



# Article Mechanism of Deoxygenation and Cracking of Fatty Acids by Gas-Phase Cationic Complexes of Ni, Pd, and Pt

Kevin Parker <sup>1</sup>, Victoria Pho <sup>1</sup>, Richard A. J. O'Hair <sup>2</sup> and Victor Ryzhov <sup>1,\*</sup>

- <sup>1</sup> Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA; kparker9@niu.edu (K.P.); victoria.pho@abbvie.com (V.P.)
- <sup>2</sup> School of Chemistry, Bio21 Institute of Molecular Science and Biotechnology, The University of Melbourne, Melbourne, VIC 3010, Australia; rohair@unimelb.edu.au
- \* Correspondence: ryzhov@niu.edu; Tel.: +1-(815)-753-6871

**Abstract:** Deoxygenation and subsequent cracking of fatty acids are key steps in production of biodiesel fuels from renewable plant sources. Despite the fact that multiple catalysts, including those containing group 10 metals (Ni, Pd, and Pt), are employed for these purposes, little is known about the mechanisms by which they operate. In this work, we utilized tandem mass spectrometry experiments ( $MS^n$ ) to show that multiple types of fatty acids (saturated, mono-, and poly-unsaturated) can be catalytically deoxygenated and converted to smaller hydrocarbons using the ternary metal complexes [(phen)M(O<sub>2</sub>CR)]<sup>+</sup>], where phen = 1,10-phenanthroline and M = Ni, Pd, and Pt. The mechanistic description of deoxygenation/cracking processes builds on our recent works describing simple model systems for deoxygenation and cracking, where the latter comes from the ability of group 10 metal ions to undergo chain-walking with very low activation barriers. This article extends our previous work to a number of fatty acids commonly found in renewable plant sources. We found that in many unsaturated acids cracking can occur prior to deoxygenation and show that mechanisms involving group 10 metals differ from long-known charge-remote fragmentation reactions.

Keywords: biomass; gas phase; mass spectrometry; cracking; hydrocarbons

# 1. Introduction

Interest in biomass-derived hydrocarbons has grown due to socio-economic and environmental pressures to transition from fossil fuel to renewable resources [1–3]. Production of paraffinic fuel and biodiesel have drawbacks, with poor storage stability of the fuels and unfavorable cold-flow properties that can be overcome with the new-generation methods of biomass conversion [1]. One of the main components of biomass suitable for biodiesel production is triglycerides containing fatty acids of varying lengths and degrees of unsaturation [4]. While thermal cracking of fatty acids was shown to produce hydrocarbons as early as the beginning of the 20th century by Sabatier [2], oxygen-containing impurities pose a problem of compatibility with modern diesel engines [3]. Through deoxygenation, access to the pure hydrocarbon chain is granted and, by cracking chemistry, diesel-like hydrocarbons are produced [5]. These "drop-in" fuels can be used with little to no modification to combustion engines on the road today.

Characterization of the hydrocarbons released by deoxygenation and cracking of fatty acids has been studied extensively in condensed-phase experiments [5–9]. Metal catalysts greatly reduce the energy (or temperature) requirements needed to afford the desired hydrocarbons, with Ni, Pd, and Pt showing the greatest potential [5]. The methods of deoxygenation have been studied in multiple experiments with saturated fatty acids such as stearic acid [5,6,10]. In these studies, three deoxygenation pathways have been observed: (i) decarbonylation paired with dehydration, (ii) decarboxylation, or (iii) a combination of both. While saturated fatty acids only exhibit cracking of the hydrocarbon chain after deoxygenation [10], it has been shown that, for unsaturated hydrocarbons like



Citation: Parker, K.; Pho, V.; O'Hair, R.A.J.; Ryzhov, V. Mechanism of Deoxygenation and Cracking of Fatty Acids by Gas-Phase Cationic Complexes of Ni, Pd, and Pt. *Reactions* 2021, *2*, 102–114. https:// doi.org/10.3390/reactions2020009

Academic Editor: Dmitry Yu. Murzin

Received: 20 April 2021 Accepted: 11 May 2021 Published: 15 May 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). oleic acid, deoxygenation is not required for cracking [11–13]. Various-length alkanes, terminal alkenes, and internal alkenes were all observed through Gas-chromatography (GC) after varying temperature and time in a heated reaction chamber [4].

Gas-phase studies, often carried out via mass spectrometry (MS) experiments, provide a different angle for looking at deoxygenation/cracking chemistry. For example, chargeremote fragmentation of unsaturated fatty acids has been shown to produce hydrocarbons via fatty acid chain cracking without deoxygenation [14,15]. These experiments have long been used to determine the number and position of double bonds in the fatty acid chain [5]. The main advantage of studying these reactions in the gas phase is that, in conjunction with theoretical calculations, they can be used to determine detailed mechanisms and pathway energetics, thus allowing for intelligent catalyst design [16,17]. Given the prevalence of unsaturated fatty acids found in biomass, it is important to understand the mechanism and chemistry involved in production of hydrocarbons from their cracking reactions. Recent work from our group has shown such details for the catalytic deoxygenation and cracking of stearic acid by Ni and Pd complexes studied by MS. The deoxygenation mechanism was calculated for propionic acid used as the simple gas-phase model for larger fatty acids, as shown in Scheme 1 [10].



