

ABSTRACT

A Computational Examination of the Transition Metal Cation Assisted Decomposition of Acetic Acid

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As the world's reserve of fossil fuels continues to deplete, the need to investigate alternative means of fuel production continues to rise in global relevance. Whether alternative fuel production arises from an established means or from a new technology, it is necessary to explore all plausible options. Ideally, one would take an industrial waste product or environmental contaminant and convert it into a green fuel source. Doing so generates a usable fuel source while minimizing waste and contamination. One potential means of such fuel production is through the transition metal assisted decay of an organic molecule. Although numerous organic compounds produce gaseous fuels after decomposition, acetic acid has been identified as a prominent byproduct of industrial processes with the potential to yield a green fuel source. This thesis examines the Ni^+ cation assisted decomposition of acetic acid into methanol and carbon monoxide.

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A COMPUTATIONAL EXAMINATION OF THE TRANSITION METAL
CATION ASSISTED DECOMPOSITION OF ACETIC ACID

A Thesis Submitted to the Faculty of
Baylor University
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Honors Program

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Lastly, I would like to thank you, the reader, for taking a small interest in the work I've done over the past few years.

DEDICATION

To

My grandmother, Norma McQueen

Thank you for your love and support, thank you for teaching me to laugh at the little things, and thank you for helping make me the person I am today.

CHAPTER ONE

Introduction

Background and Rationale

Catalysts lower the kinetic barriers that occur along the reaction coordinate, thereby the energy costs associated with the transformation of reactants into more useful products. Ideally, this process is bond specific, resulting in only the desired product in significant concentration. Realizing this obvious economic importance, scientists aggressively pursue insight into the fundamental processes underlying catalysis. To such end, this research focuses on the theoretical calculation of the energy-lowered formation of products that occurs during catalyzed chemical reactions.

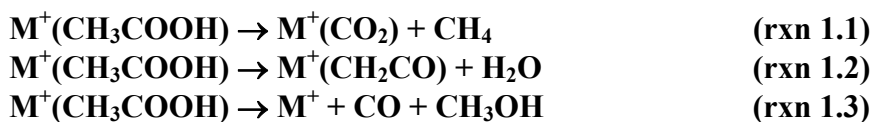
Common catalysts, such as enzymes in biological systems and zeolites utilized within the petrochemical industry, enable efficient product formation. However these extended systems are often quite complex making resolved experimental study rather challenging. This complexity arises from interactions of the ongoing reaction with the surrounding environment (i.e. negative catalysts within the system) and the possible emergent properties of the catalyst itself. As such, it is necessary to study catalytic processes in an environment that minimizes such confounding factors. It is also desirable to study catalytic centers that are significantly involved in a wide range of systems. Transition metal ions successfully fill this niche.¹

This project aims to study organic decomposition reactions where the kinetic barriers to product formation have been considerably reduced. Instrumentation has been

developed where idealized systems can be isolated and the activation energy lowering credited to transition metal ion catalysis can be studied. Computational results can further such experimental results by acting as a benchmark to which the experimental data can be compared. A primary goal of this project is to demonstrate the possible production of green fuel sources from industrial organic byproducts. Ideally, this research concerns the conversion of organic compounds into methane or methanol at reduced activation energies. These low-carbon containing molecules are considered green, as the energy producing combustion of such compounds produce fewer equivalents of CO₂ gas than traditional fossil fuel sources.

Although applicable to many organic compounds, this research will initially test the decomposition of acetic acid (CH₃COOH) into fuel sources catalyzed by transition metal cations. Acetic acid is a water-soluble organic acid and has many industrial uses. Over 10 million metric tons of acetic acid are either synthesized or extracted from bacterial fermentation each year. It is prevalently utilized as a solvent in the production of terephthalic acid, a precursor to polyester. It is also utilized as a reagent in the industrial production of paints and adhesives. Such wide spread use, as both reagent and solvent, assures that acetic acid is a byproduct in industrial waste streams.

We propose rxns 1.1-1.3 as possible transition metal ion (M⁺) assisted unimolecular decomposition reactions for acetic acid:



These possible reactions are consistent with earlier studies.²⁻⁴ The neutral products include methane, water, carbon monoxide, and methanol. It is possible that these reactions are competitive and that the resulting neutral products are a mixture of these compounds. Previous results in the laboratory suggest that various transition metal cations are capable of either C-C or C-O bond activation at lowered activation energies, however, the specificity of such reactions remains unclear.⁵ Although the reactions may be competitive, the remainder of this thesis will examine the reaction dynamics of rxn 1.3.

Rxn 1.3 produces carbon monoxide and methanol while reforming the metal cation catalyst. Although carbon monoxide is formed in this reaction, the production of methanol is highly desired as it is an easily transportable fuel source, when compared to methane gas. Methanol can be easily transported to areas where it is not feasible to build a methane pipeline.

Experimental Research Description

Although this thesis primarily examines the theoretical aspects of the transition metal assisted catalytic decomposition of acetic acid, it is important to understand the experimental methods by which this is accomplished.

Ion/organic reactants in these studies are formed as cold binary clusters under jet-cooled conditions. Energy in excess of the reaction activation requirement is provided through laser photon absorption. The quantum of photon energy approximates the total energy of the cluster as absorption occurs in the collisionless environment of the cold, supersonic expansion. Unimolecular decay ensues as the cation selectively activates

bonds within the organic moiety and mediates the formation of products. The resulting fragment ions are selectively detected and their production temporally monitored in a custom time of flight mass spectrometer. The resulting signals combine into waveforms that are analyzed to extract the rate constants for the transition metal ion assisted decomposition reaction. These studies are extended through measurement of the assisted dissociation kinetics of the deuterium labeled isotopologues. Determination of the kinetic isotope effect suggests dynamic information for the unimolecular decomposition reaction.

Experimental Procedure

In general, a large supersonic source chamber is connected to a custom time of flight mass spectrometer (TOFMS) as shown in Figure 1. The precursor ions are generated as jet-cooled clusters in the source chamber and mass analyzed in the custom TOFMS located orthogonal to the expansion axis. The cluster absorbs laser radiation which causes the complex to dissociate into fragments. This dissociative process occurs on the microsecond timescale. The ensuing fragment ions are selectively detected and temporally sampled in the TOF.

Specifically, the supersonic source chamber is a 120 L vacuum chamber. An external motor rotates a solid metal rod at a rate of 1.1 rpm. A high pressure line is coupled into the vacuum chamber connecting to the source block through a Series 9 General Valve. Momentarily opening the solenoid valve allows high pressure gas (either helium or a helium/argon mixture) doped with the vapor of the organic bonding partner to supersonically expand into the vacuum. As the expansion plume develops, 248 nm laser radiation from a pulsed KrF excimer is focused onto the rotating metal rod, ablating the

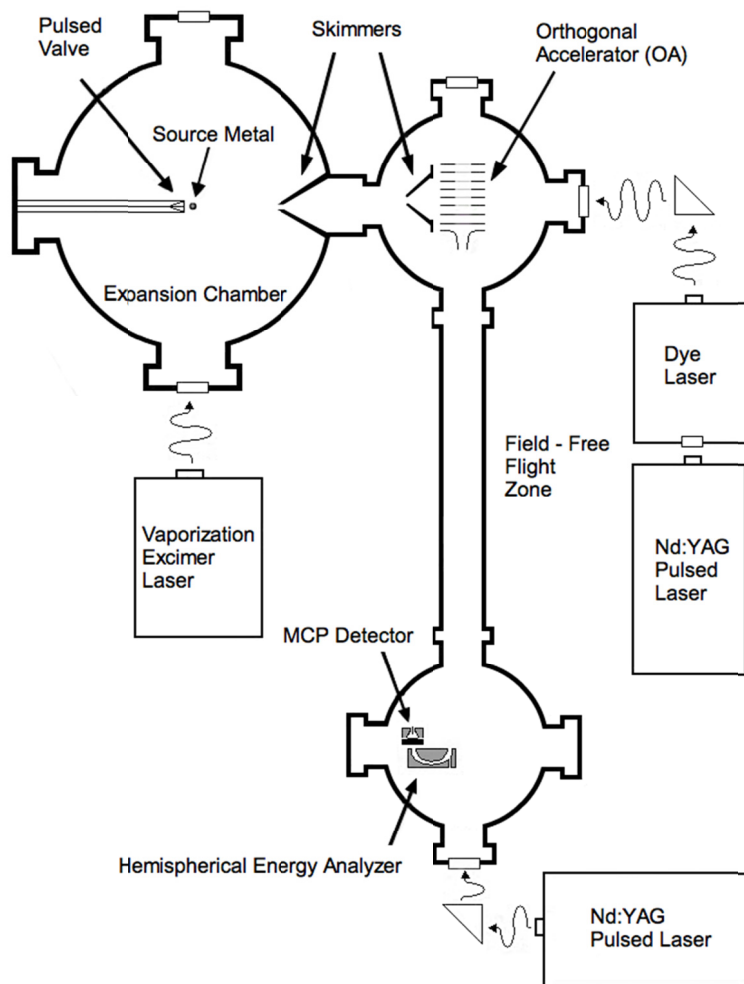


Figure 1: Instrumental diagram

metallic surface and seeding neutral and ionic atoms into the expansion. The large pressure drop (10^9) between the static gas reservoir and the vacuum chamber assures that the cluster ions are formed with minimal amounts of internal energy.

The expanding plume traverses ~ 80 cm, is skimmed twice, and enters between parallel capacitor plates of a Wiley-McLaren, pulsed orthogonal accelerator (OA) situated at the entrance to the TOFMS. As the densest portion of the ion packet enters, the OA is pulsed from ground potential to +1.75 kV, imparting this kinetic energy to the ions. Mass separation occurs as the ions drift through the 1.8 meter field free flight of the TOFMS.

The separated ion packets enter a voltage controlled hemispherical, kinetic energy analyzer (or sector). The potential difference across the halves of the sector can be selected to transmit the full kinetic energy of the ion beam, thus allowing the different ionic species produced in the expansion to strike a Chevron microchannel plate (MCP) detector located at the sector's terminus. Precursor mass spectra can then be acquired and analyzed, determining the identity of the complexes and optimizing their intensity within the beam.

Laser induced dissociation of a single precursor ion results in charged fragment ions that transmit through the sector at different characteristic voltage settings. Although the dissociation event does not significantly affect the fragment's velocity, the transmission voltage changes due to the change in fragment ion mass. To measure the unimolecular decay of a precursor ion, cations within the molecular beam must absorb a photon of energy prior to right angle extraction and mass separation. This is accomplished by guiding a YAG pumped, dye laser beam into the vacuum apparatus through a viewport along the supersonic expansion axis. The ionic molecules within the beam absorb the radiation. The excited precursor ions decay, producing fragment ions as the molecular beam approaches the OA. All fragment ions produced in the expanse between the location of photon absorption and the OA receive the same (full) kinetic energy imparted to the precursor ions during right angle extraction. These fragment ions are indistinguishable from the precursor ions in the parent beam and are therefore not sampled. Only those excited precursor ions that decay within the field free flight of the TOF produce fragments detectable via selective transmission through the sector.

The relative fragment intensity is plotted versus the timing delay between triggering the OA and dye laser pulses. These points combine into a waveform that is analyzed to extract kinetic information from the dissociative reaction. Zero microseconds is defined to be the coincident firing of both the dye laser and the OA. Since the dye laser is temporally scanned to times earlier than the OA trigger pulse, the intensity is plotted versus negative delay values.

CHAPTER TWO

Review of Literature

Unification of Theory and Experiment

The traditional disciplines of chemistry nominally separate theoretical physical chemistry from experimental physical chemistry. Although divided, this separation has become less distinct over the past several decades as theoretical methods have become more refined and as computational techniques have become more readily available to academia. Collaboration between theoreticians and experimentalists has further enabled direct integration of theory into experimental work, and vice versa.⁶ This interplay has provided a unique insight into chemical bonding, assisted in molecular structure determination, helped to establish or confirm chemical concepts, and has prompted further experimental and theoretical investigations.⁷ Combined results most importantly provide a means to clearly elucidate fundamental aspects of the world around us.

Transition Metal Assisted Decomposition of Organic Molecules

In the realms of organometallic chemistry, theoretical and experimental results have yielded valuable mechanistic and kinetic details about transition metal assisted unimolecular decomposition reactions.⁸⁻¹⁶ It has been seen that in the gas-phase, transition metal cations cleave high energy bonds in a variety of organic molecules.¹⁷⁻²¹ These transition metal cations are capable of bond activation at lowered activation

energies suggesting catalytic behavior, however, the specificity of such reactions remains unclear.

Acetone Studies

Experimental and theoretical studies examining the gas-phase unimolecular decomposition reaction of M^+ ($M = \text{Ni}, \text{Co}$) with h_6 - and d_6 -acetone have provided insight into the catalytic properties of transition metals, as well as the kinetic and mechanistic details of this reaction.

A 2009 study by Castleberry et al. monitored the $\text{Ni}^+(\text{h}_6\text{-Acetone})$ [$\text{Ni}^+(\text{h}_6\text{-Ac})$] unimolecular decomposition into Ni^+CO and C_2H_6 resulting from single photon absorption.⁸ A schematic of the dissociative mechanism is displayed in Figure 2.

