textsubscript{3}</td>
<td>88%</td>
<td>12%</td>
<td>57%</td>
</tr>
<tr>
<td>(CH\textsubscript{3})\textsubscript{2}CCO\textsubscript{2}CH\textsubscript{3}</td>
<td>76%</td>
<td>24%</td>
<td></td>
</tr>
<tr>
<td>CF\textsubscript{3}CO\textsubscript{2}CH\textsubscript{3}</td>
<td>42%</td>
<td>58%</td>
<td></td>
</tr>
<tr>
<td>PhCO\textsubscript{2}CH\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}OCO\textsubscript{2}CH\textsubscript{3}</td>
<td>68%</td>
<td>32%</td>
<td></td>
</tr>
<tr>
<td>HCO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}</td>
<td>26%</td>
<td>74%</td>
<td>19%</td>
</tr>
<tr>
<td>CH\textsubscript{3}CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}</td>
<td>26%</td>
<td>74%</td>
<td>11%</td>
</tr>
<tr>
<td>(CH\textsubscript{3})\textsubscript{2}CCO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}</td>
<td>63%</td>
<td>37%</td>
<td></td>
</tr>
<tr>
<td>CF\textsubscript{3}CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}</td>
<td>32%</td>
<td>66%</td>
<td></td>
</tr>
<tr>
<td>CF\textsubscript{3}CO\textsubscript{2}CH\textsubscript{2}CF\textsubscript{3}</td>
<td>&lt; 5%</td>
<td>&gt;95%</td>
<td></td>
</tr>
<tr>
<td>PhCO\textsubscript{2}CH\textsubscript{2}CF\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{2}CH\textsubscript{3}OCO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}</td>
<td>22%</td>
<td>78%</td>
<td></td>
</tr>
</tbody>
</table>

(a) Reference 13.
ethyl pivalate, methyl and ethyl trifluoroacetate, and 2',2',2'-trifluoroethyl trifluoroacetate were examined with H$^{18}$O$^-$. These reactions will differentiate between the coincident mechanisms for formation of the carboxylate ion (RCO$_2^-$) product. These ion-molecule reactions have other products besides those seen from BAC2 and BAL2/E2 which have been ignored for the purpose of this discussion.

When overlap occurs between our higher pressure FA studies and the results published by Takashima and Riveros, they show good agreement. Most importantly in both pressure regimes, the same pathways are observed as major products in all cases (Table 4.1).

Both NH$_2^-$ and H$^{18}$O$^-$ show a preference for BAC2 over the BAL2 reaction pathway in reactions with methyl formate (Table 4.1). The preferences are 4.3 and 3.8 to 1 in favor of the BAC2 pathway for NH$_2^-$ and H$^{18}$O$^-$, respectively. These similarities show that the nucleophilicity of the ion does not discriminate between the two pathways. The amount of BAC2, that is observed, lends support to the previous result that the CH$_3$O$^-$ product formed in the reaction (Chapter 3) is produced via a Riveros reaction. The mechanism of the CH$_3$O$^-$ formation may be due to a direct fragmentation or via nucleophilic attack on the carbonyl carbon followed by fragmentation.

Contrary to the preference for nucleophilic attack on the carbonyl carbon in methyl formate, reactions with ethyl formate prefers the E2 or BAL2 mechanisms. The BAL2 pathway must be a small contributor because the BAL2 pathway should be even less likely in the ethyl case (more steric hinderance) than in the methyl case. In fact, the preference for E2 is 2.8:1 for NH$_2^-$ and 4.2:1 for H$^{18}$O$^-$. 

92
These trends are reproduced for the methyl and ethyl acetates. Methyl acetate still favors the nucleophilic acyl substitution pathway and is independent of the chosen nucleophile. Furthermore, ethyl acetate also prefers to undergo an E2 reaction as in ethyl formate. With $\text{H}_2\text{N}^-$, the degree of the preference even matches the formate esters within experimental error. With methyl acetate and $\text{H}_2\text{N}^-$, the dominant product is proton transfer to generate the $(\text{M-H})^-$ anion; and for the $\text{Bac2}$ and $\text{Bal2}$ pathways, the only observed product is from the $\text{Bac2}$ pathway, as expected, by the ratio of $\sim 8:1$ (Table 4.1).

However, the amount of $\text{H}^{18}\text{O}^-$ reaction with methyl or ethyl acetate which occurs at the alkyl group increases by a factor of 3 and 2, respectively. This implies that the acetyl group is hindering the reaction at the carbonyl carbon. The explanation for this observation can be two-fold. The first is that the added steric bulk of $\text{CH}_3$, as compared to H, slows the reaction at the carbonyl carbon. The second explanation is that the $\alpha$-H reacts with the nucleophile as it attacks the carbonyl compound. Alas, another system must be studied that differentiates these explanations.

Therefore, the reactions of the methyl and ethyl pivalate with $\text{H}^{18}\text{O}^-$ were performed. If the steric hinderance explanation is correct, the increased steric bulk of the $\text{C(CH}_3\text{)}_3$ group, as compared to $\text{CH}_3$, should only drive the reaction away from the $\text{Bac2}$ pathway. However, the exact opposite effect is seen. The $\text{Bac2}$ reaction at the carbonyl carbon is still favored for both the methyl and the ethyl pivalates. Therefore, the $\alpha$-H reacts with the nucleophile as it approaches the carbonyl carbon, and proton transfer occurs with the acetyl derivatives.
Not only is the steric bulk not a factor in the reactivity of these compounds, but the pivalate seems to increase the amount of reaction at the carbonyl carbon. This contradicts the postulate that the carbonyl carbon would be less electrophilic with more alkyl groups that can donate electron density to the carbonyl carbon. In fact, the opposite is the case. What is, therefore, the origin of these results? We currently postulate that the tert-butyl group aids in complexing the incoming nucleophile (see Figure 3.5) and biases the system towards $\text{BAC}_2$ due to proximity effects.

The electronic preference for the $\text{BAC}_2$ pathway was studied further. The use of methyl and ethyl trifluoroacetyl esters should place strongly electron withdrawing substituents adjacent to the carbonyl carbon and should increase the electrophilicity of the carbonyl carbon. Therefore, the $\text{BAC}_2$ products were predicted to increase. However, the exact opposite trend is observed, and the $\text{BAL}_2$ pathway is favored. Therefore, it can be postulated that electron-electron repulsion between the fluorine lone pairs and the incoming anionic nucleophile could hinder the approach to the neighboring carbonyl carbon. Furthermore, $\text{CF}_3\text{CO}_2^-$ is a very good leaving group and explains the increased alkyl reactivity observed (Table 4.1).

Therefore, the reaction of $(2',2',2'$-trifluoroethyl) $2,2,2$-trifluoroacetate ($\text{CF}_3\text{CO}_2\text{CH}_2\text{CF}_3$) with $\text{H}^{18}\text{O}^-$ was studied. The trifluoroethyl group should prevent the E2 pathway and cause the same electron-electron repulsion for the nucleophile to approach either the alkyl or acyl carbon. Furthermore, the reaction is biased toward acyl addition ($\text{BAC}_2$) based on the need to undergo $\text{BAL}_2$ at a secondary center. However, the only product seen from the reaction is via the $\text{BAL}_2$ pathway. Based on our signal-to-noise the ratio of $\text{BAL}_2$ to $\text{BAC}_2$ is $>20:1$. This estimate is conservative.
Conclusions

The reactions with H^{18}O− has been a good technique to elucidate the mechanistic preferences for the reactions of hydroxide with esters. The methyl esters tend to be more reactive at the carbonyl carbon than at the methyl group. However, the ethyl esters are more reactive at the alkyl substituent. These preferences are simply guidelines for expected results from other methyl and ethyl esters.