**Scheme 1.** Catalytic deoxygenation and dehydrogenation of propionic acid by ternary 1,10-phenanthroline and metal (Ni and Pd) complexes.

Once deoxygenation has occurred, the resulting organometallic ion can undergo facile "chain walking" (when the metal is Ni or Pd). The isomerization barriers were shown to be low enough to produce a mixture of organometallic isomers prior to fragmentation (Scheme 2) [18].



**Scheme 2.** Isomerization of alkane from alpha to beta and beta to gamma is reversible and low enough in energy to be observed in simple gas-phase experiments.

The subsequent "cracking" allowed for any length of neutral alkene to be extruded from the hydrocarbon chain [19–24]. This mechanism was modeled with a hexyl chain in our recent work and can be used to describe the cracking chemistry observed in the fatty acid chemistry described in this work (Scheme 2) [18]. The compositions of unsaturated fatty acids in most vegetable oils and fats are over 90% oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3) [6]. The main goal of this study was to see if this approach

could be applied to multiple saturated and unsaturated fatty acids for the production of hydrocarbons via mass spectrometry. We also extended our previous studies to include and compare Ni, Pd, and Pt catalysts.

# 2. Materials and Methods

# 2.1. Materials

Palladium acetate, nickel acetate, acetic acid, propionic acid, butyric acid, and stearic acid were all purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Decanoic acid, linoleic acid, linolenic acid, oleic acid, and elaidic acid were all purchased from Cayman Chemicals (Ann Arbor, MI, USA) and used without any further purification. K<sub>2</sub>[PtCl<sub>4</sub>] and Ag(OAc) were purchased from Sigma-Aldrich. DMSO, THF, dichloromethane, ethanol, and diethyl ether were all used in the synthesis of [(phen)Pt (OAc)<sub>2</sub>] and were purchased from Sigma-Aldrich [7]. Solutions were prepared by mixing 100  $\mu$ L (1 mg/mL) of ligand, metal acetate, and fatty acid dissolved in MeOH and diluting them with 700  $\mu$ L of methanol to 0.1 mg/mL. Samples were allowed to react for five minutes to allow for the complexation of the metal, ligand, and fatty acid. Solutions were then introduced into the mass spectrometer via electrospray ionization (ESI).

#### 2.2. Mass Spectrometry

The primary instrument for the gas-phase studies was a ThermoFisher LTQ (ThermoFisher Scientific, San Jose, CA, USA) which was modified to allow for ion-molecule reactions; the modification is described in other sources [8]. Samples were introduced into the ion trap through ESI. Source parameters were set to 5 kV needle voltage, 275 °C inlet temperature, and 3 a.u. for nitrogen gas flow rate. The precursor carboxylate complexes were subjected to activation via collisions with the helium bath gas as a 15% NCE (normalized collision energy) for the decarboxylation to occur. An isolation window of 1 m/z was used when isolating the resulting organometallic ion. Further collision-induced dissociation (CID) MS<sup>4</sup> experiments were done between 20–22% NCE, ensuring maximum product intensity while still preserving some of the parent ion.

High resolution mass spectrometry was carried out using a Bruker Maxis II Plus (Bruker Daltonics, Billerica, MA, USA). Samples were prepared in the same manner as above and introduced into the gas phase through ESI. The ESI source was set to a nebulizing gas pressure of 40 psi and a voltage of 4.5 kV. Ions were selected with a quadrupole mass filter and, in the collision cell, CID was used to probe the neutral losses from deoxygenation and cracking. The collision cell was set to 2.5 kV.

## 3. Results

#### 3.1. Metal (Ni, Pd, Pt) Comparison in Fragmentation of Oleic Acid Complexes

Previous studies and work recently published by our group have shown that the formation of fatty acid metal complexes ([(phen)M(O<sub>2</sub>CR)]<sup>+</sup>], where phen = 1,10-phenanthroline and M = Ni, Pd, and Pt) can be easily achieved via ESI [8]. Investigation of the different mechanisms and pathways in the deoxygenation and cracking of fatty acids can be done through CID. For Ni and Pd complexes, stearic acid was shown to deoxygenate through neutral loss of CO<sub>2</sub> and H<sub>2</sub> with subsequent cracking of the hydrocarbon chain resulting in a catalytic cycle for the formation of various hydrocarbons varying in length from C<sub>2</sub>–C<sub>15</sub> [8]. Here, we expanded the metal comparison to include Pt and used oleic acid (mono-unsaturated fatty acid) to see if similar chemistry operates in the presence of a double bond in the chain.