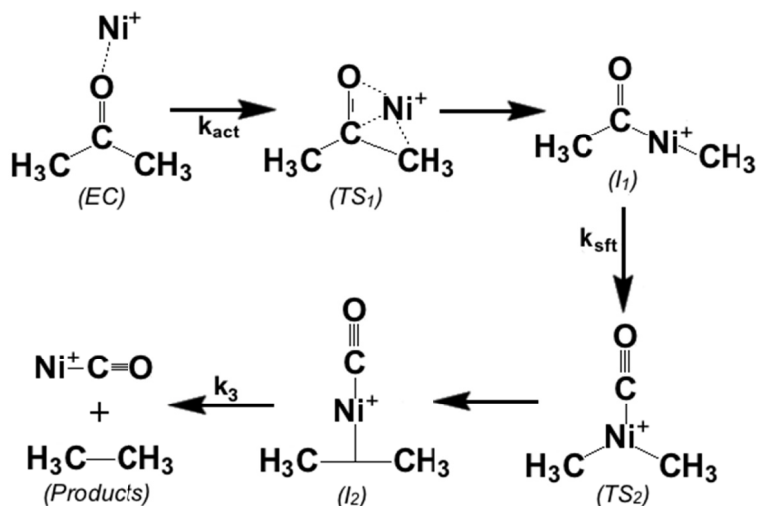


Figure 2: Proposed mechanism of the Ni^+ assisted decomposition of acetone (*TS*: transition state, *I*: intermediate)

The photon energies utilized to initiate the dissociative reaction were below the energy required to cleave C-C σ -bonds; additionally, the absorbed quantum of energy was

insufficient to directly dissociate the $\text{Ni}^+(\text{h}_6\text{-Ac})$ complex into separated $\text{Ni}^+ + \text{acetone}$ fragments. Rather, the absorbed photon promotes an electron into an excited quartet state that intersystem crosses to the high vibrational levels of the ground, doublet electronic state. This provides the necessary energy for dissociation of $\text{Ni}^+(\text{h}_6\text{-Ac})$ into $\text{Ni}^+\text{CO} + \text{C}_2\text{H}_6$. Thus the quantum of photon energy represents the internal energy available to the cluster.

This decomposition reaction is experimentally followed in real time. Rate constants between $(1.13 \pm 0.05) \times 10^5$ and $(5.5 \pm 0.03) \times 10^4 \text{ s}^{-1}$ were measured at energies between 18800 and 15600 cm^{-1} . Expectedly, the rate constant magnitudes increased as the photon energy (or internal energy) was increased. Furthermore, the data indicates that the reaction kinetics is controlled by the formation of two energetically important transition states. Both C-C σ -bond activation and methyl isomerization (figure 2) are likely rate limiting steps. Early results suggested that the latter was likely to be rate-limiting.

The follow up study by Dee et al. 2009 directly measured the rate-limiting rate constants in the unimolecular decomposition of $\text{Ni}^+(\text{h}_6\text{-Ac})$'s deuterated isotopomer $\text{Ni}^+(\text{d}_6\text{-Acetone})$ [$\text{Ni}^+(\text{d}_6\text{-Ac})$].¹⁰ By comparing kinetic results, it was seen that deuterium labeling affected both the oxidative addition as well as the reductive elimination. A considerable kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} \sim 5.5$) was measured and associated with the reaction rate-limiting. It was determined that the reductive elimination (or the isomerization of the methyl group) was rate limiting. These experimental results are in agreement with recent theoretical results.²²

A third study examining the Co^+ -assisted decomposition of h_6 - and d_6 -Ac systems comparatively demonstrated the importance of differences in the low-lying electronic structures of the different transition metals utilized.¹⁴ Figure 3 compares the low-lying electronic structures of Co^+ and Ni^+ . The reaction dynamics for Co^+ -Acetone [$\text{Co}^+(\text{Ac})$] were unique when compared to those of $\text{Ni}^+(\text{Ac})$. Although each system likely follows the same overall mechanism, the decomposition kinetics is limited by a different energetically important step. Figure 4 plots the fragment ion intensity sampled during the decomposition of h_6 -acetone by Ni^+ and Co^+ . The dissimilar waveforms presented in Figure 4 indicate significant differences in the unimolecular decay dynamics. In the case of $\text{Co}^+(\text{Ac})$, C-C σ -bond activation is rate-limiting (compared to methyl isomerization for $\text{Ni}^+(\text{Ac})$). The difference in the kinetics of the $\text{Co}^+(\text{Ac})$ reaction was attributed to a

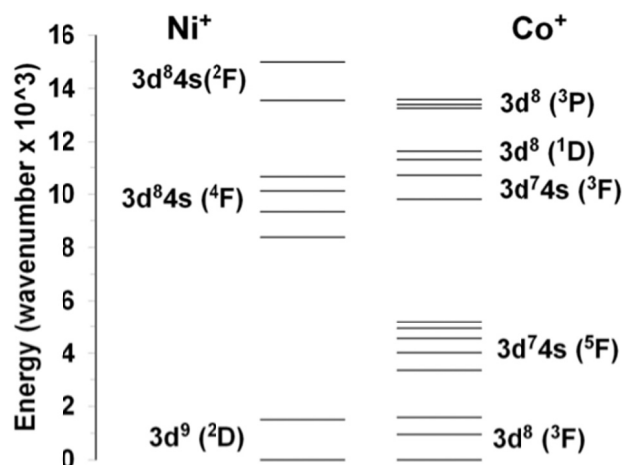


Figure 3: Electronic states of Ni^+ and Co^+

possible spin inversion junction along the potential energy surfaces between the triplet and quintet reaction coordinates. Comparatively the doublet and quartet potential energy surfaces for $\text{Ni}^+(\text{Ac})$ system are well separated as suggested by Density Functional

Theory (DFT) calculations acquired for a similar system.¹⁵ It was observed that fragment production in the $\text{Co}^+(\text{Ac})$ system was less than that in $\text{Ni}^+(\text{Ac})$, which is consistent with spin orbit coupling (SOC) arguments. It is important to note that the inefficient spin SOC between the triplet and quintet potential energy surfaces for $\text{Co}^+(\text{Ac})$ results in decreased production of $\text{Co}^+\text{CO} + \text{C}_2\text{H}_6$ fragments.

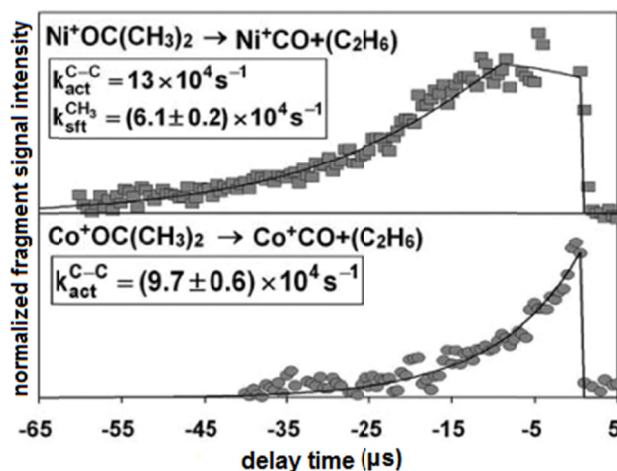


Figure 4: Comparison of the Ni^+ and Co^+ assisted decomposition of acetone performed at similar excitation energies: 16400 and 16100 cm^{-1} , respectively

Acetaldehyde Studies

Two studies, one by Dee et al. 2010 and the second by Chen et al. 2007 Dee et al. 2010, examine the Ni^+ assisted decomposition reaction of acetaldehyde into $\text{Ni}^+\text{CO} + \text{CH}_4$.^{10, 23} Both studies come to similar conclusions regarding the mechanistic details of the reaction. However, it was found that the theoretical results overestimated the activation energy barrier along each reaction coordinate for the system.²³

The 2007 study by Chen theoretically examined the Ni^+ assisted decomposition through the utilization of DFT with Becke's hybrid, three-parameter functional of Lee, Yang, and Parr (B3LYP).²³ This functional was employed at the 6-311+G(2df,2pd) level

of theory. This approach, along with computation using several smaller basis sets, has consistently been used in the treatment of small, transition metal containing systems.²⁴ It is largely accepted that this approach provides sufficiently accurate results for the unimolecular decomposition reactions being examined.²⁵⁻²⁷

The theoretical study provided insights into the mechanistic details of the decarbonylation of acetaldehyde. Results of the study suggested that both C-C σ -bond and aldehyde C-H σ -bond activations result in the production of $\text{Ni}^+\text{CO} + \text{CH}_4$.

In accordance with the theoretical study, experimental results observed that the decomposition of $\text{Ni}^+(\text{Acetaldehyde})$ [$\text{Ni}^+(\text{Aald})$] follows two parallel paths. Both paths initiate with the oxidative addition of Ni^+ ; one across the C-C σ -bond, while the other is across the aldehyde C-H σ -bond. A schematic of the $\text{Ni}^+(\text{Aald})$ dissociative mechanism is displayed in Figure 5.

Experimental results suggested that the rate-limiting step of the reaction was energy dependent. At higher energy levels, both reaction pathways are available to the system. As such, when the precursor internal energy is greater than $17200 \pm 400 \text{ cm}^{-1}$, the pathway is rate-limited by methyl isomerization. However, at lower energies, only a single reaction coordinate becomes available. This pathway involves the Ni^+ activation of the C-C σ -bond and H-migration, forming $\text{Ni}^+\text{CO} + \text{CH}_4$. This second pathway is available at energies as low as 15600 cm^{-1} .

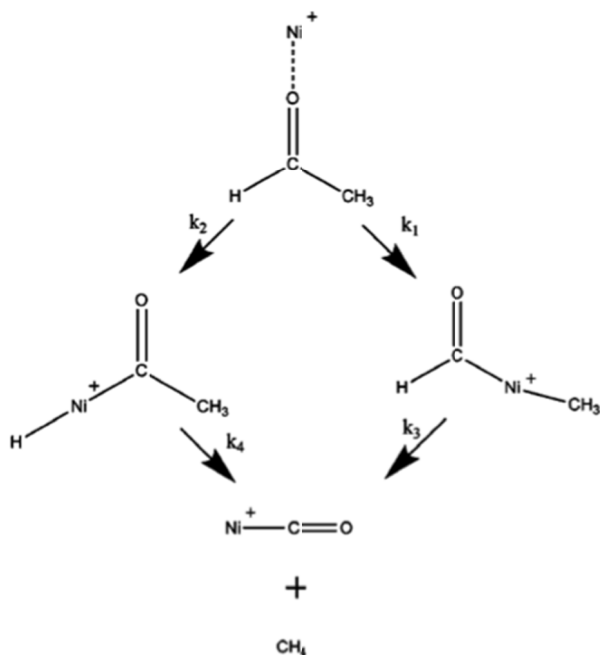


Figure 5: Proposed mechanism of the Ni^+ assisted decomposition of acetaldehyde

Two earlier theoretical studies by Zhao et al. investigated the M^+ ($\text{M} = \text{Co}$, Fe , and Cr) assisted decomposition of acetaldehyde.²⁶⁻²⁷ As seen in the acetone studies, using a different transition metal cation alters the kinetics of the reaction due to differences in the low-lying electronic structures of the cations. The use of other transition metal cations consistently displays similar decarbonylation mechanisms following four key steps: (1) encounter complex formation, (2) C-C σ -bond activation, (3) H-migration, and (4) nonreactive dissociation. However, the energy required along the reaction coordinate varies by transition metal.²⁶⁻²⁷

Butanone Studies

Researchers have studied the reaction of the asymmetric ketone, butanone, with the Ni^+ cation $[\text{Ni}^+(\text{But})]$.¹⁵ As with acetaldehyde, the dissociative mechanism of $\text{Ni}^+(\text{But})$

consists of two parallel paths. However, unlike acetaldehyde, where the two reaction pathways converge to ultimately yield the same products ($M^+CO + CH_4$), $Ni^+(But)$ dissociation results in the production of three unique complexes. The experimental results indicated the reaction is most likely rate-limited by either C-C₂H₅ ethyl insertion or C-CH₃ methyl insertion by Ni^+ . Furthermore, the mechanism depicted in Figure 5 was proposed to explain the experimental measurements. Rate constants for the activation of each C-C sigma-bond was derived from the measured rate constants, the product channel intensities, and this mechanism. The rate constant for C-C₂H₅ σ -bond insertion was slightly higher than that calculated for C-CH₃ insertion ((1.65 ± 0.04) vs. $(0.66 \pm 0.09) \times 10^5 \text{ s}^{-1}$ at 18800 cm^{-1}). As such, the reaction will more probabilistically occur along the C-C₂H₅ insertion pathway. This is in agreement with thermodynamic arguments.¹⁶

A theoretical study of the potential energy surfaces of the $Ni^+(But)$ decomposition reaction supplemented experimental findings.^(La 2012) Results confirmed that the two decomposition pathways, depicted as (B) and (C) in Figure 6, were parallel to one another and initiated with the activation of the C-C₂H₅ or C-CH₃ σ -bond by Ni^+ . Furthermore, the three neutral elimination products: ethylene, acetaldehyde, and methane were observed computationally.

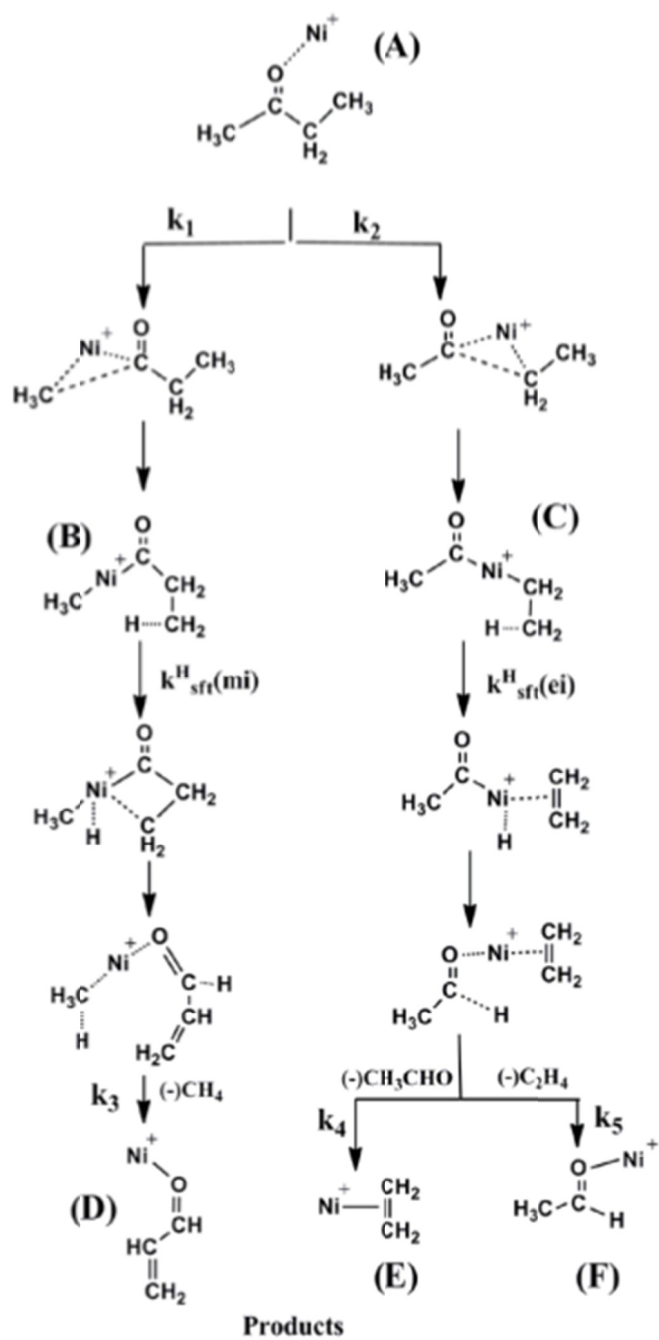


Figure 6: Proposed mechanism of the Ni^+ assisted decomposition of butanone

Carboxylic Acid Studies: M^+ -Assisted Decomposition of Acetic Acid

“These acids are not only essential in the biochemistry of living systems but also valuable resources for industrial processes... Carboxylic acids certainly represent the most relevant class of carbonyl compounds in general.”²⁸ Organic molecules studied previously by the Bellert Research Group, such as acetone, acetaldehyde, and butanone, have primarily been carbonyl compounds. However, the Group has yet to study a carboxylic acid. As such, there is interest in studying the transition metal assisted decomposition of such an organic.