Further studies must be undertaken to discern why the reactions with ethyl pivalate favors the reaction at the carbonyl carbon. Furthermore, the trifluoroacetyl esters behave very differently than expected.
LIST OF REFERENCES


CHAPTER 5

REACTIONS OF OTHER CARBOXYLIC ACID DERIVATIVES

Introduction

The reactions of carboxylic acid derivatives other than those of esters are also of interest. When the derivative is the acid halide, these reactions have been fairly well studied by Brauman, who utilized ion cyclotron resonance mass spectrometry (ICR). The comparison of these values to our flowing afterglow (FA)^2 studies, as seen in Chapter 2, have shown that the rate coefficients obtained by ICR experiments were probably in error. Therefore, the experimental results that have been published to date in this area are in doubt.

DePuy and co-workers^3 have probed the reactivity of N,N-dimethylformamide in the gas phase using both the flowing afterglow-selected ion flow tube (FA-SIFT)^4 and ICR techniques. In this study, only a few ions were used and a number of unanswered questions remain. For instance, the reaction of methoxide ion with N,N-dimethylformamide reportedly yields only a complex or adduct. Is the barrier for the BAC2 reaction too large? Furthermore, why is BAL2 not observed? These reactions, which have been observed at room temperature with esters (Chapter 3) are perhaps not accessible for the amides. Nevertheless, these reactions may become accessible at higher temperatures. Therefore, variable temperature studies of these reactions may reveal interesting information about the potential energy surfaces.
Riveros and coworkers,⁵ as well as Bartmess and coworkers,⁶ have studied the reactions of a few thioesters in the gas phase. These reactions have been observed with different ICR instruments, and the reaction rate coefficients and product distributions should be compared to the higher pressure results from a FA experiment. Other than the occasional reactivity of a carboxylic acid derivative as previously stated in earlier chapters, this area is in need of a systematic study.

Despite the sparse experimental data, Lee and coworkers⁷ have started to computationally investigate the BAc2 pathway of a variety of carboxylic acid derivatives. Jorgensen⁸ has also investigated the acid halides computationally. Jorgensen was most interested in a method for comparison of computational results to the condensed phase.

Experimental Methods

The experimental methods have been described in detail in Chapter 2. In short, the reactions are carried out in our home-built VTFA. In the flow tube, the ions are generated via electron impact (EI) ionization of bath gas (typically helium) and neutral precursors. These ions traverse the length (~1 m) of the flow tube to the detection region where the ions are extracted. The ions are then filtered by their mass-to-charge ratio and detected with an electron multiplier (EM). The resolution of the 5/8 inch quadrupole mass filter is limited to unit mass separation. Therefore, HCO₂⁻ and CH₃CH₂O⁻ (m/z = 45) are not differentiated by our mass filter.

The ion-molecule reactions are carried out in ~0.5 torr of helium gas. This acts to minimize diffusional loss of ions to the walls by establishing laminar flow, and the bath gas thermalizes the ions to a known energy. The amount of energy in the system can be
changed by increasing or decreasing the temperature of the bath gas and the walls of the flow tube.

In order to study reaction kinetics, neutral reagents are added downstream at different locations along the length of the flow tube. The ion-neutral reactions can be monitored as a function of distance/time, and rate coefficients can be determined under conditions of pseudo-first order kinetics. The reported rates are averages of at least three measurements (unless noted otherwise). Most of the rates reported here were obtained at 298 K and 0.5 torr, but some have been determined as a function of temperature.

Upon reaction with a neutral reagent, product ions can be observed. The yield of each product ion was determined by extrapolating the normalized ion percentage to the zero flow limit of the neutral reagent. This method allows for the determination of primary and secondary ions and has been well employed in the literature. Even with this extrapolation, the accuracy of the product determination should be considered as ±10%. These percent yields are taken as the average of three different initial flow rates of the neutral reagent where each is extrapolated to the zero flow limit of the neutral compound. In the cases where the rate was not determined, the product yields are not extrapolated to the zero flow rate limit of the neutral reagent. Instead, the relativistic terminology (major and minor) will be used.

In this work, the helium (Praxair, ≥99.995%) bath gas is further purified by passing the gas through a copper coil, packed with 4Å molecular sieves, that is submerged in liquid nitrogen. The purified helium is then passed over a thoriated iridium or rhenium filament of the EI source. H$_2$N$^-$ is then formed from electron impact ionization of NH$_3$ (AGA, 99.99%). For some experiments, H$_2$N$^-$ was used to deprotonate H$_2$O for generating HO$^-$, but on most occasions, HO$^-$ was generated by dissociative electron
attachment on N₂O (AGA, 99.5%) followed by hydrogen atom abstraction from CH₄
(AGA, 99.9%). HO⁻ or H₂N⁻ was subsequently used to deprotonate CH₃OH (Fisher,
99.9%), CD₃OD (Cambridge Isotopes, 99.8%), CH₃CN (Mallinckrodt, 99.9%), and
CH₃NO₂ (Aldrich, 96%) to form CH₃O⁻, CD₃O⁻, NCCH₂⁻, and O₂NCH₂⁻, respectively.
The reaction of HO⁻ with CH₃SSCH₃ (Aldrich, 98%) generated CH₃S⁻. Finally, F⁻ was
formed by electron impact upon NF₃ (Air Products, 99.5%). These compounds were used
as provided by the manufacturer. The neutral reagents, HC(=O)N(CH₃)₂ (Baker, 99.5%),
CF₃C(=O)Cl (Aldrich, 97%), CF₃CO₂CH₂CF₃ (Aldrich, 99%), CF₃C(=O)SCH₃
(Mallinckrodt, 98%), and ClCH₂CO₂CH₂CH₃ (Acros, 99%), were used as provided by
the commercial sources.

Results

The results presented here represent an attempt to study the chemistry of a wide
assortment of various carboxylic acid derivatives. The results are summarized in Table 5.1
and discussed in further detail below.

Reactions of N,N-Dimethylformamide The reaction of CH₃O⁻ with N,N-
dimethylformamide (HC(=O)N(CH₃)₂, DMF) has been studied with the FA-SIFT
technique by DePuy and coworkers.² The reported reaction rate is 3.8 x 10⁻¹⁰ cm³-
molecule⁻¹-sec⁻¹ at room temperature. The only product that was reported was the adduct.
The rate of the reaction at room temperature is reproduced in our FA experiment
Table 5.1. Reactions of Carboxylic Acid Derivatives with Various Nucleophiles.