Saturated hydrocarbons like stearic acid undergo decarboxylation with dehydrogenation (Equation (1)); however, unsaturated fatty acid deoxygenation occurs in relatively high abundance without dehydrogenation (purple peaks in Figure 1). Figure 1 shows the comparison of MS/MS spectra for ternary metal complexes ([(phen)M(OOCC<sub>16</sub>H<sub>31</sub>)]<sup>+</sup>) with oleic acid (M = Ni, Pd, and Pt). The deoxygenation of oleic acid, as well as other unsaturated fatty acids, like linoleic (18-2), linolenic (18-3), and undecanoic (10-1) acids (Figure 2/Figure S1), occurs via decarboxylation (Equation (2)).

 $[(phen)M(OOCC_{16}H_{33})]^+ \rightarrow [(phen)M(C_{16}H_{33-2n})]^+ + CO_2 + nH_2$ (1)

M = Ni (Figure 2A), Pd (Figure S1A), Pt (Figure S1F) (2)

$$[(phen)M(OOCC_{16}H_y)]^+ \rightarrow [(phen)M(C_{16}H_y)]^+ + CO_2$$

$$M = Ni, Pd, Pt$$

y = 31 (oleic), 29 (linoleic), 27 (linolenic)



**Figure 1.** CID of  $[(\text{phen})M(\text{OOCC}_{17}\text{H}_{33})]^+$  for M = Ni (A), Pd (B), and Pt (C). Red peaks correspond to dehydrogenation of the parent peak immediately to the right. Blue peaks are the result of cracking of the hydrocarbon chain without deoxygenation (number of neutral carbons lost in neutral molecule). Purple represents deoxygenation, while green indicates cracking of the hydrocarbon chain after deoxygenation. \* indicates the mass-selected precursor ion.

While dehydrogenation does occur (red peaks in Figure 1) in high abundance, the occurrence of the loss of 44 m/z (-CO<sub>2</sub>) is a significant difference in the pathway of deoxygenation for coordinated unsaturated fatty acids. After deoxygenation, cracking of the hydrocarbon chain can be observed, similar to that of stearic acid [8] (green peaks in Figure 1). In addition to the differing deoxygenation observed, a significant variance of unsaturated vs. saturated fatty acids is the appearance of cracking peaks that come from non-deoxygenated species (blue peaks in Figure 1). Confirmed via high resolution mass spectrometry, the hydrocarbons neutrally lost from the fatty acid before deoxygenation



vary in length, and this loss is observed mostly for Pd and, to a much smaller extent, for Ni and Pt.

**Figure 2.** CID of  $[(phen)Ni(OOCR)]^+$  for  $R = C_{16}H_{33}$  (**A**),  $C_{16}H_{29}$  (**B**), and  $C_{16}H_{27}$  (**C**) (A = stearate, B = linoleate, C = linolenate). Red peaks correspond to dehydrogenation of the parent peak immediately to the right. Blue peaks are the result of cracking of the hydrocarbon chain without deoxygenation (number of neutral carbons lost in neutral molecule). Purple represents deoxygenation, while green indicates cracking of the hydrocarbon chain after deoxygenation. \* indicates the mass-selected precursor ion.

One of the major differences between the metals for CID of oleate species occurs in the Pd and Ni spectrum (Figure 1B) around the neutral loss of  $C_{13}H_{26}$ . This phenomenon can be observed with higher intensity in the Pd spectrum compared with Ni, while Pt shows more uniformity across the spectrum of neutral hydrocarbon losses. Another obvious difference between the metals is the high level of dehydrogenation seen with the Pt complex. This increased dehydrogenation of platinum complexes is in agreement with investigations that our group is currently working on involving DFT calculations demonstrating the low activation energy required for Pt dehydrogenation compared to Ni and Pd. (Work describing the difference between Pt and Pd dehydrogenation is being prepared for submission. DFT calculations have shown that dehydrogenation by ternary [(phen)M(cyclohexyl)]+ complexes where M = Pd are ~38 kJ/mol less favorable than when M = Pt.) A similar stabilization has been described in the dehydrogenation of methane by bare metal ions. The difference in bond strength, 155 kJ/mol, between Ni-CH<sub>2</sub><sup>+</sup> (310 kcal mol<sup>-1</sup>) and Pt-CH<sub>2</sub><sup>+</sup> (464 kcal mol<sup>-1</sup>) made Pt dehydrogenate CH<sub>4</sub> much more easily, which was explained by a strong relativistic effect in the Pt complex [9].