Fe^+ -Acetic Acid Study

Although numerous reactions between Fe^+ and carboxylic acids, ranging from formic to nonanoic acid, were studied, only acetic acid (CH_3COOH) and its deuterated (CD_3COOH) counterpart are of primary relevance. A study by Schröder et al. 1994 examined the reaction products, directionalities, and mechanisms of iron(I) [Fe^+] mediated C-H, C-C, and C-O-bond activation of aliphatic carboxylic acids in the gas-phase.²⁸ Schröder et al. utilized tandem mass spectrometry to measure the unimolecular fragmentation from metastable $Fe^+(\text{Acetic Acid})$ [$Fe^+(AA)$] and $Fe^+(d_3\text{-Acetic Acid})$ [$Fe^+(d_3-AA)$] ions. The observed mass differences in the Metastable Ion (MI) Mass Spectra is found in Table 1. These observed mass differences indicate the stable neutral molecules that are lost from the precursor complex due to the dissociative process.

	Mass Differences (Δm amu) Observed in the MI Mass Spectra							
	Δm							
Precursor	-15	-16	-17	-18	-19	-20	-28	-30
$\text{Fe}^+(\text{AA})$	-	-	-	2	-	-	100	-
$\text{Fe}^+(d_3\text{-AA})$	1	-	-	1	2	-	100	-

Table 1. Intensities are given relative to the base peak of 100%²⁸

The Fe^+ mediated decompositions of CH_3COOH and CD_3COOH were characterized by an extremely low loss of water (2% and 1% respectively). The preferential loss of HDO from $\text{Fe}^+(d_3\text{-AA})$ ($\Delta m = -19$) indicates that dehydration can be described as a 1,2-elimination process of water from the functional group, according to Schröder et al. Although present, the loss of the methyl radical from $\text{Fe}^+(d_3\text{-AA})$ was observed with extremely low yields.

Neither molecular hydrogen nor alkenes are formed from the dissociation of $\text{Fe}^+(\text{AA})$ and $\text{Fe}^+(d_3\text{-AA})$. Both of these channels are open in reactions with carboxylic acids with longer alkyl chains. This is likely due to a competition between initial Fe^+ coordination to the longer alkyl chains and the carbonyl group. In acetic acid, Fe^+ binding to the methyl group offers little energy benefit and the metal preferentially coordinates to the carbonyl group. This in turn leads to decarbonylation, or the loss of carbon monoxide ($\Delta m = -28$), from both isomers the predominant dissociation process. Upon CO loss, the cation reorganizes into an approximate 9:1 mixture of an aquo iron carbene complex ($[\text{H}_2\text{C}=\text{Fe}-\text{OH}_2]^+$) relative to a hydroxy insertion complex ($[\text{H}_3\text{C}-\text{Fe}-\text{OH}]^+$).²⁹⁻³⁰ The importance of these two species will be discussed in terms of the conversion of methane to methanol via a metal oxide catalyst.

Conversion of Methane to Methanol by Metal Oxides

The efficient catalytic conversion of methane into methanol has been studied for more than half a century due to methanol's potential as an easily transportable fuel source. Many studies have focused on the transition-metal oxide assisted conversion of methane to methanol, as given by rxn 2.1.³¹⁻³⁶



Extensive studies examining the effects of the different transition-metal oxides, MO^+ , (M= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu) on methane to methanol conversion have provided molecular geometries of reactants and products, transition states, intermediates, as well as potential energies along the reaction pathway, reaction efficiencies (the ability of the catalyst to convert reactants into desired products), and product branching ratios.³¹⁻
³⁴ Table 2 presents reaction efficiencies (ϕ) and product branching ratios derived from the reactions of MnO^+ , FeO^+ , CoO^+ , and NiO^+ with methane. Reaction efficiencies indicate that out of the total number of collisions, a given percent of these collisions will result in the products indicated.

MO^+	ϕ	$\text{MOH}^+ + \text{CH}_3$	$\text{MCH}_2 + \text{H}_2\text{O}$	$\text{M}^+ + \text{CH}_3\text{OH}$
MnO^+	40 %	100	-	<1
FeO^+	20 %	57	2	41
CoO^+	0.5 %	-	-	100
NiO^+	20 %	-	-	100

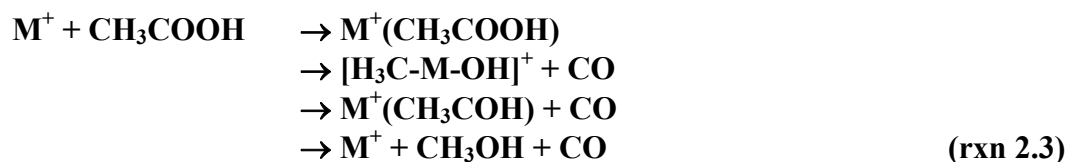
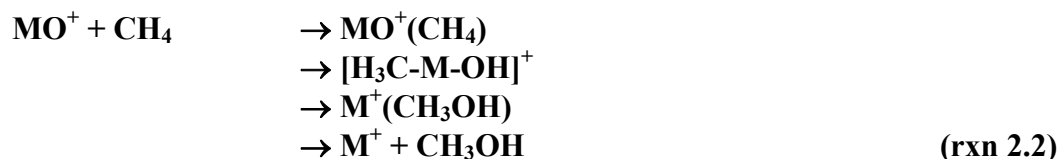
Table 2. Reaction Efficiencies (ϕ) and Product Branching Ratios of $\text{MO}^+ + \text{CH}_4$.^{32, 34}

It has been proposed that the formation of $[\text{H}_3\text{C-Fe-OH}]^+$, an intermediate of this reaction, plays a key role in the gas-phase conversion of methane to methanol.³¹⁻³⁶ Along with this key intermediate, three other inserted intermediates have been proposed: $[\text{H}_2\text{C=Fe-OH}_2]^+$, $[\text{H}_3\text{C-O-Fe-H}]^+$, and $[\text{H-Fe-CH}_2\text{OH}]^+$.³⁰ It should be noted that gas-phase experimental evidence exists only for the aquo iron carbene and the hydroxy insertion complex.

In order to examine these intermediates, Schwarz et al. employed reactions between Fe^+ and CH_3COOH as one of several precursor molecules.³⁰ Upon Fe^+ insertion into CH_3COOH , CO loss was observed; resulting in a mixture of $[\text{H}_2\text{C=Fe-OH}_2]^+$ and $[\text{H}_3\text{C-Fe-OH}]^+$ ions. One of this study's main findings is that this dissociative reaction takes place on a relatively complex potential energy surface.

The Missing Piece

By indicating the ability to convert CH_3COOH into a key intermediate found in the conversion of methane to methanol through the use of a metal oxide or transition metal cation (MO^+ or M^+), researchers have indicated a potential path intersection between two unique reactions. These two mechanisms are indicated in rxn 2.2 and rxn 2.3.



This suggests that studying metal ion catalyzed decomposition reactions of acetic acid may have impact on the economically important conversion of methane to methanol through a MO^+ catalyst. As such, it is of interest to study the dynamics and kinetics of the dissociative reaction of acetic acid, catalyzed by M^+ ($\text{M} = \text{Ni}, \text{Fe}, \text{Co}, \text{and Mn}$). The remainder of this thesis will examine the Ni^+ assisted decomposition of acetic acid into methanol and carbon monoxide as studied through computational chemistry.

CHAPTER THREE

Theoretical Studies

Method of Calculation

Computations were carried out with the Gaussian 03 program package.³⁷ Both energies and geometries of the reactants, intermediates, transition states, and products were calculated utilizing Density Functional Theory (DFT) with the hybrid, three-parameter functional of Becke, Lee, Yang and Parr (B3LYP) at the 6-311+G(d,p) and 6-311++G(d,p) levels of theory. The basis sets used were a compromise between computation accuracy and time. This level of theory has been utilized in similar studies yielding publishable results.^{25, 27} Computations using slightly larger basis sets were not done because calculations at both B3LYP/6-311++G(d,p) and B3LYP/6-311+G(2df,2pd) for similar systems, Ni⁺-Acetone and Ni⁺-Butanone, led to negligible differences.^{25, 27}

Furthermore, frequencies were calculated to determine zero point energy corrections and to confirm transition states and local minimas.

Ni⁺-Acetic Acid Decomposition: Results and Discussion

The potential energy surface (PES) for the gas-phase Ni⁺-assisted decomposition of acetic acid was explored through DFT calculations. The mechanism leading to the loss of carbon monoxide and the formation of a Ni⁺-methanol product complex was examined. The proposed mechanism for the reaction is displayed in Figure 7. The coordinate for doublet (²D) Ni⁺ is displayed in Figure 8. The energies throughout the

coordinate are relative to the encounter complex (EC), and will be discussed in a chronological manner. Table 3 displays the comparative energies calculated at the B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) levels of theory. Finally, Figure 9 shows geometries and structural parameters of key structures optimized at the B3LYP/6-311++G(d,p) level of theory. Data of the complete parameters, thermochemistry, and frequencies of the optimized structures are located in the Appendix

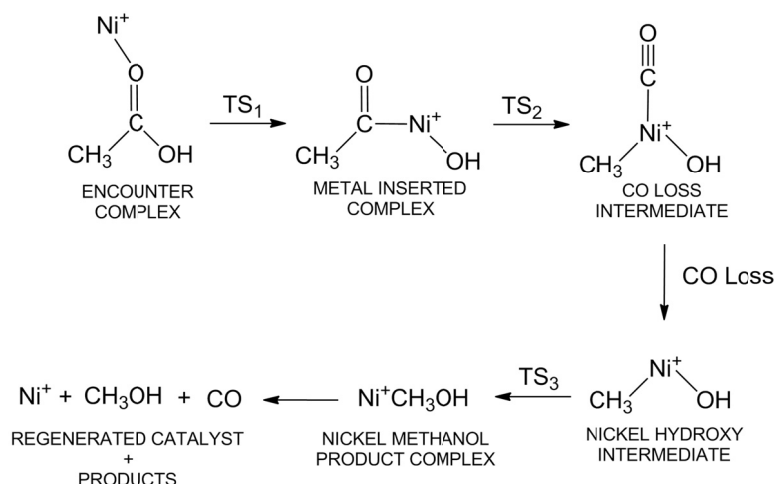


Figure 7: Proposed mechanism of the Ni^+ assisted decomposition of acetic acid

The ground electronic state bond dissociation energy (BDE) of the reactants is $\sim 17100 \text{ cm}^{-1}$. This bond likely forms from the electrostatic attraction between the dipole moment of neutral acetic acid (1.74 D) and the charged Ni^+ cation.

Complexation of the Ni^+ cation to the organic, i.e. the formation of an encounter complex (EC), leads to noticeable changes in the acetic acid molecule. The changes primarily include lengthening of the C-O carbonyl double bond, shortening of the C-C σ -

Ni⁺(CH₃COOH) Doublet Reaction Coordinate (cm⁻¹)

DFT B3LYP 6-311++G(d,p)

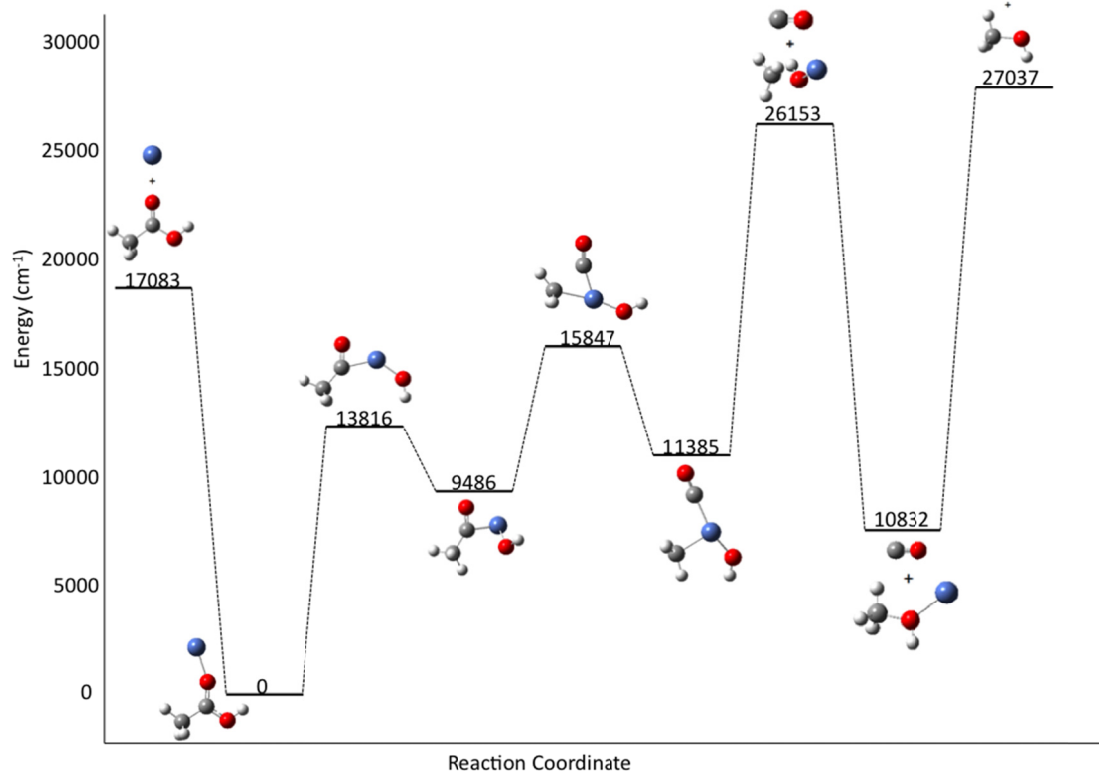


Figure 8: Doublet coordinate for Ni⁺(AA) decomposition

bond, and shortening of the C-O σ -bond. The most significant alteration to the molecule is the shortening of the C-O σ -bond (-0.0489 Å) and the consequent lengthening of the C-O carbonyl double bond (+0.0370 Å). This likely results from the interaction between the cation and the electronegative carboxylic acid functional group. It was initially hypothesized that the Ni⁺ cation would complex toward the carboxylic group of the organic. However, theoretical calculations consistently placed the Ni⁺ cation toward the methyl group of the organic.