<table>
<thead>
<tr>
<th>Acid Derivative</th>
<th>Ion (A')</th>
<th>ΔH (kJ/mol)</th>
<th>Ionic Products (Yield)</th>
<th>Rate (mM/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC(=O)N(CH₃)₂</td>
<td>HO⁻</td>
<td>391</td>
<td>HO⁻(H₂O) (100%)</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td></td>
<td>390</td>
<td>CH₃O⁻(CH₃OH) (100%)</td>
<td></td>
</tr>
<tr>
<td>F⁻</td>
<td></td>
<td>381</td>
<td>F⁻HC(=O)H(CH₃)₂ (100%)</td>
<td>10. ± 1.</td>
</tr>
<tr>
<td>CF₃C(=O)Cl</td>
<td>HO⁻</td>
<td>391</td>
<td>Cl⁻ (80%); CF₃Cl⁻ (20%)</td>
<td></td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td></td>
<td>380</td>
<td>Cl⁻ (100%)</td>
<td>11. ± 1.</td>
</tr>
<tr>
<td>NCCH₂⁻</td>
<td></td>
<td>373</td>
<td>Cl⁻ (100%)</td>
<td>14. ± 1.</td>
</tr>
<tr>
<td>F⁻</td>
<td></td>
<td>381</td>
<td>Cl⁻ (100%)</td>
<td>11.2 ± 0.5</td>
</tr>
<tr>
<td>CH₃S⁻</td>
<td></td>
<td>367</td>
<td>Cl⁻ (100%)</td>
<td>15. ± 1.</td>
</tr>
<tr>
<td>O₂NCH₂⁻</td>
<td></td>
<td>356</td>
<td>Cl⁻ (100%)</td>
<td>13. ± 1.</td>
</tr>
<tr>
<td>CF₃CO₂CH₂CF₃</td>
<td>HO⁻</td>
<td>391</td>
<td>CF₃CO₂⁻ (100%)</td>
<td></td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td></td>
<td>380</td>
<td>CF₃CO₂⁻ (100%)</td>
<td></td>
</tr>
<tr>
<td>NCCH₂⁻</td>
<td></td>
<td>373</td>
<td>CF₃CO₂⁻ (100%)</td>
<td></td>
</tr>
<tr>
<td>CH₃S⁻</td>
<td></td>
<td>357</td>
<td>CF₃CO₂⁻ (100%)</td>
<td></td>
</tr>
<tr>
<td>O₂NCH₂⁻</td>
<td></td>
<td>356</td>
<td>CF₃CO₂⁻ (100%)</td>
<td></td>
</tr>
<tr>
<td>CF₃C(=O)SCH₂</td>
<td>HO⁻</td>
<td>391</td>
<td>CH₃S⁻ (maj.); CF₃C(=O)S⁻ (maj.); (M-H)⁻ (min.)</td>
<td></td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td></td>
<td>380</td>
<td>CH₃S⁻ (maj.); (M-H)⁻ (min.)</td>
<td></td>
</tr>
<tr>
<td>NCCH₂⁻</td>
<td></td>
<td>373</td>
<td>CF₃C(=O)⁻=CHCN (100%)</td>
<td></td>
</tr>
<tr>
<td>F⁻</td>
<td></td>
<td>371</td>
<td>CH₃S⁻ (maj.); CF₃C(=O)S⁻ (min.)</td>
<td></td>
</tr>
<tr>
<td>CH₃S⁻</td>
<td></td>
<td>357</td>
<td>adduct (100%)</td>
<td></td>
</tr>
<tr>
<td>O₂NCH₂⁻</td>
<td></td>
<td>356</td>
<td>CF₃C(=O)⁻=CHNO₂ (100%)</td>
<td></td>
</tr>
<tr>
<td>ClCH₂CO₂CH₂CH₃</td>
<td>F⁻</td>
<td>371</td>
<td>F⁻(CH₂CH₃OH) (maj.)</td>
<td>23. ± 2.</td>
</tr>
</tbody>
</table>

(a) See text about secondary products that are formed.
[(5.0 ± 0.5) \times 10^{-10} \text{ cm}^3\text{-molecule}^{-1}\text{-sec}^{-1}]. However, the observed product in our experiment is the proton-bound dimer (CH$_3$O$^-$\cdot\cdot\cdotH$^+$\cdot\cdot\cdotOCH$_3$) which has a mass-to-charge ratio of 63. This is most likely due to ligand switching between the initial [CH$_3$O$^-$\cdot\cdot\cdotHC(=O)N(CH$_3$)$_2$] adduct and excess CH$_3$OH available in the reaction which is possible in the FA experiment, whereas there is no excess CH$_3$OH in the FA-SIFT experiment.

In order to probe this reaction further, the reaction was carried out at multiple temperatures. The products at all temperatures is the proton-bound dimer. However the rate of the reaction is temperature dependent (Figure 2.10). These results are also discussed in Chapter 2. However, the reaction of HO$^-$ with HC(=O)N(CH$_3$)$_2$ shows more diverse chemistry. Unfortunately, a rate for this reaction has not been obtained, but the products as a function of inlet have been determined. Besides observing the proton-bound dimer of hydroxide ion (HO$^-$\cdot\cdot\cdotH$^+$\cdot\cdot\cdotOH), other products include the Riveros product (HO$^-$\cdot\cdot\cdotHN(CH$_3$)$_2$), formate ion, the adduct [HO$^-$\cdot\cdot\cdotHC(=O)N(CH$_3$)$_2$] and the product resulting from proton transfer from DMF. The amount of each of these ions at various distances are shown in Figure 5.1.

The reaction rate for the reaction of F$^-$ with HC(=O)N(CH$_3$)$_2$ has been determined to be (1.0 ± 0.1) \times 10^{-9} \text{ cm}^3\text{-molecule}^{-1}\text{-sec}^{-1}. The only product formed in the reaction is an adduct (or complex) with m/z = 92. This adduct may be a tetrahedral intermediate but the loss of (CH$_3$)$_2$N$^-$ as a leaving group is endothermic by 37 kcal-mol$^{-1}$. In this case,
Figure 5.1. Products of $\text{HO}^- + \text{HC}(=\text{O})\text{N(CH}_3\text{)}_2$ as a function of inlet.

Inlet for addition of N,N-Dimethylformamide
ligand exchange does not take place. However, no further attempts were made to test if any ligand switching could be driven with other neutral reagents.

Reactions of Carboxylic Acid Chlorides As reported in Chapter 2, the reactions of trifluoroacetyl chloride has been investigated with $\text{F}^-$, $\text{CH}_3\text{O}^-$, $\text{CH}_3\text{S}^-$, $\text{NCCH}_2^-$, and $\text{O}_2\text{NCH}_2^-$. The reaction with $\text{HO}^-$ has also been investigated; however, the rate of this reaction has only been taken twice as there are difficulties when using trifluoroacetyl derivatives (see below). The two experimental rates obtained for this reaction are $(3.8 \pm 0.5)$ and $(1.19 \pm 0.04) \times 10^{-9}$ cm$^3$-molecule$^{-1}$-sec$^{-1}$. The observed ionic products for the reaction of $\text{HO}^-$ with $\text{CF}_3\text{C}(=\text{O})\text{Cl}$ are $\text{Cl}^-$ (major, $\sim 80\%$) and $\text{CF}_3^-$ (minor, $\sim 20\%$), and these products are unique in comparison to the other nucleophiles explored.

For $\text{F}^-$, $\text{CH}_3\text{O}^-$, $\text{CH}_3\text{S}^-$, $\text{NCCH}_2^-$, and $\text{O}_2\text{NCH}_2^-$, the only observed product is $\text{Cl}^-$. However, the rate of formation for $\text{Cl}^-$ ion was much, much greater than the rate of depletion of the reagent ion and is evidence that another mechanism was occurring other than displacement of $\text{Cl}^-$ by the nucleophile. Presumably this mechanism is dissociative electron attachment as electrons are present in the FA's plasma. This hypothesis was supported by simply flowing the $\text{CF}_3\text{C}(=\text{O})\text{Cl}$ reagent into the flow tube where only helium was flowing over the electron impact filament, and large quantities of $\text{Cl}^-$ were then produced.

Another major problem with trifluoroacetyl derivatives, that were alluded to earlier, is that the neutral flow rates continuously decrease, despite their high volatility. The reason
for the decrease in flow is directly due to interactions of the trifluoroacetyl derivatives with the Viton® O-rings that are used throughout our neutral inlet system. The interaction causes decomposition of the O-rings and the inlets subsequently get clogged and renders the inlet useless. Nevertheless, we did pursue studies with other trifluoroacetyl derivatives.

**Reactions with (2',2',2'-Trifluoroethyl) 2,2,2-Trifluoroacetate**

Products were determined for the reactions of HO⁻, CH₃O⁻, CH₃S⁻, NCCH₂⁻, and O₂NCH₂⁻ with (2',2',2'-trifluoroethyl) 2,2,2-trifluoroacetate (CF₃CO₂CH₂CF₃). The major product in these reactions is CF₃CO₂⁻. In two cases, CH₃S⁻ and NCCH₂⁻, the proton-bound adduct with CF₃CO₂⁻ ion is formed. The adduct ions are obviously due to secondary reactions and should be ignored. The interesting trend is that the reaction in these cases are all occurring at the methylene group, via a BAL2 reaction pathway, and not at the acyl carbon. However, this trend shows that the most electrophilic site of CF₃CO₂CH₂CF₃ is the methylene group and is not dependent on the nucleophile strength. Furthermore, this cannot be simply a matter of the enthalpy of reaction. For example, take the case of H¹⁸O⁻ + CF₃CO₂CH₂CF₃, where the products of the reaction at the the methylene and acyl carbons yield the same product with the exception of the label (Table 4.1). In this case, as discussed in Chapter 4, shows a greater than 20:1 preference for attack at the methylene group.
Reactions of Trifluoroacetyl Thioesters The reactions of F\(^-\), HO\(^-\), CH\(_3\)O\(^-\), CH\(_3\)S\(^-\), NCCH\(_2\)\(^-\), and O\(_2\)NCH\(_2\)\(^-\) with CF\(_3\)C(=O)SCH\(_3\) have been studied. The reaction of F\(^-\) produced two product ions which are CH\(_3\)S\(^-\) (major) and CF\(_3\)C(=O)S\(^-\) (minor) resulting from \(\text{Bac}_2\) and \(\text{Bal}_2\) pathways, respectively. As the flow rate of CF\(_3\)C(=O)SCH\(_3\) decreases, the amount of CH\(_3\)S\(^-\) increases. Again due to flow rate complications with trifluoroacetyl derivatives, accurate rate coefficients for these reactions could not be determined.