#### 3.2. CID for Various Ternary Nickel Complexes with Fatty Acids

In addition to the oleic acid fragmentation shown in Figure 1, we investigated several other saturated (stearic acid) and unsaturated (linoleic and linolenic) fatty acids. Comparison of deoxygenation and cracking for these fatty acids in Ni complexes is shown in Figure 2 (and Figure 1A). In the unsaturated fatty acid complex fragmentation spectrum (Figure 2A), cracking after deoxygenation is observed (green peaks). While deoxygenation in the saturated fatty acids like stearic acid usually corresponds to a loss of 46 m/z (-CO<sub>2</sub>, -H<sub>2</sub>), the unsaturated fatty acids all have deoxygenation without dehydrogenation (purple peak, Figures 1A and 2B,C). The largest difference between the fatty acids is when the hydrocarbon chain is unsaturated. Stearic acid only shows cracking chemistry after deoxygenation (Figure 1A). Blue peaks, indicating cracking without deoxygenation, only appear in the unsaturated fatty acid spectra. The CID of ternary Ni complexes with unsaturated fatty acids yields similar spectra for oleic acid (Figure 1A), linoleic acid (Figure 2B), and linolenic acid (Figure 2C), with a similar level of cracking with and without deoxygenation across all fatty acids.

Similar comparisons can be made for Pd and Pt complexes of unsaturated fatty acids. Like with oleic acid (Figure 1B), the CID spectra of other unsaturated fatty acid Pd complexes yield a lone peak around the loss of  $C_{13}H_{26}$  for both linoleic acid (Figure S1C) and linolenic acid (Figure 1C). The increased level of dehydrogenation for Pt with oleic acid (Figure 1C) is mirrored in the spectrum of Pt with linoleic acid (Figure S1F). High resolution mass spectrometry identified the neutral loss of  $C_{13}H_{26}$  within an 8 ppm error (Table S1).

We also compared fragmentation of cis versus trans isomers of unsaturated fatty acids. Fragmentation of oleic acid (cis) for Ni, Pd, and Pt (Figure 1) was compared with the trans isomer of the fatty acid, elaidic acid. (Figure S2). No discernable differences could be seen in fragmentation of cis and trans isomers. This shows the effectiveness of deoxygenation and cracking towards a wide range of fatty acids found in nature or converted during thermal isomerization [10].

Metal ion complexes of fatty acids have long been used for determination of the location of double bonds in unsaturated acids [11]. Recent work by Randolph and McLuckey [5,12] showed that ternary Mg complexes of unsaturated fatty acids formed by ion–ion reactions demonstrate a double bond location with depressions in the cracking region surrounding the double bond. We formed similar Mg complexes in solution, and they showed identical results (Figure S3). In contrast to Mg, none of group 10 metals (Ni, Pd, and Pt) show similar depressions in the intensity of the cracking peaks in their CID spectra (Figure 1, Figure 2B,C, and Figure S1). The differences in mechanisms between fragmentation of Mg and group 10 metal complexes are discussed in the Section 4 below.

Multi-stage tandem mass spectrometry (MS<sup>n</sup>) experiments provide continuous collisional "heating" of the activated ions, leading to an increased extent of fragmentation. Previously, we showed that saturated fatty acids complexes of Ni and Pd subjected to MS<sup>n</sup> eventually lead to the formation of the hydride and methyl species [13]. For example, MS<sup>3</sup> on the deoxygenated ion in the stearate complex (purple peak in Figure 2A) leads to the enhanced production of "cracking" ions (green peaks) (Figure S4). Further MS<sup>4</sup> on one of the green peaks leads to lower m/z green peaks, and so on, until the formation of [(phen)M(H)]<sup>+</sup> or [(phen)M(CH<sub>3</sub>)]<sup>+</sup>, which are obviously incapable of further cracking.

Similarly, unsaturated fatty acids complexes of Ni, Pd, and Pt display sequential fragmentation leading to the formation of the hydride and methyl species, as shown in Figure S3. The observed cracking without deoxygenation (red peaks in Figure 2B, for example) does not change the result—these peaks eventually lose carbon dioxide (i.e., deoxygenate) and fragment via cracking (Figure S5B).

As previously described in our recent work,  $[(phen)M(H)]^+$ ,  $[(phen)M(CH_3)]^+$ , and  $[(phen)M(C_2H_3)]^+$  are all capable of reacting with volatile carboxylic acids (acetic, propionic, and butyric acids) and regenerating a ternary carboxylate ion (Equation (3)) [13].

$$[(phen)M(X)]^{+} + HOOCR \rightarrow [(phen)M(OOCR)]^{+} + HX$$
(3)  
$$(X = H, CH_3, C_2H_3)$$
$$(R = CH_3, C_2H_5, C_3H_7)$$

This chemistry allowed us to close the catalytic cycle for the deoxygenation and cracking of propionic acid (Scheme 1).

# 4. Discussion

4.1. Mechanism for Decarboxylation

The mechanisms for decarboxylation of ternary cationic complexes [LM(OOCR)]<sup>+</sup> have been studied in detail by our group [13–17] and others [19–21] and are well established. The first step always involves the dissociation of one of the M-O bonds of the symmetrically bound carboxylate **1** forming the intermediate **1a** (Scheme 3):



Scheme 3. Decarboxylation mechanism.