Regardless of structure of the EC, it is proposed that Ni⁺ preferentially inserts into the C-O σ -bond. Calculations were performed examining initial insertion into both the C-

O σ -bond and C-C σ -bond. The C-O σ -bond activation yielded a smaller barrier height (9485.91298 cm^{-1} versus 14644.8836 cm^{-1}) as the reaction progressed through the first

	6-311+G(d,p)	6-311++G(d,p)
Separated Reactants	16984.4832	17083.4662
EC	0	0
TS₁	13829.7549	13816.3669
I₁	9502.59306	9485.91298
TS₂	15832.2414	15846.5072
I₂	11383.7101	11384.8075
TS₃	26170.5938	26153.4748
Product Complex (I₃)	10832.3898	10832.6093
Separated Products	26929.7566	27036.6407

Table 3. Calculated zero point corrected energies for the Ni⁺(AA) reaction coordinate (cm^{-1})

transition state. Upon Ni⁺ insertion, the reaction moves through the first of three transition states (**TS₁**). **TS₁** is associated with obvious rupture of the C-O σ -bond. Of the three transition states, **TS₁** presents the lowest barrier height, and as such, the formation of **TS₁** is not likely a kinetically important step in this dissociative reaction. **TS₁**, as is essential with transition state calculations, presented one imaginary frequency, 205i.

Once the reaction passes through **TS₁**, intermediate **I₁** is formed. Intermediate **I₁** presents as a Ni⁺ inserted complex, $\sim 9490 \text{ cm}^{-1}$ above the EC. The intermediate exhibits C_s symmetry with a plane defined along the C¹-C²-Ni⁺-O² axis. A slightly extended C-O carbonyl double bond (1.195 Å) is also present in this intermediate.

Intermediate **I₁** progresses to a second intermediate, **I₂**, through a second transition state (**TS₂**). **TS₂** is located $\sim 15800 \text{ cm}^{-1}$ above the EC, and $\sim 1300 \text{ cm}^{-1}$ below the energy of the separated reactants. This transition state is more energetically demanding than the initial transition state by 2000 cm^{-1} . As such, the less stable

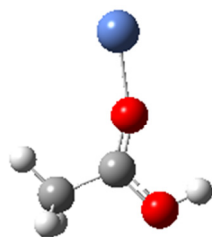
molecule, is characterized by more costly structural alterations. The single methyl group shifts onto the Ni^+ cation forming a tri-coordinate molecule with a transition metal center. The I_2 intermediate stabilizes as the carbonyl CO of acetic acid begins to extract from the molecule. The loss of CO from I_2 leads to the formation of a hydroxy insertion complex ($[\text{H}_3\text{C-Ni-OH}]^+$).

This hydroxy insertion complex is the same intermediate formed in the conversion of methane by MO^+ ($\text{M}=\text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) as studied by Schwarz et al. and Yoshizawa et al.²⁸⁻³⁴ The conversion of acetic acid by Ni^+ to the hydroxy insertion complex suggests a potential path intersection between these two, separate reactions.

The final transition state, TS_3 , presents the highest barrier height along the reaction coordinate. TS_3 is situated 12400 cm^{-1} above TS_1 and 10400 cm^{-1} above TS_2 . As such, this transition state is the most energetically demanding and will likely be rate determining. The formation of this transition state involves bond coupling between the methyl and hydroxyl groups.

As the reaction moves from TS_3 to products, minor structural changes within the molecule occur. The C-O σ -bond shortens upon formation of the product complex ($-0.605\text{ \AA}$) while the bond between the Ni^+ cation and remaining oxygen elongates ($+0.121\text{ \AA}$).

Upon complete dissociation, the reaction regenerates the Ni^+ catalyst, as well as methanol and carbon monoxide. Separating these individual products proves to be the most energetically demanding step within the reaction at $\sim 27000\text{ cm}^{-1}$.



Ni⁺-O¹-C²: 159.37681
 C¹-C²-O²: 114.47117
 C²-O²-H: 111.52843

EC



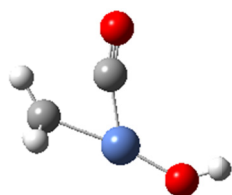
O¹-C²-Ni⁺: 85.74617
 C¹-C²-O¹: 143.36329
 C²-Ni⁺-O²: 72.86288

TS₁



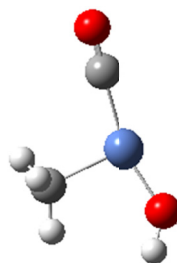
O¹-C²-Ni⁺: 76.01304
 C¹-C²-O¹: 139.89310
 C²-Ni⁺-O²: 131.63296

I₁



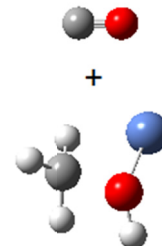
C¹-Ni⁺-C²: 61.03543
 C²-Ni⁺-O²: 170.13979
 O²-C²-Ni⁺: 163.52316

TS₂



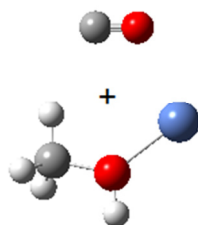
C¹-Ni⁺-C²: 97.86526
 C²-Ni⁺-O²: 96.58353
 O²-Ni⁺-C²: 155.11014

I₂



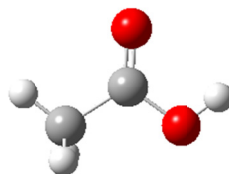
C¹-O²-Ni⁺: 64.3827

TS₃



C¹-O²-Ni⁺: 130.1021

Product Complex/I₃



C¹-C²-O¹: 126.18774
 O¹-C²-O²: 122.31260
 C¹-C²-O²: 111.49966

CH₃COOH

Figure 9: Geometries and structural parameters of key structures optimized at the B3LYP/6-311++G(d,p) level of theory

Ni⁺-Acetic Acid Decomposition: Conclusions

The present theoretical work adds new insight into the reaction between Ni⁺ and acetic acid. The formation of a Ni⁺-methanol product complex proceeds through six fundamental steps: encounter complex formation, C-O σ -bond activation by Ni⁺, a methyl shift forming a tri-coordinate molecule with a transition metal center, CO loss, bond coupling, and nonreactive dissociation. Theory also suggests that the final steps along the reaction coordinate are the most energetically demanding processes that occur during this dissociative reaction.

The theoretical results illuminate the various challenges associated with the experimental study of this reaction. The first challenge is that the complete catalytic cycle cannot be studied experimentally since it is endothermic by roughly 10,000 cm⁻¹. The technique pioneered by the Bellert Research Group is limited to studying reactions that are exothermic with respect to the separated reactants. Thus, the reaction that may be studied is the Ni⁺ assisted decomposition of acetic acid to yield Ni⁺(CH₃OH) + CO (the decomposition of the **EC** to the formation the third intermediate (**Product Complex/I₃**) in Figure 8). However, the formidable barrier height associated with formation of **TS₃** will make even the study of the “catalytic half cycle” nearly impossible. The theory indicates that photon energies in excess of 26000 cm⁻¹ are required to overcome this energetically demanding step. Supplying this amount of energy will likely result in reflection along the reaction coordinate which is simply the direct dissociation of the **EC** into Ni⁺ + CH₃COOH.

Altering one's perspective from driving the reaction forward toward decomposition, which is experimentally unlikely, to driving an association reaction

(combining CO and CH₃OH with a Ni⁺ catalyst to form acetic acid) provides an alternative direction for future experimental studies.

CHAPTER FOUR

Conclusion

General Conclusions

This study presents the utility of theoretical computations as a tool to preface experimental examination. Here, Density Functional Theory suggests that the barrier heights of the Ni^+ assisted decomposition of acetic acid reaction are too formidable to permit the experimental study of the forward reaction. As such, this saves time, money, and other laboratory resources. Moreover, the theoretical results indicate that the reverse reaction shows potential for experimental study. Thus, the combination of carbon monoxide and methanol to form acetic acid may be facilitated by a Ni^+ cation. Such association reactions have yet to be attempted by the Bellert Research Group and may provide a new direction for future research.

Additionally, the theoretical approach provides atomistic detail to reaction coordinates. As such, key intermediates can be identified; these are proposed to play roles in presumably unrelated reactions. Thus, these points where reaction pathways intersect indicate stable intermediate structures that may be common to multiple reaction coordinates. Here theory suggests that the hydroxyl metal inserted complex is a common point between the Ni^+ assisted decomposition of acetic acid and the industrially important conversion of methane to methanol via a NiO^+ catalyst.

Finally, the synergistic union of theory and experiment can provide a far more complete phenomenological description than either can muster independently. Theory

provides significant reaction detail but must be verified through experimental study. Experimental observations alone lack specificity of the reaction coordinate. Their combination provides the complete picture and the results of this thesis are a step toward that direction.

APPENDIX

APPENDIX

Computational data at the B3LYP/6-311++G(d,p) level of theory

ACETIC ACID (CH₃COOH)

Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!
! R1	R(1,2)	1.2049	-DE/DX = 0.0	!
! R2	R(1,3)	1.504	-DE/DX = 0.0	!
! R3	R(1,7)	1.3587	-DE/DX = 0.0	!
! R4	R(3,4)	1.0875	-DE/DX = 0.0	!
! R5	R(3,5)	1.0924	-DE/DX = 0.0	!
! R6	R(3,6)	1.0924	-DE/DX = 0.0	!
! R7	R(7,8)	0.9691	-DE/DX = 0.0	!
! A1	A(2,1,3)	126.1914	-DE/DX = 0.0	!
! A2	A(2,1,7)	122.3154	-DE/DX = 0.0	!
! A3	A(3,1,7)	111.4932	-DE/DX = 0.0	!
! A4	A(1,3,4)	109.5843	-DE/DX = 0.0	!
! A5	A(1,3,5)	109.833	-DE/DX = 0.0	!
! A6	A(1,3,6)	109.8309	-DE/DX = 0.0	!
! A7	A(4,3,5)	110.0844	-DE/DX = 0.0	!
! A8	A(4,3,6)	110.083	-DE/DX = 0.0	!
! A9	A(5,3,6)	107.3978	-DE/DX = 0.0	!
! A10	L(1,7,8,3,-1)	179.5697	-DE/DX = 0.0	!
! A11	L(1,7,8,3,-2)	359.9994	-DE/DX = 0.0	!
! D1	D(2,1,3,4)	0.0154	-DE/DX = 0.0	!
! D2	D(2,1,3,5)	121.0657	-DE/DX = 0.0	!
! D3	D(2,1,3,6)	-121.032	-DE/DX = 0.0	!
! D4	D(7,1,3,4)	-179.9852	-DE/DX = 0.0	!
! D5	D(7,1,3,5)	-58.9348	-DE/DX = 0.0	!
! D6	D(7,1,3,6)	58.9675	-DE/DX = 0.0	!