The reaction with HO\(^-\) as the nucleophile results in the formation of two major product ions: CH\(_3\)S\(^-\) (\(\text{Bac}_2\)) and CF\(_3\)C(=O)S\(^-\) (\(\text{Bal}_2\)). A minor ion (m/z = 143) derived from proton transfer is also observed. The structure of the ion was not conclusively determined, but it is either CF\(_3\)C(=O)SCH\(_2\)\(^-\) or CF\(_3\)C(=O)CH\(_2\)S\(^-\). The latter ion is formed by the loss of thioformaldehyde from the former ion followed by subsequent recombination in the ion-dipole complex.
Reaction of $\text{CH}_3\text{O}^-$ with $\text{CF}_3\text{C}(=\text{O})\text{SCH}_3$ forms $\text{CH}_3\text{S}^-$ and $\text{CF}_3\text{C}(=\text{O})\text{SCH}_2^-$ or $\text{CF}_3\text{C}(=\text{O})\text{CH}_2\text{S}^-$ as the major and minor product ions, respectively. The proton transfer reactions seen in reactions of $\text{HO}^-$ and $\text{CH}_3\text{O}^-$ with $\text{CF}_3\text{C}(=\text{O})\text{SCH}_3$ as well as the reaction of $\text{HO}^-$ with $\text{HC}(=\text{O})\text{N(CH}_3)_2$ are the only examples of proton transfer from an alkyl group observed in these kinds of compounds.

Complexation, or the formation of an adduct, is seen in the reaction of $\text{CH}_3\text{S}^-$ and $\text{CF}_3\text{C}(=\text{O})\text{SCH}_3$. However, with $\text{NCCH}_2^-$ and $\text{O}_2\text{NCH}_2^-$ as nucleophiles, the major product is derived from a $\text{Bac}2$ pathway, followed by proton transfer ($\text{CF}_3\text{C}(=\text{O})^-=\text{CHCN}$ and $\text{CF}_3\text{C}(=\text{O})=\text{CHNO}_2$, respectively).

Reactions of $\alpha$-Chloro Acetyl Esters Finally, the reaction of $\text{ClCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ has been studied with fluoride ion. The rate of the reaction has been determined to be $(2.3 \pm 0.2) \times 10^{-9} \text{ cm}^3\text{-molecule}^{-1}\text{-sec}^{-1}$. The observed products are $\text{Cl}^-$ ($43\%$), $(\text{M-H})^-$ ($37\%$) and $\text{F}^-(\text{HOCH}_2\text{CH}_3)$ ($20\%$). The $\text{Cl}^-$ ion product can be formed via a $\text{Bac}2$ attack on the methylene carbon or via dissociative electron attachment. The $\text{F}^-(\text{HOCH}_2\text{CH}_3)$ product is most likely being formed via an $\text{S}\text{N}2$ pathway which is followed by elimination to form the chloroketene.
However, it may also result from the subsequent fragmentation of the (M-H)$^-$ species to also form chloroketene as a neutral product.

**Conclusions**

We have been able to demonstrate the versatility of our VTFA. Some of the reactions presented here are preliminary, yet the chemistry has been shown to be very diverse. The diversity of the chemistry that can be and has been studied by our FA demonstrates the viability of this technique for the study of a wide array of carbonyl reactions.

There are some concerns noted here that can be avoided with the use of a SIFT (i.e. the fragmentation of neutral reagents via dissociative electron attachment). Other concerns, like the decomposition of O-rings by trifluoroacetyl derivatives, will require more modifications to already existing equipment. However, neither problem is insurmountable as a SIFT is in construction in our laboratory,$^{10}$ and an improved inlet system could be developed.
LIST OF REFERENCES


CHAPTER 6

FUTURE WORK

Introduction

This project has the potential to be extended in many ways. Here are some brief comments, and these topics will be expanded below. First, there are many other esters that can be studied in order to further elucidate the reactivity differences of the methyl and ethyl esters. For instance, the reactions of pivalate and other trifluoroacetyl derivatives should be investigated.

In addition, the reactions of the esters presented here still leave some unanswered questions. For example, the $\text{H}^{18}\text{O}^- + \text{HCO}_2\text{CH}_2\text{CH}_3$ reaction is not definitive enough to differentiate two ions, $\text{HCO}_2^-$ and $\text{CH}_3\text{CH}_2\text{O}^-$, which have common mass-to-charge ratios in our instrument. Another isotopic label is needed in order to discern these two products.

In addition to the labelling studies for the discrimination of product ions, the isotope effect of each for these pathways can be investigated. The isotopic labelling of more lactones should also be investigated. Furthermore, the reactions of other carboxylic acid derivatives should be more exhaustively studied. For example, what occurs in reactions with thioesters (RC(=O)--SR') vs thionoesters (RC(=S)--OR')? And imines and oximes? Another long-term goal is to look at the effects of micro-solvation. Finally, the last major
experimental addition to this work is probing linear free energy relationships in the gas phase.

Furthermore, these reactions should be compared to computational models. For example, the gas-phase reaction of \( F^- + HCO_2CH_3 \) has been probed both experimentally and computationally. The results, seen in Chapter 3, show that the computational model reproduces the experimental results and provides insight into the mechanism of action. In addition, the model can even predict possible changes in product distributions as a function of temperature. Therefore, computational chemistry should be used to further explore carbonyl addition reactions.

**Reactions with Other Esters**

The reactions of methyl and ethyl esters have been studied. The role of the electronic and steric properties of the acyl group needs further study. Reactions of pivalate \(((CH_3)_3CC(=O)-OR)\) and trifluoroacetyl \((CF_3C(=O)-OR)\) esters need to be exhaustively investigated. The pivalate esters should have similar electronic properties as their acetyl counterparts, but the steric bulk of the tertiary butyl group should change the reactivity. And most importantly, the proton transfer reaction that dominates the acetyl ester reactions will be eliminated or minimized for pivalate esters. On the other hand, the trifluoroacetyl derivatives should add very little steric bulk but should change the electronic properties significantly. In this manner, the reactivity of the carbonyl group can be probed over a wide range of steric and electronic characteristics.

Furthermore, the alkyl group of the ester should be varied. For example, the use of propyl and isopropyl groups will elucidate the role that elimination reactions play in the reactivity observed with the ethyl esters. The elimination pathway may also be blocked with fluorines or methyl groups. The fluorines will change the acidity of the leaving group.
thereby changing the reactivity observed. A neopentyl ester would not have an E2 pathway available, and this substitution probably would prevent the BAL2 pathway as well. The neopentyl esters should be studied after the reactions of propyl and isobutyl esters are examined.