The step  $\mathbf{1} \rightarrow \mathbf{1a}$  is highly endothermic. For example, for dissociation in [(phen) Zn(OOCH)]<sup>+</sup> it has been calculated to be 128 kJ/mol [16], while in [(phen)Pd(OOCC<sub>2</sub>H<sub>5</sub>)]<sup>+</sup>, it is 174 kJ/mol [13]. The species  $\mathbf{1a}$  has a coordinatively unsaturated metal ion that can get stabilized by forming a metal–carbon bond to the  $\alpha$ -carbon, eventually expelling carbon dioxide (purple peaks) and forming the organometallic, species  $\mathbf{2}$ , [(L)M(R)]<sup>+</sup>, which is often stabilized via  $\beta$ -H agostic interaction with the metal ion, especially when the metal is Ni, Pd, or Pt [22].

## 4.2. Cracking and Dehydrogenation of the Deoxygenated Hydrocarbon Chain

The organometallic ternary metal complex  $[(phen)M(CH_2CH_2R)]^+$  can undergo further fragmentation when additional energy is supplied through MS<sup>n</sup> experiments (Figure S5C). The initial structure of species **2** immediately after the loss of carbon dioxide has a terminal carbon bound to the metal center (Scheme 3). This species **2** can either decompose via the loss of a 1-alkene RCH=CH<sub>2</sub>, leaving the hydride species **3**,  $[(phen)M(H)]^+$ , or via the loss of hydrogen, forming an unsaturated organometallic species (red peaks). Both of these channels proceed via a common intermediate **2a** (Scheme 4):



Scheme 4. Mechanism of alkene loss or dehydrogenation of organometallic species 2.

We showed that these two competitive channels have similar energetics. For example, for the C<sub>2</sub> chain, the loss of alkene C<sub>2</sub>H<sub>4</sub> from the Pd complex requires 162 vs. 149 kJ/mol for the loss of H<sub>2</sub> [17]. The respective numbers for the C<sub>6</sub> chain are 182 and 140 kJ/mol [15].

This  $\beta$ -hydride shift mechanism has been well studied in alkene polymerization and depolymerization [23,24]. We showed theoretically and experimentally that it operates in the decomposition of a C<sub>6</sub> chain in a recent work [15]. The common intermediate **2a** can be formed independently by a reaction of the hydride species **3** and a terminal alkene. We studied this reaction and showed that the decomposition products of **2a** are very similar, independent of the way this intermediate was formed (Figure S6).

As mentioned before, species **2** can undergo isomerization via chain walking (Scheme 5).



**Scheme 5.** Chain-walking isomerization from  $\alpha - \beta$  and  $\beta - \gamma$ . This type of mechanism has been described before [23,24].

As we showed earlier, the barriers for sequential chain walking via  $\beta$ -hydride shift are very small. For instance, barriers for  $\alpha - \beta$  and  $\beta - \gamma$  isomerization of the Pd-hexyl complex [(phen)Pd(C<sub>6</sub>H<sub>13</sub>)]<sup>+</sup> are 19 and 42 kJ/mol, respectively, which are much lower than is typically required for fragmentation. Thus, in a saturated alkyl chain R (like in stearic acid), the metal can "travel" along the whole chain with very small energy input. If there is a double bond in the fatty acid chain (e.g., oleic acid), the metal can "chain walk" up to the  $\alpha$ -carbon next to the double bond, forming an allylic intermediate. Our calculations show that this type of structure is the most stable by as much as 20 kJ/mol [25]. The chain walking can be observed experimentally through the appearance of peaks in the mass spectrum, indicating an almost equal distribution of hydrocarbon losses from C<sub>2</sub>-C<sub>14</sub> in stearic acid complexes (Figure 2A and Figure S1A,E).

The isomeric species 2c formed by this chain-walking mechanism can then undergo a  $\beta$ -alkide shift, leading to the loss of a smaller alkene and leaving behind the shortened chain (Scheme 6).



Scheme 6. Mechanism of cracking of organometallic species 2c.

Obviously, alkene  $CH_2=CH-R_2$  can also be formed (scheme not shown). The losses of alkenes after deoxygenation correspond to the green ions in the mass spectra (Figure 1, Figure 2 and Figure S1).

This process, combined with chain walking, can occur multiple times if sufficient energy is supplied, as it is here via multi-stage CID (Figure S5). Fragmentation via alkene extrusion continues until either a hydride or methyl complex is formed. If the chain contains double bonds, some of the extruded hydrocarbons will contain two double bonds or a triple bond (Figure S5C).