ACETIC ACID (CH₃COOH)

Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 8 and mass 15.99491

Atom 3 has atomic number 6 and mass 12.00000

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 8 and mass 15.99491

Atom 8 has atomic number 1 and mass 1.00783

Molecular mass: 60.02113 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	159.32265	191.03536	339.19987
X	0.99828	-0.05864	0.00000
Y	0.05864	0.99828	0.00000
Z	0.00000	0.00000	1.00000

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.54364 0.45339 0.25535

Rotational constants (GHZ): 11.32759 9.44716 5.32058

Zero-point vibrational energy 161440.3 (Joules/Mol)

38.58517 (Kcal/Mol)

Warning -- explicit consideration of 4 degrees of freedom as
vibrations may cause significant error

Vibrational temperatures: 81.67 611.10 781.22 843.07 951.53

(Kelvin) 1236.21 1437.24 1535.47 1733.17 1916.63

2025.25 2117.84 2123.89 2616.05 4390.45

4475.91 4548.08 5408.79

Zero-point correction= 0.061489 (Hartree/Particle)

Thermal correction to Energy= 0.066094

Thermal correction to Enthalpy= 0.067038

Thermal correction to Gibbs Free Energy= 0.034103

Sum of electronic and zero-point Energies= -229.103339

Sum of electronic and thermal Energies= -229.098734

Sum of electronic and thermal Enthalpies= -229.097790

Sum of electronic and thermal Free Energies= -229.130725

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	41.475	14.347	69.318
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	38.196

Rotational	0.889	2.981	23.850
Vibrational	39.697	8.385	7.272
Vibration 1	0.596	1.975	4.567
Vibration 2	0.787	1.416	0.876
Vibration 3	0.898	1.155	0.559
Vibration 4	0.943	1.062	0.474
	Q	Log10(Q)	Ln(Q)
Total Bot	0.205928D-15	-15.686284	-36.119003
Total V=0	0.395193D+13	12.596809	29.005225
Vib (Bot)	0.309767D-27	-27.508965	-63.341733
Vib (Bot) 1	0.363921D+01	0.561007	1.291767
Vib (Bot) 2	0.411907D+00	-0.385201	-0.886958
Vib (Bot) 3	0.290969D+00	-0.536153	-1.234538
Vib (Bot) 4	0.258499D+00	-0.587542	-1.352865
Vib (V=0)	0.594467D+01	0.774128	1.782496
Vib (V=0) 1	0.417340D+01	0.620490	1.428731
Vib (V=0) 2	0.114782D+01	0.059873	0.137862
Vib (V=0) 3	0.107850D+01	0.032820	0.075572
Vib (V=0) 4	0.106287D+01	0.026480	0.060972
Electronic	0.100000D+01	0.000000	0.000000
Translational	0.182773D+08	7.261911	16.721169
Rotational	0.363722D+05	4.560770	10.501561

ACETIC ACID (CH₃COOH)
Frequencies (cm⁻¹)

56.7646
424.7363
542.9747
585.9641
661.3469
859.2111
998.9321
1067.2056
1204.6136
1332.1290
1407.6208
1471.9719
1476.1796
1818.2494
3051.5219
3110.9196
3161.0749
3759.3027

ENCOUNTER COMPLEX ($\text{Ni}^+ + \text{CH}_3\text{COOH}$)

Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!
! R1	R(1,2)	1.2419	-DE/DX = 0.0	!
! R2	R(1,3)	1.4885	-DE/DX = 0.0	!
! R3	R(1,7)	1.3098	-DE/DX = 0.0	!
! R4	R(2,9)	1.8873	-DE/DX = 0.0	!
! R5	R(3,4)	1.087	-DE/DX = 0.0	!
! R6	R(3,5)	1.0933	-DE/DX = 0.0	!
! R7	R(3,6)	1.0933	-DE/DX = 0.0	!
! R8	R(7,8)	0.9724	-DE/DX = 0.0	!
! A1	A(2,1,3)	125.016	-DE/DX = 0.0	!
! A2	A(2,1,7)	120.5128	-DE/DX = 0.0	!
! A3	A(3,1,7)	114.4712	-DE/DX = 0.0	!
! A4	A(1,2,9)	159.3769	-DE/DX = 0.0	!
! A5	A(1,3,4)	111.1303	-DE/DX = 0.0	!
! A6	A(1,3,5)	109.1678	-DE/DX = 0.0	!
! A7	A(1,3,6)	109.1603	-DE/DX = 0.0	!
! A8	A(4,3,5)	110.18	-DE/DX = 0.0	!
! A9	A(4,3,6)	110.1799	-DE/DX = 0.0	!
! A10	A(5,3,6)	106.9201	-DE/DX = 0.0	!
! A11	A(1,7,8)	111.5284	-DE/DX = 0.0	!
! D1	D(3,1,2,9)	-0.0198	-DE/DX = 0.0	!
! D2	D(7,1,2,9)	-179.9808	-DE/DX = 0.0	!
! D3	D(2,1,3,4)	0.0315	-DE/DX = 0.0	!
! D4	D(2,1,3,5)	121.7595	-DE/DX = 0.0	!
! D5	D(2,1,3,6)	-121.6911	-DE/DX = 0.0	!
! D6	D(7,1,3,4)	-180.0053	-DE/DX = 0.0	!
! D7	D(7,1,3,5)	-58.2774	-DE/DX = 0.0	!
! D8	D(7,1,3,6)	58.272	-DE/DX = 0.0	!
! D9	D(2,1,7,8)	-0.0176	-DE/DX = 0.0	!
! D10	D(3,1,7,8)	-179.9825	-DE/DX = 0.0	!

ENCOUNTER COMPLEX (Ni^+ + CH_3COOH)

Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 8 and mass 15.99491

Atom 3 has atomic number 6 and mass 12.00000

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 8 and mass 15.99491

Atom 8 has atomic number 1 and mass 1.00783

Atom 9 has atomic number 28 and mass 57.93535

Molecular mass: 117.95648 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	187.46920	1207.30163	1383.66253
X	0.99973	-0.02338	0.00000
Y	0.02338	0.99973	0.00000
Z	0.00000	0.00000	1.00000

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.46202 0.07174 0.06260

Rotational constants (GHZ): 9.62687 1.49486 1.30432

Zero-point vibrational energy 164329.2 (Joules/Mol)

39.27562 (Kcal/Mol)

Warning -- explicit consideration of 7 degrees of freedom as vibrations may cause significant error

Vibrational temperatures: 38.94 75.86 89.37 412.23 659.82

(Kelvin) 803.60 845.80 977.48 1312.90 1484.98

1528.76 1774.97 1997.45 2096.18 2103.20

2104.27 2437.56 4391.08 4474.24 4560.82

5358.99

Zero-point correction= 0.062590 (Hartree/Particle)

Thermal correction to Energy= 0.069266

Thermal correction to Enthalpy= 0.070210

Thermal correction to Gibbs Free Energy= 0.028424

Sum of electronic and zero-point Energies= -1737.140641

Sum of electronic and thermal Energies= -1737.133964

Sum of electronic and thermal Enthalpies= -1737.133020

Sum of electronic and thermal Free Energies= -1737.174806

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	43.465	19.713	87.946

Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.210
Rotational	0.889	2.981	27.240
Vibrational	41.688	13.752	19.118
Vibration 1	0.593	1.984	6.034
Vibration 2	0.596	1.977	4.712
Vibration 3	0.597	1.972	4.389
Vibration 4	0.684	1.699	1.494
Vibration 5	0.817	1.342	0.770
Vibration 6	0.914	1.121	0.527
Vibration 7	0.945	1.058	0.471
	Q	Log10(Q)	Ln(Q)
Total Bot	0.842878D-13	-13.074235	-30.104539
Total V=0	0.518757D+16	15.714964	36.185041
Vib (Bot)	0.417794D-26	-26.379037	-60.739978
Vib (Bot) 1	0.765113D+01	0.883725	2.034853
Vib (Bot) 2	0.391954D+01	0.593235	1.365973
Vib (Bot) 3	0.332354D+01	0.521601	1.201030
Vib (Bot) 4	0.668716D+00	-0.174758	-0.402395
Vib (Bot) 5	0.371319D+00	-0.430253	-0.990695
Vib (Bot) 6	0.278670D+00	-0.554910	-1.277727
Vib (Bot) 7	0.257173D+00	-0.589775	-1.358007
Vib (V=0)	0.257135D+03	2.410162	5.549602
Vib (V=0) 1	0.816745D+01	0.912086	2.100157
Vib (V=0) 2	0.445130D+01	0.648487	1.493196
Vib (V=0) 3	0.386094D+01	0.586693	1.350910
Vib (V=0) 4	0.133497D+01	0.125473	0.288912
Vib (V=0) 5	0.112280D+01	0.050302	0.115824
Vib (V=0) 6	0.107241D+01	0.030362	0.069912
Vib (V=0) 7	0.106226D+01	0.026231	0.060400
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.503544D+08	7.702038	17.734598
Rotational	0.200325D+06	5.301734	12.207694

ENCOUNTER COMPLEX (Ni^+ + CH_3COOH)
Frequencies (cm^{-1})

27.0650
52.7274
62.1179
286.5121
458.5964
558.5283
587.8583
679.3816
912.5111
1032.1159
1062.5415
1233.6657
1388.2963
1456.9173
1461.8019
1462.5427
1694.1885
3051.9583
3109.7556
3169.9291
3724.6878

TS_I (Ni⁺ + CH₃COOH)
Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	TS	Reactant	Product	Derivative Info.	!

! R1	R(1,2)	1.1733	1.2419	1.1953	-DE/DX = 0.0	!
! R2	R(1,3)	1.4676	1.4885	1.463	-DE/DX = 0.0	!
! R3	R(1,7)	2.232	1.3098	3.2479	-DE/DX = 0.0	!
! R4	R(2,9)	2.1939	1.8873	1.9544	-DE/DX = 0.0001	!
! R5	R(3,4)	1.0954	1.087	1.0934	-DE/DX = 0.0	!
! R6	R(3,5)	1.0872	1.0933	1.0955	-DE/DX = 0.0	!
! R7	R(3,6)	1.097	1.0933	1.0954	-DE/DX = 0.0	!
! R8	R(7,8)	0.9695	0.9724	0.9667	-DE/DX = 0.0	!
! R9	R(1,9)	1.9429	3.0809	1.862	-DE/DX = 0.0	!
! R10	R(7,9)	1.8113	4.0876	1.6976	-DE/DX = 0.0	!
! A1	A(2,1,3)	143.3633	125.0161	139.8931	-DE/DX = 0.0	!
! A2	A(2,1,7)	115.4549	120.5128	99.0087	-DE/DX = 0.0	!
! A3	A(3,1,7)	96.4156	114.4712	121.0981	-DE/DX = 0.0	!
! A4	A(1,2,9)	62.0245	159.3768	67.5832	-DE/DX = 0.0	!
! A5	A(1,3,4)	107.6265	111.1303	109.7212	-DE/DX = 0.0	!
! A6	A(1,3,5)	111.322	109.1679	108.546	-DE/DX = 0.0	!
! A7	A(1,3,6)	106.6529	109.1603	108.6062	-DE/DX = 0.0	!
! A8	A(4,3,5)	112.2996	110.18	111.2421	-DE/DX = 0.0	!
! A9	A(4,3,6)	109.5709	110.1799	111.2728	-DE/DX = 0.0	!
! A10	A(5,3,6)	109.1984	106.9201	107.358	-DE/DX = 0.0	!
! A11	A(1,7,8)	122.1268	111.5284	107.4438	-DE/DX = 0.0	!
! A12	A(3,1,9)	130.1401	112.5552	144.0938	-DE/DX = 0.0	!
! A13	A(8,7,9)	114.6141	78.0611	132.8151	-DE/DX = 0.0	!
! A14	A(1,9,7)	72.8629	13.559	131.633	-DE/DX = 0.0	!
! A15	A(2,9,7)	93.7178	5.3967	168.0366	-DE/DX = 0.0	!
! D1	D(3,1,2,9)	-169.5044	-0.0196	-179.9021	-DE/DX = 0.0	!
! D2	D(7,1,2,9)	42.558	-179.9808	0.0336	-DE/DX = 0.0	!
! D3	D(2,1,3,4)	48.3602	0.0315	-0.3136	-DE/DX = 0.0	!
! D4	D(2,1,3,5)	171.8243	121.7594	121.4375	-DE/DX = 0.0	!
! D5	D(2,1,3,6)	-69.1496	-121.6912	-122.1403	-DE/DX = 0.0	!
! D6	D(7,1,3,4)	-160.4775	179.9947	179.7606	-DE/DX = 0.0	!
! D7	D(7,1,3,5)	-37.0134	-58.2773	-58.4883	-DE/DX = 0.0	!
! D8	D(7,1,3,6)	82.0128	58.272	57.9339	-DE/DX = 0.0	!
! D9	D(2,1,7,8)	39.4897	-0.0175	-179.9663	-DE/DX = 0.0	!
! D10	D(3,1,7,8)	-121.9217	-179.9826	-0.0148	-DE/DX = 0.0	!
! D11	D(9,1,3,4)	-117.8933	0.0269	179.8484	-DE/DX = 0.0	!
! D12	D(9,1,3,5)	5.5708	121.7548	-58.4005	-DE/DX = 0.0	!

! D13	D(9,1,3,6)	124.597	-121.6958	58.0217	-DE/DX =	0.0	!
! D14	D(3,1,9,7)	-60.1262	179.96	-0.1924	-DE/DX =	0.0	!
! D15	D(8,7,9,1)	-113.4236	179.978	0.1522	-DE/DX =	0.0	!
! D16	D(8,7,9,2)	-88.5346	179.9438	0.3952	-DE/DX =	0.0	!

TS_I (Ni⁺ + CH₃COOH)
Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 8 and mass 15.99491

Atom 3 has atomic number 6 and mass 12.00000

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 8 and mass 15.99491

Atom 8 has atomic number 1 and mass 1.00783

Atom 9 has atomic number 28 and mass 57.93535

Molecular mass: 117.95648 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	320.41789	583.58586	758.87555
X	0.99852	0.03953	-0.03728
Y	-0.03865	0.99896	0.02400
Z	0.03819	-0.02252	0.99902

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.27032 0.14842 0.11413

Rotational constants (GHZ): 5.63246 3.09250 2.37818

1 imaginary frequencies ignored.