**Isotopic Labelling of Esters**

The reactions of hydroxide ion with methyl and ethyl formate as well as methyl and ethyl acetate have shown that many pathways occur in the gas phase. In order to determine the reaction pathways that dominate the reactions, more labelling studies need to be undertaken. For example, the \( \text{HO}^- + \text{HCO}_2\text{CH}_2\text{CH}_3 \) reaction yields an anionic product with a mass-to-charge of 45. This peak can be the \( \text{HCO}_2^- \) anion formed via \( \beta \)-elimination (E2) and/or BAL2 reactions and it can also include \( \text{CH}_3\text{CH}_2\text{O}^- \) from either a Riveros reaction or the BAL2 pathway. The reaction of \( \text{H}^{18}\text{O}^- \) with \( \text{HCO}_2\text{CH}_2\text{CH}_3 \) allows the determination of the BAL2 pathway followed by facile proton transfer mechanism, but this does not answer whether the \( m/z = 45 \) ion is \( \text{HCO}_2^- \) or \( \text{CH}_3\text{CH}_2\text{O}^- \) ion. Reacting \( \text{H}^{18}\text{O}^- \) with the mono-deuterated ethyl formate (\( \text{HCO}_2\text{CHDCH}_3 \)) would allow for the resolution of these questions.

But how is the ethoxide ion being formed for \( \text{HO}^- \) reactions with ethyl esters? At this point, we believe that the ethoxide (and other alkoxides) are formed exclusively via the Riveros reaction because facile proton transfer should occur between the alkoxide ion and the carboxylic acid produced within the ion-molecule complex. However, a direct deprotonation of the formyl hydrogen and then subsequent fragmentation would also
generate $\text{CH}_3\text{CH}_2\text{O}^-$. Therefore, to further differentiate between the Riveros pathway and the $\text{BA}2$ mechanism, which could lead to both the formation of $\text{CH}_3\text{CH}_2\text{O}^-$, the isotope effect for the Riveros reaction should be determined for $\text{HCO}_2\text{CH}_2\text{CH}_3$ vs $\text{DCO}_2\text{CH}_2\text{CH}_3$.

Because the formyl deuterium would be intimately involved in the rate determining step, there should be a large normal (primary) isotope effect for the direct deprotonation. If the ethoxide (or any alkoxide) is produced via the $\text{BA}2$ mechanism (with the more basic nucleophiles), the isotope effect should be a small inverse (secondary) isotope effect. The isotope effect for the Riveros reactions should be large no matter which mechanism (direct or indirect) is operational as long as the deprotonation of the hydrogen is involved in the rate determining step.

Furthermore, the reactions of other isotopically labelled ethyl formates can further probe the reactivity of the ethyl ester. If the majority of the m/z = 45 product is formate ion, then the comparison of those results to the $\text{HCO}_2\text{CHDCD}_3$ reaction should be made. An intra-molecular isotopic labelling study is difficult because of the $\text{H}^{18}\text{O}^-$ used in the reaction.

There are many opportunities for isotopic labelling studies. The isotope effect for other reactions of these methyl and ethyl esters can also be probed. By labelling the methyl group of the methyl esters, the inter-molecular isotope effect can be determined. For example, the reactions of $\text{HCO}_2\text{CD}_3$ would allow for the $\text{BA}2$ reaction to be investigated for the isotope effect. The comparison of the rate of formation of product ions may be more illustrative in this case. Furthermore the reaction with the $\text{HCO}_2\text{CH}_3$ has been
investigated with both CH$_3$O$^-$ and CD$_3$O$^-$, and the HCO$_2$CD$_3$ reaction would further elucidate the reactivity preferences.

Reactivity of Lactones

The enhanced acidity of the lactones dominates the gas-phase reactivity at room temperature. With deuterium labelling, the regioselectivity of the deprotonation can be investigated. Using γ-butyrolactone as the cyclic version of ethyl acetate, one can envision proton transfer from the α-carbon or the β-carbon (analogous to the E2 pathway of ethyl acetate). The latter pathway violates Baldwin’s rules. Another way to probe the other reactivity is to block the proton transfer (with fluorine of methyl groups) that has been determined to occur. Our VTFA should provide insight into these questions.

Furthermore, can other pathways become accessible at higher temperatures? In order to investigate the less volatile reagents such as δ-valerolactone and ε-capriolactone, a heated inlet system may be desirable. This will be discussed in further detail below.
Reactions of Analogs

Reactions with carboxylic acid derivatives (other than esters) are also in need of further investigation. Reactions of the thioesters studied here show that the thioester is more likely to undergo nucleophilic acyl substitution than the oxygen analogs. What makes this leaving group so unique? Does the reactivity of the alkyl group lessen due to sulfur's more electronegative nature? Or is the sulfur anion as a leaving group sufficiently stable to promote this reaction? In order to differentiate between these two effects, the reaction needs to be carried out with a significant number of different thioesters such as

\[
\begin{align*}
\text{H C} & \text{C(=O)S C H}_2 \text{CH}_3, \\
\text{CH}_3 \text{C(=O)S C H}_2 \text{CH}_3, \\
\text{(CH}_3\text{)}_3 \text{C(=O)S C H}_2 \text{CH}_3, \\
\text{HC(=O)S C H}_2 \text{CH}_3, \\
\text{CH}_3 \text{(C(=O)S C H}_2 \text{CH}_3, \\
\text{(CH}_3\text{)}_3 \text{C(=O)S C H}_2 \text{CH}_3, \\
\text{and C F}_3 \text{C(=O)S C H}_2 \text{CH}_3.}
\end{align*}
\]

The reactivity of each one will give some of these answers.

In addition, the leaving group ability of RS\(^-\) can be compared with O\(_2\)NCH\(_2\)\(^-\) and others because of their similar gas phase acidities (CH\(_3\)SH has a \(\Delta H_{\text{acid}} = 357\) while O\(_2\)NCH\(_3\) has a \(\Delta H_{\text{acid}} = 356\) kcal-mol\(^{-1}\)). Therefore, the contribution to the stability of the leaving group can be examined. In the nitro-substituted ketones and aldehydes, the complication of proton transfer arises, therefore deuterated reactions should also be investigated. Even more interestingly, can the reaction of X\(^-\) with an \(\alpha\)-substituted ketone or aldehyde break the carbon-carbon bond? In solution, we have seen that a halogenated carbon can act as a leaving group in the haloform reaction. Is this reactivity also available in the gas phase? How many halides are needed? Does the substituent(s) need to be halides for this reactivity?

Furthermore, the leaving group should not be the only parameter that should be changed. The C=O group can be changed for C=S, C=NH, C=NCH\(_3\), C=NOH, etc.
C=NSH, C=NNH₂, C=CH₂, etc. Each of these groups have a unique partial positive charge on the C=X carbon, and the electrophilic requirements of the carbonyl group can be explored. For example, the reactivity of thionyl (C=S) esters should be less than the corresponding carbonyl (C=O) group.

Micro-Solvation of the Anion

The reactions of anionic nucleophiles with carboxylic acid derivatives represented in this thesis (and the above reactions) only account for reactions of the "naked" anion. However, reactions in solution have solvent molecules associated with the nucleophile and the substrate. These "naked" ion nucleophilic reactions, while important on their own, will gain more significance once they are accompanied by micro-solvation studies (i.e. X⁻(H₂O)ₙ). This extension into the micro-solvation realm should allow for an understanding of the number of solvent molecules that are need for nucleophilic acyl substitution (Bac₂) reactions to dominate the product distribution, as in solution. Nucleophilic acyl substitution reactions do occur in the gas phase, but they are not the favored pathway and may undergo subsequent reactions. For example, the gas-phase reaction of F⁻ with HCO₂CH₃ yields a Riveros product (decarbonylation) via a Bac₂ reaction. Is the addition of just one molecule of solvent (i.e. water) sufficient in order to prevent the Bac₂ reaction from subsequent decarbonylation? Or do you need two? Or three? Or is the number of water molecules deependant on the incoming nucleophile? Micro-solvation studies will be able to answer some of these questions.

Furthermore, does the reaction care what the hydrogen bond donor is for the change in reactivity? Are all hydrogen bond donors the same? In the one solvent molecule case, perhaps all that matters is the hydrogen bond but additional solvent molecules may
provide a network for stabilization. Therefore, does water and methanol impact the reactivity in the same way but just to different degrees? Is the hydrogen bond of the solvent to the ion the most important part of the solvation effect? In other words, what role does the intimate interaction play compared to the role of the pure dielectric effect?