#### 4.3. Cracking and Dehydrogenation of the Hydrocarbon Chain without Deoxygenation

There is a series of peaks in the mass spectra (Figures 1 and 2, shown in blue) that corresponds to losses of neutral alkenes *without* losing carbon dioxide first. These losses were confirmed by high resolution MS (Figure S7). By inspecting Figure 1, it is obvious that this channel is more pronounced in the case of Pd and Pt (Figure 1B,C), while it is almost absent in Ni complexes (Figure 1A). This channel is only observed in the complexes of unsaturated fatty acids (Figure 1, Figure 2 and Figure S1). To explain the origin of these peaks, we need to consider decomposition of activated carboxylate species **1a** alternative to Scheme 3. Subsequent collisional heating of intermediate **1a** can also lead to its coordinatively unsaturated metal ion, which undergoes oxidative addition (OA) via insertion into a C-C bond of the fatty acid chain forming **1c** (Scheme 7). This lactone-type intermediate has been found in some Ni(II) complexes [26].



**Scheme 7.** Mechanism for cracking of hydrocarbon chain without deoxygenation. This channel is only observed when R is unsaturated.

The subsequent activation of this intermediate **1c** leads to alkene extrusion via reductive elimination (RE). It can proceed via abstraction of a  $\beta$ -H atom by one of the metal-bound carbons. If the carbon is part of the chain containing the R group then the lactone portion is converted to an unsaturated carboxylate, as shown in Scheme 7. Alternatively, the lactone carbon bound to the metal can abstract hydrogen from the free R-containing chain, forming a saturated carboxylate complex and extruding R-CH=CH<sub>2</sub>, as shown in Scheme S1. The initial size of the cyclic lactone shown by *n* in Scheme 7 explains the series of "cracking" peaks shown in blue (Figures 1 and 2). The length of the fatty acid hydrocarbon chain is a factor here, as the chain cannot be too short for this mechanism to operate. Indeed, our data for shorter fatty acids (C<sub>2</sub>–C<sub>4</sub>) show no cracking without deoxygenation (Figure S8). The dominant loss of C<sub>13</sub>H<sub>26</sub> from the oleic acid complexes of Pd and Pt (Figure 1) corresponds to the six-membered cyclic lactone in Scheme 1. This type of OA–RE mechanism is known for the group 10 metals (Ni, Pd, and Pt). It involves transition between M(II) and M(IV) and, thus, is more prevalent for Pd and, especially, Pt [16,26]. However, it has been postulated as a viable pathway in Ni systems as well [27].

There is a stark difference between this OA–RE mechanism and charge-remote fragmentation that operates in gas-phase fragmentation of fatty-acid/alkali or alkaline–earth metal complexes (Scheme 8). The charge-remote mechanism, as the name suggests, occurs *away* from the charge, which in this case is the metal cation.



**Scheme 8.** Charge = remote fragmentation of fatty-acid/alkaline–earth metal ternary cationic complexes. M = Mg, Ca, Ba.

There has been extensive work done on identification of fatty acids by MS via chargeremote fragmentation [5,12]. The key feature of this mechanism is that the breakage is minimized or even absent at the position of the double bond(s), leading to "dips" in the peaks corresponding to neutral alkene extrusion. For example, fragmentation of the oleic acid complex, [(phen)Mg(OOC(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)]<sup>+</sup>, shown in Figure S3, shows no peaks corresponding to the extrusion of C9 hydrocarbon, where the double bond is located. Our results are consistent with the recently published work from McLuckey's group using the same complexes but prepared in a different way (via gas-phase ion–ion reactions) [12]. In contrast, the fragmentation of the Pd complex (Figure 1B) displays no "dips" in the blue peaks (extrusion of alkenes), indicating that Pd complexes fragment via a different mechanism.

There is also a series of peaks in the mass spectra (Figures 1 and 2, shown in red) spaced by 2 m/z immediately to the left of the activated precursor that correspond to the loss of one (or more) molecules of hydrogen *without* decarboxylation. The intermediate **1a** can also undergo another variation of OA–RE process via insertion into a C-H bond of the fatty acid chain (Scheme 9), forming **1d**.



Scheme 9. Mechanism for loss of H<sub>2</sub> or protonated ligand from common intermediate.

The activation of this intermediate **1d** can lead to decomposition via RE, forming molecular hydrogen and the unsaturated carboxylate complex. The process can be repeated, leading to the losses of additional  $H_2$  molecules. The fact that the OA–RE mechanism is much more likely to occur with Pt and Pd than with Ni [26] is consistent with our results.

It should be noted that hydrogen losses are more prevalent for oleic acid (monounsaturated) than for stearic acid (saturated), as can be seen by comparing the intensity of "red' peaks in Figure 1, Figure 2, and Figure S1. This can be explained by the fact that abstracting a hydrogen atom from an allylic position demands much less energy (bond dissociation energy of a saturated C-H is as much as 58 kJ/mol higher than those for allylic C-H [27]. The ease of hydrogen abstraction seems to increase even more when going from oleic to linoleic (doubly unsaturated) acid complexes (compare Figures 1 and 2 for Ni or 1 and Figure S1 for Pd and Pt). However, complexes of linoleic (triply unsaturated) acid display less dehydrogenation because at this point the number of hydrogen atoms on the fatty acid chain available for removal is diminished. The length of the hydrocarbon chain in the fatty acids also plays a role in the ability to perform cracking/dehydrogenation chemistry without deoxygenation. Shorter chains like butyric acid and heptanoic acid show no dehydrogenation or cracking without deoxygenation [13]. Chains longer than  $C_{10}$  begin to exhibit these pathways as they are long enough to interact with the metal.