Zero-point vibrational energy 153152.0 (Joules/Mol)

36.60420 (Kcal/Mol)

Warning -- explicit consideration of 8 degrees of freedom as
vibrations may cause significant error

Vibrational temperatures: 135.12 186.01 284.89 372.95 606.57

(Kelvin) 622.49 733.67 892.23 1116.21 1308.62

1415.36 1524.72 1964.04 2038.68 2067.10

2784.89 4350.95 4453.61 4562.49 5419.26

Zero-point correction= 0.058333 (Hartree/Particle)

Thermal correction to Energy= 0.064792

Thermal correction to Enthalpy= 0.065736

Thermal correction to Gibbs Free Energy= 0.026884

Sum of electronic and zero-point Energies= -1737.077689

Sum of electronic and thermal Energies= -1737.071230

Sum of electronic and thermal Enthalpies= -1737.070285

Sum of electronic and thermal Free Energies= -1737.109137

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	40.658	20.687	81.771

Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.210
Rotational	0.889	2.981	26.453
Vibrational	38.880	14.725	13.729
Vibration 1	0.603	1.954	3.577
Vibration 2	0.612	1.924	2.957
Vibration 3	0.637	1.843	2.151
Vibration 4	0.668	1.747	1.667
Vibration 5	0.784	1.423	0.887
Vibration 6	0.794	1.399	0.850
Vibration 7	0.865	1.228	0.634
Vibration 8	0.980	0.989	0.416
	Q	Log10(Q)	Ln(Q)
Total Bot	0.430676D-12	-12.365850	-28.473421
Total V=0	0.291867D+15	14.465186	33.307321
Vib (Bot)	0.317132D-25	-25.498760	-58.713065
Vib (Bot) 1	0.218786D+01	0.340019	0.782923
Vib (Bot) 2	0.157719D+01	0.197885	0.455646
Vib (Bot) 3	0.100775D+01	0.003353	0.007720
Vib (Bot) 4	0.749611D+00	-0.125164	-0.288201
Vib (Bot) 5	0.415986D+00	-0.380921	-0.877103
Vib (Bot) 6	0.401887D+00	-0.395896	-0.911584
Vib (Bot) 7	0.319457D+00	-0.495588	-1.141133
Vib (Bot) 8	0.235791D+00	-0.627473	-1.444810
Vib (V=0)	0.214919D+02	1.332275	3.067678
Vib (V=0) 1	0.274427D+01	0.438426	1.009513
Vib (V=0) 2	0.215455D+01	0.333357	0.767582
Vib (V=0) 3	0.162497D+01	0.210846	0.485490
Vib (V=0) 4	0.140106D+01	0.146458	0.337232
Vib (V=0) 5	0.115042D+01	0.060856	0.140126
Vib (V=0) 6	0.114149D+01	0.057473	0.132337
Vib (V=0) 7	0.109334D+01	0.038755	0.089238
Vib (V=0) 8	0.105281D+01	0.022349	0.051461
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.503544D+08	7.702038	17.734598
Rotational	0.134847D+06	5.129842	11.811899

TS_I (Ni⁺ + CH₃COOH)
Frequency (cm⁻¹)

-205.1081
93.9102
129.2817
198.0116
259.2105
421.5902
432.6528
509.9266
620.1294
775.8089
909.5399
983.7240
1059.7371
1365.0788
1416.9534
1436.7073
1935.5954
3024.0675
3095.4191
3171.0922
3766.5755

I_1 ($Ni^+ + CH_3COOH$)
Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!

! R1	R(1,2)	1.1953	-DE/DX = 0.0	!
! R2	R(1,3)	1.463	-DE/DX = 0.0	!
! R3	R(1,9)	1.862	-DE/DX = 0.0	!
! R4	R(3,4)	1.0934	-DE/DX = 0.0	!
! R5	R(3,5)	1.0955	-DE/DX = 0.0	!
! R6	R(3,6)	1.0954	-DE/DX = 0.0	!
! R7	R(7,8)	0.9667	-DE/DX = 0.0	!
! R8	R(7,9)	1.6976	-DE/DX = 0.0	!
! A1	A(2,1,3)	139.8931	-DE/DX = 0.0	!
! A2	A(2,1,9)	76.013	-DE/DX = 0.0	!
! A3	A(3,1,9)	144.0938	-DE/DX = 0.0	!
! A4	A(1,3,4)	109.7212	-DE/DX = 0.0	!
! A5	A(1,3,5)	108.546	-DE/DX = 0.0	!
! A6	A(1,3,6)	108.6062	-DE/DX = 0.0	!
! A7	A(4,3,5)	111.2421	-DE/DX = 0.0	!
! A8	A(4,3,6)	111.2728	-DE/DX = 0.0	!
! A9	A(5,3,6)	107.358	-DE/DX = 0.0	!
! A10	A(8,7,9)	132.815	-DE/DX = 0.0	!
! A11	A(1,9,7)	131.633	-DE/DX = 0.0	!
! D1	D(2,1,3,4)	-0.3136	-DE/DX = 0.0	!
! D2	D(2,1,3,5)	121.4375	-DE/DX = 0.0	!
! D3	D(2,1,3,6)	-122.1403	-DE/DX = 0.0	!
! D4	D(9,1,3,4)	179.8484	-DE/DX = 0.0	!
! D5	D(9,1,3,5)	-58.4005	-DE/DX = 0.0	!
! D6	D(9,1,3,6)	58.0217	-DE/DX = 0.0	!
! D7	D(2,1,9,7)	179.9151	-DE/DX = 0.0	!
! D8	D(3,1,9,7)	-0.1924	-DE/DX = 0.0	!
! D9	D(8,7,9,1)	0.1521	-DE/DX = 0.0	!

I₁ (Ni⁺ + CH₃COOH)
Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 8 and mass 15.99491

Atom 3 has atomic number 6 and mass 12.00000

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 8 and mass 15.99491

Atom 8 has atomic number 1 and mass 1.00783

Atom 9 has atomic number 28 and mass 57.93535

Molecular mass: 117.95648 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	216.36015	735.41913	940.56407
X	0.99946	-0.03272	-0.00003
Y	0.03272	0.99946	0.00003
Z	0.00003	-0.00003	1.00000

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.40032 0.11777 0.09209

Rotational constants (GHZ): 8.34138 2.45403 1.91879

Zero-point vibrational energy 153959.4 (Joules/Mol)
36.79717 (Kcal/Mol)

Warning -- explicit consideration of 8 degrees of freedom as
vibrations may cause significant error

Vibrational temperatures: 105.11 145.87 163.36 398.55 411.39
(Kelvin) 548.96 572.32 796.67 931.52 1124.08
1336.57 1453.60 1573.47 1960.58 2032.98
2061.60 2635.60 4348.19 4450.45 4495.35
5487.86

Zero-point correction=	0.058640 (Hartree/Particle)
Thermal correction to Energy=	0.065768
Thermal correction to Enthalpy=	0.066712
Thermal correction to Gibbs Free Energy=	0.026173
Sum of electronic and zero-point Energies=	-1737.097420
Sum of electronic and thermal Energies=	-1737.090292
Sum of electronic and thermal Enthalpies=	-1737.089348
Sum of electronic and thermal Free Energies=	-1737.129887

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	41.270	22.414	85.322

Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.210
Rotational	0.889	2.981	26.506
Vibrational	39.492	16.452	17.227
Vibration 1	0.599	1.967	4.069
Vibration 2	0.604	1.948	3.428
Vibration 3	0.607	1.938	3.208
Vibration 4	0.678	1.716	1.552
Vibration 5	0.684	1.700	1.498
Vibration 6	0.751	1.510	1.033
Vibration 7	0.764	1.475	0.971
Vibration 8	0.909	1.132	0.537
	Q	Log10(Q)	Ln(Q)
Total Bot	0.914693D-12	-12.038725	-27.720188
Total V=0	0.858538D+15	14.933759	34.386252
Vib (Bot)	0.655859D-25	-25.183189	-57.986436
Vib (Bot) 1	0.282203D+01	0.450561	1.037455
Vib (Bot) 2	0.202369D+01	0.306145	0.704924
Vib (Bot) 3	0.180252D+01	0.255880	0.589185
Vib (Bot) 4	0.695152D+00	-0.157920	-0.363625
Vib (Bot) 5	0.670286D+00	-0.173740	-0.400050
Vib (Bot) 6	0.473358D+00	-0.324810	-0.747903
Vib (Bot) 7	0.448800D+00	-0.347947	-0.801178
Vib (Bot) 8	0.282409D+00	-0.549121	-1.264399
Vib (V=0)	0.615595D+02	1.789295	4.120004
Vib (V=0) 1	0.336598D+01	0.527111	1.213719
Vib (V=0) 2	0.258455D+01	0.412384	0.949550
Vib (V=0) 3	0.237058D+01	0.374855	0.863135
Vib (V=0) 4	0.135629D+01	0.132353	0.304754
Vib (V=0) 5	0.133623D+01	0.125882	0.289854
Vib (V=0) 6	0.118853D+01	0.075009	0.172714
Vib (V=0) 7	0.117188D+01	0.068883	0.158608
Vib (V=0) 8	0.107424D+01	0.031102	0.071616
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.503544D+08	7.702038	17.734598
Rotational	0.138483D+06	5.141397	11.838503

$I_1 (Ni^+ + CH_3COOH)$
Frequencies (cm⁻¹)

73.0524
101.3851
113.5385
277.0097
285.9305
381.5495
397.7833
553.7109
647.4377
781.2768
928.9617
1010.3023
1093.6195
1362.6731
1412.9962
1432.8835
1831.8325
3022.1486
3093.2229
3124.4252
3814.2572

TS₂ (Ni⁺ + CH₃COOH)
Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	TS	Reactant	Product	Derivative Info.	!

! R1	R(1,2)	1.1327	1.1953	1.1168	-DE/DX = 0.0	!
! R2	R(1,3)	1.9384	1.463	2.9612	-DE/DX = 0.0	!
! R3	R(1,9)	1.7683	1.862	1.9606	-DE/DX = 0.0001	!
! R4	R(2,9)	2.8725	1.9544	3.0764	-DE/DX = 0.0	!
! R5	R(3,4)	1.0875	1.0934	1.0924	-DE/DX = 0.0	!
! R6	R(3,5)	1.0994	1.0955	1.084	-DE/DX = 0.0	!
! R7	R(3,6)	1.0961	1.0954	1.0882	-DE/DX = 0.0	!
! R8	R(7,8)	0.9679	0.9667	0.9679	-DE/DX = 0.0	!
! R9	R(7,9)	1.7102	1.6976	1.6947	-DE/DX = 0.0	!
! R10	R(3,9)	2.0242	3.1654	1.9692	-DE/DX = 0.0	!
! A1	A(2,1,3)	130.4618	139.8931	139.6638	-DE/DX = 0.0001	!
! A2	A(3,1,9)	66.0133	144.0938	41.2109	-DE/DX = 0.0	!
! A3	A(1,3,4)	87.2702	109.7212	78.7616	-DE/DX = 0.0	!
! A4	A(1,3,5)	115.0628	108.546	149.2121	-DE/DX = 0.0	!
! A5	A(1,3,6)	115.0247	108.6062	80.9973	-DE/DX = -0.0001	!
! A6	A(4,3,5)	110.106	111.2421	113.8477	-DE/DX = 0.0	!
! A7	A(4,3,6)	110.8174	111.2728	115.1178	-DE/DX = 0.0	!
! A8	A(5,3,6)	115.0929	107.358	114.5772	-DE/DX = 0.0	!
! A9	A(8,7,9)	133.9358	132.8151	133.2659	-DE/DX = 0.0	!
! A10	A(1,9,7)	127.7863	131.633	155.121	-DE/DX = 0.0	!
! A11	A(2,9,7)	121.3832	168.0366	154.0533	-DE/DX = -0.0001	!
! A12	A(4,3,9)	140.1114	129.9006	98.6453	-DE/DX = 0.0	!
! A13	A(5,3,9)	87.6831	97.3064	108.2201	-DE/DX = 0.0	!
! A14	A(6,3,9)	91.416	97.2578	104.3848	-DE/DX = -0.0001	!
! A15	A(1,9,3)	61.0354	15.7267	97.7959	-DE/DX = 0.0	!
! A16	A(3,9,7)	170.1398	115.9063	96.5815	-DE/DX = 0.0	!
! A17	L(2,1,9,3,-1)	196.4751	283.9869	180.8747	-DE/DX = 0.0001	!
! A18	L(2,1,9,3,-2)	180.2813	179.838	184.496	-DE/DX = 0.0	!
! D1	D(2,1,3,4)	3.465	-0.3136	66.9624	-DE/DX = 0.0	!
! D2	D(2,1,3,5)	114.4193	121.4375	-174.8842	-DE/DX = 0.0	!
! D3	D(2,1,3,6)	-108.275	-122.1403	-51.0496	-DE/DX = 0.0	!
! D4	D(9,1,3,4)	-176.8163	179.8484	-117.5336	-DE/DX = 0.0	!
! D5	D(9,1,3,5)	-65.862	-58.4005	0.6198	-DE/DX = 0.0	!
! D6	D(9,1,3,6)	71.4436	58.0217	124.4543	-DE/DX = 0.0	!
! D7	D(3,1,9,7)	-174.713	-0.1924	-124.765	-DE/DX = 0.0	!
! D8	D(8,7,9,1)	-8.4905	0.1522	117.5608	-DE/DX = 0.0	!

! D9	D(8,7,9,2)	-7.8974	0.3952	116.84	-DE/DX = 0.0	!
! D10	D(4,3,9,1)	4.9625	-0.186	61.6101	-DE/DX = 0.0	!
! D11	D(4,3,9,7)	159.796	179.6541	-138.7488	-DE/DX = 0.0	!
! D12	D(5,3,9,1)	124.176	125.5005	-179.666	-DE/DX = 0.0	!
! D13	D(5,3,9,7)	-80.9906	-54.6594	-20.0249	-DE/DX = 0.0	!
! D14	D(6,3,9,1)	-120.7643	-125.8642	-57.2224	-DE/DX = 0.0	!
! D15	D(6,3,9,7)	34.0692	53.9759	102.4187	-DE/DX = 0.0	!
! D16	D(8,7,9,3)	-160.4054	0.0942	-7.424	-DE/DX = 0.0	!

TS₂ (Ni⁺ + CH₃COOH)

Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 8 and mass 15.99491

Atom 3 has atomic number 6 and mass 12.00000

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 8 and mass 15.99491

Atom 8 has atomic number 1 and mass 1.00783

Atom 9 has atomic number 28 and mass 57.93535

Molecular mass: 117.95648 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	263.06597	658.82524	908.86043
X	0.99630	0.08592	0.00056
Y	-0.08592	0.99630	0.00223
Z	-0.00036	-0.00227	1.00000

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.32925 0.13147 0.09530

Rotational constants (GHZ): 6.86041 2.73933 1.98572

1 imaginary frequencies ignored.