Another question that needs to be answered is the nature of the ion-solvent cluster. Is the ion surface-bound or internalized? It has been shown that fluoride ion is internalized in a water cluster, but the larger halides (i.e. iodide ion) are surface-bound ions. How much “solvation” occurs if the micro-solvated structure is a surface-bound ion? Does a surface bound-ion have the same reactivity with one or two solvent molecules as it does with ten or more?

**Linear Free Energy Relationships**

While linear free energy relationships for benzoyl derivatives have been extensively investigated in solution, there have not been any gas-phase studies to date. Mostly, this is due to the low-volatility of the benzoic acid derivatives. The amount of the \( B\text{AC2} \) pathway that occurs for para-substituted benzoate esters can be monitored as a function of substituent, and the rate of the overall reaction can also be measured. The reactivity of the carbonyl group can therefore be subtly changed.

The problem with these experiments is not synthesizing the para- or meta-substituted methyl benzoate esters, but simply their volatility. Methyl benzoate has been investigated in our laboratory with minimal success because of a lack of sufficient vapor pressure. The only limitation for a linear free energy relationship study is the initial vaporization. Once vaporized, the condensation process can be ignored as the temperature of FA flow tube can be elevated.

Currently, however, we do not have the capability to increase the temperature of our neutral reagent in the vacuum rack, where neutral flow rates are measured. To gain the
ability of a heated vacuum rack, the solution may be as simple as wrapping the entire vacuum rack in heating tape, or it may as complex as designing a jacketed vacuum rack that can be temperature controlled with a constant temperature circulating bath. The latter gives greater control over the temperature of the vacuum rack, but the drawback is the time and expense needed.

The information that would be gained by studying the linear free energy relationships is worth the effort and expense. The implications of defining a reactivity scale for gas phase reactions, whether \( \text{Bac}_2 \) or \( \text{Bal}_2 \) or even proton transfer, will allow for a more intimate understanding of what makes gas-phase ions stable and/or reactive and what the driving forces are for the reaction based on the substituent attached to the carbonyl group.

**Computational Chemistry**

One computational surface for a reaction studied experimentally has been shown in Chapter 3. In this example, the products of \( \text{F}^- + \text{HCO}_2\text{CH}_3 \) were predicted and found to be \( \text{F}^-(\text{CH}_3\text{OH}) + \text{CO} \) and \( \text{HCO}_2^- + \text{CH}_3\text{F} \). However, the more exothermic enthalpy of reaction would predict that \( \text{HCO}_2^- + \text{CH}_3\text{F} \) should be the major product. This is not the case, as the Riveros product \( (\text{F}^-(\text{CH}_3\text{OH}) + \text{CO}) \) is observed in greater excess. The surface of this reaction would even suggest that the barrier for cleaving the C–OCH\(_3\) bond should preclude the reaction. The surface, however, matches all of the experimental data at present and also confirmed a small barrier for the Bac2 mechanism. Therefore, the computations or experiments alone are not as informative as both together.
The other reactions that have been studied would also benefit from computational studies. The potential energy surfaces of the reaction of other nucleophiles with $\text{HCO}_2\text{CH}_3$ along with a study of $\text{F}^-$ with other carboxylic acid derivatives should be examined. In this way, the experiments can be checked by theory. Knowing that the computational model for anionic reactions with carbonyl groups is quantitatively accurate, the extension to the reactions of synthetically difficult or unstable molecules can also be performed.

Conclusions

We have designed, fabricated and implemented a variable temperature flowing afterglow. We have demonstrated its utility for studying the reactions for carbonyl groups. We have gained a significant understanding of the reactivity of carbonyl compounds, but there is still more chemistry to explore. Hopefully, this chapter has demonstrated that we have made some progress, but there are many exciting studies that remain to be explored.
LIST OF REFERENCES

LIST OF REFERENCES

Chapter 1


Chapter 2


125


Chapter 3


Chapter 4


Chapter 5


Chapter 6
Flowing Afterglow Variable Temperature Flow Tube

Overview (Top View)

Notes:
- Lo Standard
- PV 84 100 and Style
- Afterglow to be related to a 253 cu. ft. 11 tube. The 100 cu. ft. tube is the same size as the 253 cu. ft. tube.
Flowing Afterglow Variable Temperature Flow Tube

Overview (Side View)
Flowing Afterglow Variable Temperature Flow Tube
Top View (Dimensions)
Flowing Afterglow Variable Temperature Flow Tube

Side View (Dimensions)
Flowing Afterglow Variable Temperature Flow Tube
Pressure Gauge Inlet

Drill notch with a 1/4 in. drill. Then drill thru center with a 1/16 in. drill, keeping the inner surface smooth.

Standard NW16 ISO flange bored to 1/4 in. The NW16 flange will be provided.

All material is 304 SS unless otherwise noted.
All dimensions in Inches
All angles in degrees

Drawing 5 Port FP
Drawn by: Brian T. Frink, Christopher M. Hadad
The Ohio State University
Date: April 30, 1995
Tolerances: 0.X +/-.01 0.0X +/-.001 0.00X +/-.005
NOT TO SCALE
Flowing Afterglow Variable Temperature Flow Tube
Solenoid Inlets (a closer look)

See also Notes
4A-1 and 4A-2

Drill thru with #79.
Details see note 4B-1

Weld here

Notes:
4B-1 For each hole, drill about 0.040 in. deep with a 1/8 in. drill
to within about 0.020 in. of the inner wall. Drill thru center with a
#79 drill. Uniformity among the 17 equally spaced holes (see note
4A-2) is desired. The inner surface is to be kept smooth.

Drawing 4B: Ports FS1-FS7 (Detail) All material is 304 SS unless
otherwise noted.
Drawn by: Brian T. Frink,
Christopher M. Hadad
The Ohio State University
Date: April 30, 1995
Tolerances:
0.X +/- 0.1 0.0X +/- 0.01 0.00X +/- 0.005
NOT TO SCALE

All dimensions in Inches
All angles in degrees

NOT TO SCALE
Flowing Afterglow Variable Temperature Flow Tube
Solenoid Inlets

Make 7 such ports, see
Drawing 2A for positioning.

For details see note 4A-1 and Drawing 4B

For details see note 4A-2 and Drawing 4B

Weld here

Weld here

Weld here

Weld here

Ports FS1 - FS7 have welded NW 16 ISO flanges bored to 1/4 in.
The NW16 flanges will be provided.

Notes:

4A-1: The gap in the inner tube must be at least 0.100 in. thick.
Dimensions given on Drawing 4B

4A-2: Seventeen such holes 20 degrees apart.
There is not a hole in line with the 1/4 in. inlet.

Drawing 4A: Ports FS1-FS7
Drawn by: Brian T. Frink,
Christopher M. Hadad
The Ohio State University
Date: April 30, 1995

Tolerances:
0.0X +/- 0.1  0.0XX +/- 0.01  0.00X +/- 0.005
NOT TO SCALE

All material is 304 SS unless otherwise noted.
All dimensions in inches
All angles in degrees
Flowing Afterglow Variable Temperature Flow Tube
Flange FA and Flange FB

Flange FA

Flange FB

Port FS7

Weld here

Drilled thru for 1/4-20 screws

9.38
10.00

3.25
6.357
6.425

0.25
2.00

0.75

1.00

3.250

0.625

NOT TO SCALE

Drawing & Flange FA & FB
Drawn by: Brian T. Frese
Christopher K. Hadad
The Ohio State University
Date: April 30, 1995

All material is 304 SS unless otherwise noted.
All dimensions in inches
All angles in degrees

Tolerances:
±0.01
±0.005
NOT TO SCALE
Ionizer Can Modification:
drill and tap, shown in red
Macor Insulator

4 holes drilled and tapped for 2-56 bolts, equally spaced on a 1.25 in dia bc. Top depth = 0.125 in.