While the hydrocarbon products afforded by this cracking chemistry are in the form of olefins, with a high enough pressure of H<sub>2</sub> gas in the reaction chamber, alkane formation could be favored [28]. It is known that bidentate N ligands, similar to the phenanthroline used in this work, when bound to Ni catalyze hydrogenation of olefins [29]. Ni catalysts have also been used in partial hydrogenation of oils [30,31]. The unique capacity of group 10 metals to catalyze both cracking (i.e., depolymerization) and hydrogenation thus shows their advantage in producing biofuels from renewable sources.

# 4.4. Closing a Catalytic Cycle for Deoxygenation and Cracking

Industrial scale processes for the production of hydrocarbons from fatty acids would be bolstered by the ability to make these reactions catalytic. Closing the catalytic cycle in the gas phase can be easily achieved through ion–molecule reactions (IMRs) of neutral carboxylic acids with ions generated from CID experiments, as described in our previous work detailing stearic acid deoxygenation and cracking. One of the key findings in that work was that the agostic interactions of hydrocarbons longer than  $C_2$  were too great to overcome for gas-phase IMRs (an issue that, most likely, will not be as important for condensed-phase reactions) but, through multiple stages of CID, metal hydride, methyl, and ethene can be produced, which all react with carboxylic acids to reform a carboxylate metal complex (Scheme 10).



**Scheme 10.** Catalytic deoxygenation and cracking of stearic acid by  $[(phen)M(OOCC_{17}H_{35})]^+$  (M = Ni, Pd, and Pt).

# 5. Conclusions

This work expanded upon our recent study of deoxygenation and cracking of saturated fatty acid complexes of Ni and Pd. We showed that all three group 10 metals (Ni, Pd, and Pt) in the +2 oxidation state, when complexed with 1,10-phenanthroline, can induce decarboxylation of mono- and polyunsaturated fatty acids. While the detailed mechanisms of decarboxylation and fatty acid chain cracking have been described by us previously for model systems, this study expanded the scope of the proposed mechanisms and summarized multiple processes occurring upon collisional activation of these cationic complexes in the gas phase.

A common theme for all systems under study is that multiple stages of collisional activation (via MS<sup>n</sup>) lead to decarboxylation of fatty acid (via loss of CO<sub>2</sub>) followed by "cracking" of the carbon chain, which occurs via "chain walking" of the coordinatively unsaturated metal ion. In addition to these two processes, dehydrogenation is also observed, especially for Pt.

A unique feature of unsaturated fatty acid complexes is that they can undergo cracking *before* deoxygenation, thus requiring a different mechanism. While we did not investigate this process computationally, the most likely scenario is that this occurs via an oxidative addition/reductive elimination mechanism, consistent with the fact that this channel is much more pronounced for Pd and Pt than for Ni.

The order of the deoxygenation and cracking notwithstanding, the ultimate products of MS<sup>n</sup> are the hydride and methide complexes, which are reactive towards carboxylic acids (or esters), thus completing a catalytic cycle. These processes are common for all three metals and any type of fatty acid.

Thinking about the relevance to the industrial deoxygenation/cracking processes that employ the metals Ni, Pd, or Pt on carbon, the metal surface often terminates in M-OH or M-H [32,33] (in the presence of molecular hydrogen) groups that would react with neutral fatty acids by forming carboxylates. Then, mechanisms similar to those described in this study can operate. The main difference is that the gas-phase mechanism for cracking produces *alkenes*, while industrial biodiesel production demands *alkanes*, but the latter are formed from alkenes in hydrogen atmosphere. It is advantageous that group 10 metals are effective catalysts for both cracking and hydrogenation.

Lastly, while the OA–RE mechanism proposed in this work requires initial oxidation of +2 metals to the +4 oxidation state, under the conditions of heterogeneous catalysis, the carboxylate binding and C-C (or C-H) bond insertion can occur at different metal atoms, thus requiring a more feasible  $M^0$  to  $M^{2+}$  transition.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/reactions2020009/s1. Figure S1: Spectra for CID of ternary metal complexes, Table S1: High resolution mass spectral neutral losses.