Zero-point vibrational energy 146420.5 (Joules/Mol)

34.99534 (Kcal/Mol)

Warning -- explicit consideration of 9 degrees of freedom as vibrations may cause significant error

Vibrational temperatures: 65.46 158.36 191.81 450.53 518.00
(Kelvin) 535.13 573.39 761.22 879.93 1046.56

1073.07 1229.96 1765.69 2005.56 2050.80

3132.97 4292.63 4458.71 4562.77 5468.08

Zero-point correction= 0.055769 (Hartree/Particle)

Thermal correction to Energy= 0.062885

Thermal correction to Enthalpy= 0.063829

Thermal correction to Gibbs Free Energy= 0.023152

Sum of electronic and zero-point Energies= -1737.068439

Sum of electronic and thermal Energies= -1737.061323

Sum of electronic and thermal Enthalpies= -1737.060378

Sum of electronic and thermal Free Energies= -1737.101055

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	39.461	22.687	85.612
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.210
Rotational	0.889	2.981	26.557
Vibrational	37.684	16.725	17.467
Vibration 1	0.595	1.979	5.004
Vibration 2	0.606	1.941	3.268
Vibration 3	0.613	1.920	2.898
Vibration 4	0.701	1.649	1.346
Vibration 5	0.735	1.555	1.122
Vibration 6	0.744	1.530	1.072
Vibration 7	0.765	1.473	0.968
Vibration 8	0.884	1.186	0.589
Vibration 9	0.971	1.007	0.430
	Q	Log10(Q)	Ln(Q)
Total Bot	0.224265D-10	-10.649238	-24.520776
Total V=0	0.100577D+16	15.002498	34.544529
Vib (Bot)	0.156741D-23	-23.804818	-54.812619
Vib (Bot) 1	0.454567D+01	0.657598	1.514175
Vib (Bot) 2	0.186076D+01	0.269690	0.620985
Vib (Bot) 3	0.152791D+01	0.184097	0.423898
Vib (Bot) 4	0.602769D+00	-0.219849	-0.506222
Vib (Bot) 5	0.509095D+00	-0.293201	-0.675121
Vib (Bot) 6	0.488840D+00	-0.310834	-0.715721
Vib (Bot) 7	0.447719D+00	-0.348995	-0.803590
Vib (Bot) 8	0.302538D+00	-0.519220	-1.195548
Vib (Bot) 9	0.241242D+00	-0.617547	-1.421954
Vib (V=0)	0.702939D+02	1.846918	4.252686
Vib (V=0) 1	0.507309D+01	0.705272	1.623949
Vib (V=0) 2	0.242677D+01	0.385028	0.886559
Vib (V=0) 3	0.210764D+01	0.323796	0.745567
Vib (V=0) 4	0.128315D+01	0.108279	0.249321
Vib (V=0) 5	0.121357D+01	0.084064	0.193564
Vib (V=0) 6	0.119926D+01	0.078913	0.181704
Vib (V=0) 7	0.117116D+01	0.068615	0.157992
Vib (V=0) 8	0.108441D+01	0.035192	0.081031
Vib (V=0) 9	0.105516D+01	0.023317	0.053688
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.503544D+08	7.702038	17.734598
Rotational	0.142073D+06	5.152512	11.864098

TS₂ (Ni⁺ + CH₃COOH)
Frequencies (cm⁻¹)

-243.4563
45.4959
110.0673
133.3157
313.1345
360.0261
371.9377
398.5276
529.0782
611.5796
727.3966
745.8224
854.8690
1227.2176
1393.9339
1425.3805
2177.5233
2983.5288
3098.9648
3171.2895
3800.5107

I₂ (Ni⁺ + CH₃COOH)
Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!

! R1	R(1,2)	1.1168	-DE/DX = 0.0	!
! R2	R(1,9)	1.9606	-DE/DX = 0.0	!
! R3	R(3,4)	1.0924	-DE/DX = 0.0	!
! R4	R(3,5)	1.084	-DE/DX = 0.0	!
! R5	R(3,6)	1.0882	-DE/DX = 0.0	!
! R6	R(3,9)	1.9692	-DE/DX = 0.0	!
! R7	R(7,8)	0.9679	-DE/DX = 0.0	!
! R8	R(7,9)	1.6947	-DE/DX = 0.0	!
! A1	A(4,3,5)	113.8477	-DE/DX = 0.0	!
! A2	A(4,3,6)	115.1178	-DE/DX = 0.0	!
! A3	A(4,3,9)	98.6453	-DE/DX = 0.0	!
! A4	A(5,3,6)	114.5772	-DE/DX = 0.0	!
! A5	A(5,3,9)	108.2201	-DE/DX = 0.0	!
! A6	A(6,3,9)	104.3848	-DE/DX = 0.0	!
! A7	A(8,7,9)	133.2659	-DE/DX = 0.0	!
! A8	A(1,9,3)	97.7959	-DE/DX = 0.0	!
! A9	A(1,9,7)	155.121	-DE/DX = 0.0	!
! A10	A(3,9,7)	96.5815	-DE/DX = 0.0	!
! A11	L(2,1,9,3,-1)	180.8747	-DE/DX = 0.0001	!
! A12	L(2,1,9,3,-2)	184.496	-DE/DX = 0.0	!
! D1	D(4,3,9,1)	61.6101	-DE/DX = 0.0	!
! D2	D(4,3,9,7)	-138.7488	-DE/DX = 0.0	!
! D3	D(5,3,9,1)	-179.666	-DE/DX = 0.0	!
! D4	D(5,3,9,7)	-20.0249	-DE/DX = 0.0	!
! D5	D(6,3,9,1)	-57.2224	-DE/DX = 0.0	!
! D6	D(6,3,9,7)	102.4187	-DE/DX = 0.0	!
! D7	D(8,7,9,1)	117.5608	-DE/DX = 0.0	!
! D8	D(8,7,9,3)	-7.424	-DE/DX = 0.0	!

I₂ (Ni⁺ + CH₃COOH)
Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 8 and mass 15.99491

Atom 3 has atomic number 6 and mass 12.00000

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 8 and mass 15.99491

Atom 8 has atomic number 1 and mass 1.00783

Atom 9 has atomic number 28 and mass 57.93535

Molecular mass: 117.95648 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	227.90705	839.18472	1032.44143
X	0.99979	-0.01913	-0.00775
Y	0.01914	0.99982	0.00106
Z	0.00772	-0.00121	0.99997

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.38004 0.10321 0.08389

Rotational constants (GHZ): 7.91876 2.15059 1.74803

Zero-point vibrational energy 148708.5 (Joules/Mol)
35.54219 (Kcal/Mol)

Warning -- explicit consideration of 9 degrees of freedom as
vibrations may cause significant error

Vibrational temperatures: 122.89 152.07 154.39 291.35 433.31
(Kelvin) 457.73 529.00 570.81 648.12 998.31
1026.28 1077.46 1145.89 1711.46 2021.82
2072.54 3311.30 4374.68 4568.78 4640.95
5461.87

Zero-point correction=	0.056640 (Hartree/Particle)
Thermal correction to Energy=	0.064399
Thermal correction to Enthalpy=	0.065344
Thermal correction to Gibbs Free Energy=	0.023704
Sum of electronic and zero-point Energies=	-1737.088773
Sum of electronic and thermal Energies=	-1737.081014
Sum of electronic and thermal Enthalpies=	-1737.080070
Sum of electronic and thermal Free Energies=	-1737.121709

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	40.411	24.784	87.638

Electronic	0.000	0.000	1.377
Translational	0.889	2.981	40.210
Rotational	0.889	2.981	26.782
Vibrational	38.634	18.822	19.269
Vibration 1	0.601	1.959	3.762
Vibration 2	0.605	1.945	3.347
Vibration 3	0.606	1.943	3.317
Vibration 4	0.639	1.836	2.110
Vibration 5	0.693	1.671	1.410
Vibration 6	0.705	1.639	1.320
Vibration 7	0.740	1.539	1.089
Vibration 8	0.763	1.477	0.975
Vibration 9	0.809	1.360	0.794
	Q	Log10(Q)	Ln(Q)
Total Bot	0.125034D-10	-10.902973	-25.105023
Total V=0	0.141126D+16	15.149606	34.883257
Vib (Bot)	0.780499D-24	-24.107628	-55.509864
Vib (Bot) 1	0.240898D+01	0.381833	0.879204
Vib (Bot) 2	0.193956D+01	0.287704	0.662463
Vib (Bot) 3	0.190972D+01	0.280970	0.646957
Vib (Bot) 4	0.983739D+00	-0.007120	-0.016395
Vib (Bot) 5	0.631055D+00	-0.199933	-0.460362
Vib (Bot) 6	0.591538D+00	-0.228018	-0.525030
Vib (Bot) 7	0.495943D+00	-0.304568	-0.701293
Vib (Bot) 8	0.450330D+00	-0.346469	-0.797775
Vib (Bot) 9	0.380548D+00	-0.419591	-0.966144
Vib (V=0)	0.880951D+02	1.944952	4.478416
Vib (V=0) 1	0.296032D+01	0.471339	1.085298
Vib (V=0) 2	0.250297D+01	0.398456	0.917480
Vib (V=0) 3	0.247409D+01	0.393416	0.905873
Vib (V=0) 4	0.160351D+01	0.205073	0.472197
Vib (V=0) 5	0.130513D+01	0.115653	0.266301
Vib (V=0) 6	0.127454D+01	0.105354	0.242588
Vib (V=0) 7	0.120424D+01	0.080715	0.185852
Vib (V=0) 8	0.117290D+01	0.069262	0.159481
Vib (V=0) 9	0.112834D+01	0.052442	0.120751
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.503544D+08	7.702038	17.734598
Rotational	0.159069D+06	5.201587	11.977096

$I_2 (Ni^+ + CH_3COOH)$
Frequencies (cm^{-1})

85.4158
105.6916
107.3076
202.4968
301.1652
318.1389
367.6773
396.7344
450.4633
693.8582
713.3012
748.8759
796.4351
1189.5249
1405.2372
1440.4905
2301.4689
3040.5612
3175.4616
3225.6263
3796.1946

TS₃ (Ni⁺ + CH₃COOH)
Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	TS	Reactant	Product	Derivative Info.	!

! R1	R(1,2)	1.1054	1.1034	1.0861	-DE/DX = 0.0	!
! R2	R(1,3)	1.0824	1.0894	1.0887	-DE/DX = 0.0	!
! R3	R(1,4)	1.0815	1.0863	1.0887	-DE/DX = 0.0	!
! R4	R(1,7)	2.0808	1.9127	3.0851	-DE/DX = 0.0	!
! R5	R(5,6)	0.9689	0.9712	0.9664	-DE/DX = 0.0	!
! R6	R(5,7)	1.7999	1.6944	1.9208	-DE/DX = 0.0	!
! R7	R(1,5)	2.0804	2.8095	1.4755	-DE/DX = 0.0	!
! A1	A(2,1,3)	112.8765	115.2348	110.5036	-DE/DX = 0.0	!
! A2	A(2,1,4)	114.7509	113.6722	110.4995	-DE/DX = 0.0	!
! A3	A(2,1,7)	77.7806	92.5213	78.3082	-DE/DX = 0.0	!
! A4	A(3,1,4)	115.7797	115.1715	111.6945	-DE/DX = 0.0	!
! A5	A(3,1,7)	117.8572	105.9406	120.0084	-DE/DX = 0.0	!
! A6	A(4,1,7)	112.2756	111.6546	120.0747	-DE/DX = 0.0	!
! A7	A(6,5,7)	119.322	125.9929	119.8596	-DE/DX = 0.0	!
! A8	A(1,7,5)	64.3571	102.1463	21.459	-DE/DX = 0.0	!
! A9	A(2,1,5)	129.0252	126.4325	106.7471	-DE/DX = 0.0	!
! A10	A(3,1,5)	92.6293	97.8888	108.6176	-DE/DX = 0.0	!
! A11	A(4,1,5)	89.0218	84.7481	108.615	-DE/DX = 0.0	!
! A12	A(1,5,6)	100.3277	84.3361	110.0383	-DE/DX = 0.0	!
! A13	A(1,5,7)	64.3827	41.7253	130.1021	-DE/DX = 0.0	!
! D1	D(2,1,7,5)	-178.6521	161.4256	179.9233	-DE/DX = 0.0	!
! D2	D(3,1,7,5)	-69.053	-81.4204	-73.0067	-DE/DX = 0.0	!
! D3	D(4,1,7,5)	69.3721	44.6889	72.8606	-DE/DX = 0.0	!
! D4	D(6,5,7,1)	87.6341	3.8116	179.9732	-DE/DX = 0.0	!
! D5	D(2,1,5,6)	-115.993	159.7992	179.9463	-DE/DX = 0.0	!
! D6	D(2,1,5,7)	1.6958	-23.2991	-0.0785	-DE/DX = 0.0	!
! D7	D(3,1,5,6)	6.5647	-70.615	-60.8872	-DE/DX = 0.0	!
! D8	D(3,1,5,7)	124.2535	106.2867	119.0881	-DE/DX = 0.0	!
! D9	D(4,1,5,6)	122.3277	44.1227	60.786	-DE/DX = 0.0	!
! D10	D(4,1,5,7)	-119.9834	-138.9756	-119.2388	-DE/DX = 0.0	!

TS₃ (Ni⁺ + CH₃COOH)
Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 1 and mass 1.00783

Atom 3 has atomic number 1 and mass 1.00783

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 8 and mass 15.99491

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 28 and mass 57.93535

Molecular mass: 89.96156 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	136.96460	220.74013	340.95867
X	0.99556	0.09346	-0.01138
Y	-0.09308	0.99520	0.03032
Z	0.01416	-0.02913	0.99948

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 0.63238 0.39238 0.25403

Rotational constants (GHZ): 13.17670 8.17586 5.29314

1 imaginary frequencies ignored.