Stainless Steel Sink

4 clearance holes for 2-56 bolts, equally spaced on a 1.025 in dia bc. Countersunk for side.
Modification to Macor Insulator:
drill thru hole shown in red
"BRINKS" TYPE INHIBITOR ASSY. 1 REQD
FILE: A\SA\101\J\R DATE 3/4/90

PURCHASED PARTS
SS-4-VC0 1 FITTING, 1 REQD
ISO "LARGE FLANGE" #812008 (NW80), 1 REQD
POWER FEEDTHRU, DEL-WELD, #9411020, 4 REQD
Weld on VEE body (SS-4 VEE-1) here

Modify atmospheric side of NW80 flange so this groove is 0.50" wide as shown

Drill and blind top 3 holes for 82-56 bolts - on a 1" line to a run path of 0.250"

Drill 1/4" hole (with std 1/8" drill bit) and weld in 1/4" tube

Note: Weld Groove

Note: Drill as small as possible

Note: Weld Groove
Drill Clearance
Hole for #4-40 bolt

Round Corners
and all surfaces
should be smooth

REPELLE R PLATE, 1 REQD
ELECTROPOLISHED
MATL: 1/16 SHEET 304 SS
6 Holes Drilled thru and countersink for #8-32 bolts

Drill and Blind tap 4 holes on a 1813° b.h.c., a min depth of 0.313°

IONIZER CAN, 1 REQD
MATL: DELRIN ROD, HOLLOWED
Drill and blind tap 6 holes for #10-80 bolts to a min depth of 0.313. Drill 3 clearance holes and counterbore for #2-56 bolts on a 1" bhc.
Drill and Blind top 1 hole for #2-56 bolt a run depth of 0.313".

Drill 4 holes, 0.125" dia on a 0.75" b/c.

Drill 4 Clearance holes and counterbore for #2-56 bolts on a 1.813" b/c.

IONIZER CAN CLUSURE, 1 REQD
ELECTRUPOLISHED
MATL: 304 SS
FEEDTHRU TERMINAL, 7 REQD
MAIL: 1/8 RD 304 SS

FEEDTHRU TERMINAL, 1 REQD
MAIL: 1/8 RD 304 SS
APPENDIX B

ADO RATE DATA
beta-lactone/CH3O-

Data used to calculate rate coefficient:

<table>
<thead>
<tr>
<th>Mass</th>
<th>Dipole</th>
<th>Polarizability</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>4.18 (crc)</td>
<td>5.612553E-24 (approximated)</td>
</tr>
</tbody>
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Reduced Mass = 21.6699
Langevin rate coefficient = 1.191842E-09
ADO correction factor = 0.2560066
ADO rate coefficient = 3.309524E-09
VTST Factor = 6.150155
VTST Rate Coefficient = 4.233161E-09

beta-lactone/OH-

Data used to calculate rate coefficient:

<table>
<thead>
<tr>
<th>Mass</th>
<th>Dipole</th>
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</thead>
<tbody>
<tr>
<td>72</td>
<td>4.18 (crc)</td>
<td>5.612553E-24 (approximated)</td>
</tr>
</tbody>
</table>

Reduced Mass = 13.75281
Langevin rate coefficient = 1.496069E-09
ADO correction factor = 0.2560066
ADO rate coefficient = 4.154304E-09
VTST Factor = 6.150155
VTST Rate Coefficient = 5.313706E-09
beta-lactone/F-

Data used to calculate rate coefficient:

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<thead>
<tr>
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<th>ION DATA</th>
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<td>4.18 (crc)</td>
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<tr>
<td>Polarizability</td>
<td>5.612553E-24</td>
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</tbody>
</table>

Reduced Mass = 15.03297
Langevin rate coefficient = 1.430952E-09
ADO correction factor = .2560066
ADO rate coefficient = 3.973486E-09
VTST Factor = 6.150155
VTST Rate Coefficient = 5.082424E-09

beta-lactone/CH3S-

Data used to calculate rate coefficient:

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<td>Polarizability</td>
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Reduced Mass = 28.43698
Langevin rate coefficient = 1.040413E-09
ADO correction factor = .2560066
ADO rate coefficient = 2.889031E-09
VTST Factor = 6.150155
VTST Rate Coefficient = 3.695316E-09
Methyl Formate/NH2-

Data used to calculate rate coefficient:

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<tr>
<th>NEUTRAL DATA</th>
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<tbody>
<tr>
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<tr>
<td>Dipole</td>
<td>1.77 (crc)</td>
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<tr>
<td>Polarizability</td>
<td>4.950232E-24 (approximated)</td>
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</table>

Reduced Mass = 12.63158
Langevin rate coefficient = 1.466058E-09
ADO correction factor = 0.1948797
ADO rate coefficient = 2.36013E-09
VTST Factor = 2.773004
VTST Rate Coefficient = 2.846924E-09

Methyl Formate/OH-

Data used to calculate rate coefficient:

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Reduced Mass = 13.24675
Langevin rate coefficient = 1.431611E-09
ADO correction factor = 0.1948797
ADO rate coefficient = 2.304677E-09
VTST Factor = 2.773004
VTST Rate Coefficient = 2.780033E-09
Methyl Formate/CH$_3$O$^-$

Data used to calculate rate coefficient:

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Reduced Mass = 20.43956
Langevin rate coefficient = 1.152508E-09

ADO correction factor = .1948797
ADO rate coefficient = 1.855363E-09

VTST Factor = 2.773004
VTST Rate Coefficient = 2.238046E-09

Methyl Formate/CD$_3$O$^-$

Data used to calculate rate coefficient:

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<tr>
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Reduced Mass = 21.70213
Langevin rate coefficient = 1.118481E-09

ADO correction factor = .1948797
ADO rate coefficient = 1.800585E-09

VTST Factor = 2.773004
VTST Rate Coefficient = 2.171969E-09
Methyl Formate/NCCH2-

Data used to calculate rate coefficient:

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Reduced Mass = 24
Langevin rate coefficient = 1.06359E-09
ADO correction factor = 0.1948797
ADO rate coefficient = 1.712218E-09
VTST Factor = 2.773004
VTST Rate Coefficient = 2.065376E-09

Methyl Formate/F-

Data used to calculate rate coefficient:

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Reduced Mass = 14.43038
Langevin rate coefficient = 1.371643E-09
ADO correction factor = 0.1948797
ADO rate coefficient = 2.208136E-09
VTST Factor = 2.773004
VTST Rate Coefficient = 2.065376E-09

164
Methyl Formate/CH3C(=O)CH2-

Data used to calculate rate coefficient:

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<tr>
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Reduced Mass = 29.23077
Langevin rate coefficient = 9.637398E-10

ADO correction factor = .1948797
ADO rate coefficient = 1.551475E-09

VTST Factor = 2.773004
VTST Rate Coefficient = 1.871478E-09

Methyl Formate/CH3S-

Data used to calculate rate coefficient:

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Reduced Mass = 26.35514
Langevin rate coefficient = 1.014956E-09

ADO correction factor = .1948797
ADO rate coefficient = 1.633925E-09

VTST Factor = 2.773004
VTST Rate Coefficient = 1.970934E-09
Mrthyl Formate/O2NCH2-

Data used to calculate rate coefficient:

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Reduced Mass = 30
Langevin rate coefficient = 9.513038E-10

ADO correction factor = .1948797
ADO rate coefficient = 1.531455E-09

VTST Factor = 2.773004
VTST Rate Coefficient = 1.847328E-09
Ethyl Formate/NH2-  

Data used to calculate rate coefficient:

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<td>8.01E-24 (crc)</td>
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Reduced Mass = 13.15556  
Langevin rate coefficient = 1.82738E-09  
ADO correction factor = 0.1816145  
ADO rate coefficient = 2.717636E-09  
VTST Factor = 2.37701  
VTST Rate Coefficient = 3.203617E-09

Ethyl Formate/OH-  

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<td>8.01E-24 (crc)</td>
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Reduced Mass = 13.82418  
Langevin rate coefficient = 1.78264E-09  
ADO correction factor = 0.1816145  
ADO rate coefficient = 2.651101E-09  
VTST Factor = 2.37701  
VTST Rate Coefficient = 3.125184E-09
**Ethyl Formate/CH3O-**

Data used to calculate rate coefficient:

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<td><strong>Dipole</strong></td>
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<td><strong>Polarizability</strong></td>
<td>8.01E-24 (crc)</td>
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Reduced Mass = 21.84762
Langevin rate coefficient = 1.418017E-09

ADO correction factor = .1816145
ADO rate coefficient = 2.108841E-09

VTST Factor = 2.37701
VTST Rate Coefficient = 2.485955E-09

**Ethyl Formate/NCCH2-**

Data used to calculate rate coefficient:

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<td><strong>Polarizability</strong></td>
<td>8.01E-24 (crc)</td>
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Reduced Mass = 25.96491
Langevin rate coefficient = 1.300738E-09

ADO correction factor = .1816145
ADO rate coefficient = 1.934427E-09

VTST Factor = 2.37701
VTST Rate Coefficient = 2.280351E-09
Ethyl Formate/F-

Data used to calculate rate coefficient:

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Reduced Mass = 15.1128
Langevin rate coefficient = 1.704638E-09
ADO correction factor = 0.1816145
ADO rate coefficient = 2.535097E-09
VTST Factor = 2.37701
VTST Rate Coefficient = 2.988436E-09

Ethyl Formate/CH3S-

Data used to calculate rate coefficient:

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Reduced Mass = 28.7438
Langevin rate coefficient = 1.236264E-09
ADO correction factor = 0.1816145
ADO rate coefficient = 1.838543E-09
VTST Factor = 2.37701
VTST Rate Coefficient = 2.16732E-09
Ethyl Formate/O2NCH2-

Data used to calculate rate coefficient:

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Reduced Mass = 33.13433
Langevin rate coefficient = 1.151448E-09
ADO correction factor = .1816145
ADO rate coefficient = 1.712406E-09

VTST Factor = 2.37701
VTST Rate Coefficient = 2.018627E-09
**Methyl Acetate/NH2-**

Data used to calculate rate coefficient:

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Reduced Mass = 13.15556
Langevin rate coefficient = 1.700953E-09

ADO correction factor = 1.723722
ADO rate coefficient = 2.453966E-09

VTST Factor = 2.275824
VTST Rate Coefficient = 2.89993E-09

**Methyl Acetate/OH-**

Data used to calculate rate coefficient:

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Reduced Mass = 13.82418
Langevin rate coefficient = 1.659309E-09

ADO correction factor = 1.723722
ADO rate coefficient = 2.393886E-09

VTST Factor = 2.275824
VTST Rate Coefficient = 2.828932E-09
Methyl Acetate/CH₃O-

Data used to calculate rate coefficient:

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<tr>
<td>Polarizability</td>
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Reduced Mass = 21.84762
Langevin rate coefficient = 1.319911E-09

ADO correction factor = .1723722
ADO rate coefficient = 1.904237E-09

VTST Factor = 2.275824
VTST Rate Coefficient = 2.250298E-09

Methyl Acetate/CD₃O-

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Reduced Mass = 23.2963
Langevin rate coefficient = 1.278213E-09

ADO correction factor = .1723722
ADO rate coefficient = 1.84408E-09

VTST Factor = 2.275824
VTST Rate Coefficient = 2.179207E-09
**Methyl Acetate/NCCH2-**

Data used to calculate rate coefficient:

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<td>Polarizability</td>
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Reduced Mass = 25.96491
Langevin rate coefficient = 1.210747E-09
ADO correction factor = 0.1723722
ADO rate coefficient = 1.746746E-09
VTST Factor = 2.275824
VTST Rate Coefficient = 2.064185E-09

**Methyl Acetate/F-**

Data used to calculate rate coefficient:

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Reduced Mass = 15.11828
Langevin rate coefficient = 1.586703E-09
ADO correction factor = 0.1723722
ADO rate coefficient = 2.289138E-09
VTST Factor = 2.275824
VTST Rate Coefficient = 2.705147E-09
Methyl Acetate/CH$_3$C(=O)CH$_2$-

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<td>Polarizability</td>
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Reduced Mass = 32.19847
Langevin rate coefficient = 1.087249E-09
ADO correction factor = 0.1723722
ADO rate coefficient = 1.568576E-09
VTST Factor = 2.275824
VTST Rate Coefficient = 1.853636E-09

Methyl Acetate/CH$_3$S-

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</table>

Reduced Mass = 28.7438
Langevin rate coefficient = 1.150733E-09
ADO correction factor = 0.1723722
ADO rate coefficient = 1.660164E-09
VTST Factor = 2.275824
VTST Rate Coefficient = 1.961869E-09
Methyl Acetate/O2NCH2-

Data used to calculate rate coefficient:

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<td>Polarizability</td>
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Reduced Mass = 33.13433
Langevin rate coefficient = 1.071785E-09

ADO correction factor = 0.1723722
ADO rate coefficient = 1.546265E-09

VTST Factor = 2.275824
VTST Rate Coefficient = 1.827271E-09
Ethyl Acetate/NH2-

Data used to calculate rate coefficient:

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<tbody>
<tr>
<td>Mass</td>
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<tr>
<td>Dipole</td>
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<tr>
<td>Polarizability</td>
<td>9.7E-24 (crc)</td>
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Reduced Mass = 13.53846
Langevin rate coefficient = 1.982295E-09

ADO correction factor = 0.1647475
ADO rate coefficient = 2.716498E-09

VTST Factor = 1.99216
VTST Rate Coefficient = 3.111646E-09

Ethyl Acetate/OH-

Data used to calculate rate coefficient:

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<tbody>
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<tr>
<td>Polarizability</td>
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Reduced Mass = 14.24762
Langevin rate coefficient = 1.932332E-09

ADO correction factor = 0.1647475
ADO rate coefficient = 2.64803E-09

VTST Factor = 1.99216
VTST Rate Coefficient = 3.033218E-09
### Ethyl Acetate/CH₃O⁻

Data used to calculate rate coefficient:

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<tr>
<td>Dipole</td>
<td>1.78 (crc)</td>
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<tr>
<td>Polarizability</td>
<td>9.7E-24 (crc)</td>
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</table>

Reduced Mass: 22.92437  
Langevin rate coefficient: 1.523366E-09

ADO correction factor: 0.1647475  
ADO rate coefficient: 2.08759E-09

VTST Factor: 1.99216  
VTST Rate Coefficient: 2.391256E-09

### Ethyl Acetate/NCCH₂⁻

Data used to calculate rate coefficient:

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<td>Polarizability</td>
<td>9.7E-24 (crc)</td>
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</table>

Reduced Mass: 27.5  
Langevin rate coefficient: 1.39087E-09

ADO correction factor: 0.1647475  
ADO rate coefficient: 1.906021E-09

VTST Factor: 1.99216  
VTST Rate Coefficient: 2.183275E-09
Ethyl Acetate/$F^-$

Data used to calculate rate coefficient:

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 Reduced Mass = 15.62617
 Langevin rate coefficient = 1.845129E-09
 ADO correction factor = 0.1647475
 ADO rate coefficient = 2.528528E-09

 VTST Factor = 1.99216
 VTST Rate Coefficient = 2.896333E-09

Ethyl Acetate/CH3S-

Data used to calculate rate coefficient:

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 Reduced Mass = 30.63704
 Langevin rate coefficient = 1.31774E-09
 ADO correction factor = 0.1647475
 ADO rate coefficient = 1.805804E-09

 VTST Factor = 1.99216
 VTST Rate Coefficient = 2.06848E-09

178
Ethyl Acetate/O2NCH2-

Data used to calculate rate coefficient:

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<td>Polarizability</td>
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Reduced Mass = 35.67567
Langevin rate coefficient = 1.221144E-09
ADO correction factor = 0.1647475
ADO rate coefficient = 1.673431E-09
VTST Factor = 1.99216
VTST Rate Coefficient = 1.916852E-09