Zero-point vibrational energy 126088.0 (Joules/Mol)

30.13576 (Kcal/Mol)

Warning -- explicit consideration of 4 degrees of freedom as
vibrations may cause significant error

Vibrational temperatures: 145.07 421.18 632.83 877.38 1075.96

(Kelvin) 1160.75 1283.55 1740.27 1989.58 2075.75

4211.62 4576.11 4702.65 5437.07

Zero-point correction=	0.048024 (Hartree/Particle)
Thermal correction to Energy=	0.052704
Thermal correction to Enthalpy=	0.053648
Thermal correction to Gibbs Free Energy=	0.019696
Sum of electronic and zero-point Energies=	-1623.677465
Sum of electronic and thermal Energies=	-1623.672786
Sum of electronic and thermal Enthalpies=	-1623.671842
Sum of electronic and thermal Free Energies=	-1623.705794

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	33.072	14.286	71.459
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	39.403
Rotational	0.889	2.981	23.848

Vibrational	31.295	8.324	6.831
Vibration 1	0.604	1.948	3.438
Vibration 2	0.688	1.687	1.458
Vibration 3	0.800	1.383	0.827
Vibration 4	0.969	1.011	0.433
	Q	Log10(Q)	Ln(Q)
Total Bot	0.872395D-09	-9.059287	-20.859779
Total V=0	0.107240D+14	13.030356	30.003504
Vib (Bot)	0.357850D-21	-21.446299	-49.381929
Vib (Bot) 1	0.203514D+01	0.308594	0.710563
Vib (Bot) 2	0.652285D+00	-0.185562	-0.427273
Vib (Bot) 3	0.393080D+00	-0.405519	-0.933742
Vib (Bot) 4	0.242388D+00	-0.615488	-1.417214
Vib (V=0)	0.439889D+01	0.643343	1.481353
Vib (V=0) 1	0.259566D+01	0.414248	0.953840
Vib (V=0) 2	0.132187D+01	0.121190	0.279050
Vib (V=0) 3	0.113601D+01	0.055383	0.127524
Vib (V=0) 4	0.105565D+01	0.023522	0.054161
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.335383D+08	7.525541	17.328198
Rotational	0.363448D+05	4.560442	10.500806

TS₃ (Ni⁺ + CH₃COOH)
Frequencies (cm⁻¹)

-414.6544
100.8260
292.7354
439.8417
609.8109
747.8340
806.7632
892.1145
1209.5474
1382.8265
1442.7230
2927.2229
3180.5588
3268.5103
3778.9588

PRODUCT COMPLEX
Final Optimized Structure

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.	!

! R1	R(1,2)	1.0861	-DE/DX = 0.0	!
! R2	R(1,3)	1.0887	-DE/DX = 0.0	!
! R3	R(1,4)	1.0887	-DE/DX = 0.0	!
! R4	R(1,5)	1.4755	-DE/DX = 0.0	!
! R5	R(5,6)	0.9664	-DE/DX = 0.0	!
! R6	R(5,7)	1.9208	-DE/DX = 0.0	!
! A1	A(2,1,3)	110.5037	-DE/DX = 0.0	!
! A2	A(2,1,4)	110.4995	-DE/DX = 0.0	!
! A3	A(2,1,5)	106.7471	-DE/DX = 0.0	!
! A4	A(3,1,4)	111.6945	-DE/DX = 0.0	!
! A5	A(3,1,5)	108.6176	-DE/DX = 0.0	!
! A6	A(4,1,5)	108.615	-DE/DX = 0.0	!
! A7	A(1,5,6)	110.0383	-DE/DX = 0.0	!
! A8	A(1,5,7)	130.1021	-DE/DX = 0.0	!
! A9	A(6,5,7)	119.8596	-DE/DX = 0.0	!
! D1	D(2,1,5,6)	179.9462	-DE/DX = 0.0	!
! D2	D(2,1,5,7)	-0.0785	-DE/DX = 0.0	!
! D3	D(3,1,5,6)	-60.8872	-DE/DX = 0.0	!
! D4	D(3,1,5,7)	119.0881	-DE/DX = 0.0	!
! D5	D(4,1,5,6)	60.786	-DE/DX = 0.0	!
! D6	D(4,1,5,7)	-119.2387	-DE/DX = 0.0	!

PRODUCT COMPLEX

Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 1 and mass 1.00783

Atom 3 has atomic number 1 and mass 1.00783

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 8 and mass 15.99491

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 28 and mass 57.93535

Molecular mass: 89.96156 amu.

Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	38.73101	497.72865	524.77435
X	0.99994	0.01119	0.00000
Y	-0.01119	0.99994	0.00004
Z	0.00000	-0.00004	1.00000

This molecule is an asymmetric top.

Rotational symmetry number 1.

Rotational temperatures (Kelvin) 2.23629 0.17402 0.16505

Rotational constants (GHZ): 46.59681 3.62595 3.43908

Zero-point vibrational energy 139535.8 (Joules/Mol)
33.34986 (Kcal/Mol)

Warning -- explicit consideration of 4 degrees of freedom as
vibrations may cause significant error

Vibrational temperatures: 91.52 285.64 577.94 580.68 1344.54
(Kelvin) 1598.41 1669.72 1982.79 2122.81 2138.21
2155.16 4417.94 4556.37 4582.89 5459.94

Zero-point correction=	0.053146 (Hartree/Particle)
Thermal correction to Energy=	0.058077
Thermal correction to Enthalpy=	0.059021
Thermal correction to Gibbs Free Energy=	0.024198
Sum of electronic and zero-point Energies=	-1623.747272
Sum of electronic and thermal Energies=	-1623.742342
Sum of electronic and thermal Enthalpies=	-1623.741398
Sum of electronic and thermal Free Energies=	-1623.776221

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	36.444	14.012	73.291
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	39.403
Rotational	0.889	2.981	23.829

Vibrational	34.666	8.050	8.682
Vibration 1	0.597	1.972	4.342
Vibration 2	0.637	1.842	2.147
Vibration 3	0.767	1.466	0.956
Vibration 4	0.769	1.462	0.950
	Q	Log10(Q)	Ln(Q)
Total Bot	0.740798D-11	-11.130300	-25.628463
Total V=0	0.206675D+14	13.315288	30.659583
Vib (Bot)	0.306740D-23	-23.513229	-54.141211
Vib (Bot) 1	0.324483D+01	0.511193	1.177064
Vib (Bot) 2	0.100494D+01	0.002139	0.004925
Vib (Bot) 3	0.443164D+00	-0.353436	-0.813816
Vib (Bot) 4	0.440464D+00	-0.356090	-0.819928
Vib (V=0)	0.855774D+01	0.932359	2.146836
Vib (V=0) 1	0.378313D+01	0.577851	1.330552
Vib (V=0) 2	0.162245D+01	0.210172	0.483939
Vib (V=0) 3	0.116813D+01	0.067490	0.155402
Vib (V=0) 4	0.116634D+01	0.066825	0.153870
Electronic	0.200000D+01	0.301030	0.693147
Translational	0.335383D+08	7.525541	17.328198
Rotational	0.360046D+05	4.556358	10.491403

PRODUCT COMPLEX

Frequencies (cm^{-1})

63.6129
198.527
401.6920
403.5902
934.5047
1110.9485
1160.5148
1378.1066
1475.4299
1486.1338
1497.9138
3070.6270
3166.8382
3185.2728
3794.8536

BIBLIOGRAPHY

- (1) Böhme, D.K.; Schwarz, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 2336-2354.
- (2) Fang, W.; Lui, R.; Zheng, X.; Philips, D.L. *J. Org. Chem.* **2002**, *67*, 8407.
- (3) Hunnicutt, S.S.; Waits, L.D.; Guest, J.A. *J. Phys. Chem.* **1989**, *93*, 5188-5195.
- (4) Hunnicutt, S.S.; Waits, L.D.; Guest, J.A. *J. Phys. Chem.* **1991**, *95*, 562-570.
- (5) Metz, R.B. *Int. Rev. Phys. Chem.* **2004**, *23*, 79-108.
- (6) Lin, Z. *Accounts Chem. Res.* **2010**, *43*, 602-611.
- (7) Johnson, M.A. *Nature Chem.* **2009**, *1*, 8-9.
- (8) Castleberry, V.A.; Dee, S.J.; Villarroel, O.J.; Laboren, I.E.; Frey, S.E.; Bellert, D.J. *J. Phys. Chem. A* **2009**, *113*, 10417-10424.
- (9) Castleberry, V.A. Construction and calibration of a custom time-of-flight mass spectrometer and its use in measuring the reaction kinetics of transition metal ion-organic interactions, Ph.D. Dissertation, Baylor University, Waco, TX, May 2010.
- (10) Dee, S.J.; Castleberry, V.A.; Villarroel, O.J.; Laboren, I.E.; Frey, S.E.; Ashley, D.; Bellert, D.J. *J. Phys. Chem. A* **2009**, *113*, 14074-14080.
- (11) Dee, S.J.; Castleberry, V.A.; Villarroel, O.J.; Laboren, I.E.; Bellert, D.J. *J. Phys. Chem. A* **2010**, *114*, 1783-1789.
- (12) Dee, S.J. Rates of Photon Induced, Metal Ion Assisted, Unimolecular Decomposition of Gaseous Organometallic Complexes Using a Custom Built Molecular Beam Apparatus, Ph.D. Dissertation, Baylor University, Waco, TX, August 2010.
- (13) Villarroel, O.J. Metal Ion Assisted Unimolecular Decomposition of Gaseous Organometallic Complexes: Acquisition of Reaction Rate Constants and Dynamics of the Dissociative Mechanism, Ph.D. Dissertation, Baylor University, Waco, TX, December 2012.
- (14) Villarroel, O.J.; Laboren, I.E.; Bellert, D.J. *J. Phys. Chem. A* **2012**, *116*, 3081-3088.
- (15) Laboren, I.E.; Villarroel, O.J.; Dee, S.J.; Castleberry, V.A.; Klausmeyer, K.; Bellert, D.J. *J. Phys. Chem. A* **2011**, *115*, 1810-1820.

- (16) Laboren, I.E. Kinetics and Mechanistic Detail of Ni⁺ Assisted Organic Decomposition Reaction at Low Internal Energies, Ph.D. Dissertation, Baylor University, Waco, TX, December 2012.
- (17) Karrass, S.; Schwarz, H. *Organometallics*. **1990**, *8*, 2034-2040.
- (18) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121-1177.
- (19) Schröder, D.; Shaik, S.I. Schwarz, H. *Acc. Chem. Res.* **2000**, *33*, 139-145.
- (20) Zhang, D.; Wang, R.; Zhu, R. *Aust. J. Chem.* **2005**, *58*, 82-85.
- (21) Ding, N.; Zhang, S.; Chen, X. *Chem. Phys. Lett.* **2008**, *459*, 33-38.
- (22) Chen, X.; Guo, W.; Zhao, L.; Fu, Q. *Chem. Phys. Lett.* **2006**, *432*, 27-32.
- (23) Chen, X.; Guo, W.; Zhao, L.; Fu, Q.; Ma, Y. *J. Phys. Chem. A*. **2007**, *111*, 3566-3570.
- (24) Jensen, K.P.; Roos, B.O.; Ryde, U. *J. Chem. Phys.* **2007**, *126*, 014103.
- (25) La, M.-J.; Wang, Y.-C.; Wang, C.-L.; Ji, D.-F.; Jin, Y.-Z.; Nian, J.-Y.; Ma, W.-P. *Comput. Theor. Chem.* **2012**, *979*, 128-134.
- (26) Zhao, L.; Zhang, R.; Guo, W.; Wu, S.; Lu, X. *Chem. Phys. Lett.* **2005**, *414*, 28-33.
- (27) Zhao, L.; Guo, W.; Zhang, R.; Wu, S.; Lu, X. *Chem. Phys. Chem.* **2006**, *7*, 1345-1354.
- (28) Schröder, D.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 5857-5864.
- (29) Schröder, D.; Schwarz, H.; Clemmer, D.E.; Chen, Y.; Armentrout, P.B.; Baranov, V.I.; Böhme, D.K. *Int. J. Mass Spectrom. Ion Processes* **1997**, *161*, 175-191.
- (30) Schröder, D.; Fiedler, A.; Hrusák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215-1222.
- (31) Yoshizawa, K.; Shiota, Y.; Yamabe, T. *Chem. Eur. J.* **1997**, *3*, 1160-1169.
- (32) Yoshizawa, K.; Shiota, Y.; Yamabe, T. *J. Am. Chem. Soc.* **1998**, *120*, 564-572.
- (33) Yoshizawa, K.; Shiota, Y.; Yamabe, T. *J. Chem. Phys.* **1999**, *111*, 538-545.
- (34) Yoshizawa, K.; Shiota, Y.; Kagawa, Y.; Yamabe, T. *J. Phys. Chem. A* **2000**, *104*, 2552-2561.

- (35) Chen, Y.-M.; Clemmer, D.E.; Armentrout, P.B. *J. Am. Chem. Soc.* **1994**, *116*, 7815-7826.
- (36) Aguirre, F.; Husband, J.; Thompson, C.J.; Stringer, K.L.; Metz, R.B. *J. Chem. Phys.* **2002**, *116*, 4071-4078.
- (37) Gaussian 03, Revision D.02, Gaussian Inc, Quinncipiac Street, Building 40, Wallingford, CT, 0649; Copyright C 1994-2003, Gaussian, Inc. M.J. Frisch; G. W. Trucks; H.B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; J.A. Montgomery, Jr. T. Vreven; K.N. Kudin; J.C. Burant; J.M. Millam; S.S. Iyengar; J. Tomasi; V. Barone; B. Mennucci; M. Cossi; G. Scalmani; N. Rega; G.A. Petersson; H. Nakatsuji; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; M. Klene; X. Li; J.E. Knox; H.P. Hratchian; J.B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R.E. Stratmann; O. Yazyev; A.J. Austin; R. Cammi; C. Pomelli; J.W. Ochterski; P.Y. Ayala; K. Morokuma; G.A. Voth; P. Salvador; J.J. Dannenberg; V.G. Zakrzewski; S. Dapprich; A.D. Daniels; M.C. Strain; O. Farkas; D.K. Malick; A.D. Rabuck; K. Raghavachari; J.B. Foresman; J.V. Ortiz; Q. Cui; A.G. Baboul; S. Clifford; J. Cioslowski; B.B. Stefanov; G. Liu; A. Liashenko; P. Piskorz; I. Komaromi; R.L. Martin; D.J. Fox; T. Keith; M.A. Al-Laham; C.Y. Peng; A. Nanayakkara; M. Challacombe; P.M.W. Gill; B. Johnson; W. Chen; M.W. Wong; C. Gonzalez; J. A. Pople, Gaussian 03, Revision C.02. **2004**.