**Author Contributions:** Conceptualization, V.R. and K.P.; methodology, K.P.; data curation, V.P., K.P.; writing—original draft preparation, K.P., V.R.; writing—review and editing, R.A.J.O., K.P., and V.R.; funding acquisition, V.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** We acknowledge The Department of Chemistry and Biochemistry of Northern Illinois University and the NIU Office of VP for Research and Innovation Partnership and the NSF MRI program (award #CHE:1726931 to VR) for the purchase of the high-resolution mass spectrometer.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- Naik, S.; Goud, V.V.; Rout, P.K.; Dalai, A.K. Production of first and second generation biofuels: A comprehensive review. *Renew. Sustain. Energy Rev.* 2010, 14, 578–597. [CrossRef]
- 2. Sabatier, P. Catalysis in Organic Chemistry; David Van Nostrand Company: New York, NY, USA, 1922.
- 3. Hassan, M.H.; Kalam, M.A. An overview of biofuel as a renewable energy source: Development and challenges. *Procedia Eng.* **2013**, *56*, 39–53. [CrossRef]
- Asomaning, J.; Mussone, P.; Bressler, D.C. Thermal deoxygenation and pyrolysis of oleic acid. J. Anal. Appl. Pyrolysis 2014, 105, 1–7. [CrossRef]
- Randolph, C.E.; Foreman, D.J.; Blanksby, S.J.; McLuckey, S.A. Generating Fatty Acid Profiles in the Gas Phase: Fatty Acid Identification and Relative Quantitation Using Ion/Ion Charge Inversion Chemistry. J. Anal. Chem. 2019, 91, 9032–9040. [CrossRef] [PubMed]
- 6. Zambiazi, R.C.; Przybylski, R.; Zambiazi, M.W.; Mendonça, C.B. Fatty acid composition of vegetable oils and fats. *Bol. Cent. Pesqui. Process. Aliment.* **2007**, 25. [CrossRef]
- Dai, S.; Zhou, S.; Zhang, W.; Chen, C. Systematic Investigations of Ligand Steric Effects on α-Diimine Palladium Catalyzed Olefin Polymerization and Copolymerization. *Macromolecules* 2016, 49, 8855–8862. [CrossRef]
- 8. Gronert, S. Quadrupole ion trap studies of fundamental organic reactions. Mass Spectrom. Rev. 2004, 24, 100–120. [CrossRef]
- 9. Armentrout, P. Guided ion beam studies of transition metal-ligand thermochemistry. *Int. J. Mass Spectrom.* 2003, 227, 289–302. [CrossRef]
- 10. Li, C.; Zhang, Y.; Li, S.; Wang, G.; Xu, C.; Deng, Y.; Wang, S. Mechanism of Formation of Trans Fatty Acids under Heating Conditions in Triolein. *J. Agric. Food Chem.* **2013**, *61*, 10392–10397. [CrossRef]
- Trimpin, S.; Clemmer, D.E.; McEwen, C.N. Charge-remote fragmentation of lithiated fatty acids on a TOF-TOF instrument using matrix-ionization. J. Am. Soc. Mass Spectrom. 2007, 18, 1967–1972. [CrossRef]
- Randolph, C.E.; Foreman, D.J.; Betancourt, S.K.; Blanksby, S.J.; McLuckey, S.A. Gas-Phase Ion/Ion Reactions Involving Tris-Phenanthroline Alkaline Earth Metal Complexes as Charge Inversion Reagents for the Identification of Fatty Acids. *J. Anal. Chem.* 2018, 90, 12861–12869. [CrossRef]
- 13. Parker, K.; Weragoda, G.K.; Pho, V.; Canty, A.J.; Polyzos, A.; O'Hair, R.A.J.; Ryzhov, V. Gas-Phase Models for the Nickel- and Palladium-Catalyzed Deoxygenation of Fatty Acids. *ChemCatChem* **2020**, *12*, 5476–5485. [CrossRef]

- 14. Piacentino, E.L.; Rodriguez, E.; Parker, K.; Gilbert, T.M.; O'Hair, R.A.J.; Ryzhov, V. Gas-phase functionalized carbon-carbon coupling reactions catalyzed by Ni (II) complexes. *J. Mass Spectrom.* **2019**, *54*, 520–526. [CrossRef]
- Parker, K.; Geethika, W.; Canty, A.; Ryzhov, V.; O'Hair, R.A.J. Modeling Metal-Catalyzed Polyethylene Depolymerization: [(phen)Pd(X)]+ (X = H and CH3) Catalyze Decomposition of Hexane into a Mixture of Alkenes via a Complex Reaction Network. Organometallics 2021, 40, 857–868. [CrossRef]
- Piacentino, E.L.; Parker, K.; Gilbert, T.M.; O'Hair, R.A.J.; Ryzhov, V. Role of Ligand in the Selective Production of Hydrogen from Formic Acid Catalysed by the Mononuclear Cationic Zinc Complexes [(L)Zn(H)] + (L=tpy, phen, and bpy). *Chem. A Eur. J.* 2019, 25, 9959–9966. [CrossRef] [PubMed]
- 17. Parker, K.; Weragoda, G.K.; Canty, A.J.; Polyzos, A.; Ryzhov, V.; O'Hair, R.A.J. A Two-Step Catalytic Cycle for the Acceptorless Dehydrogenation of Ethane by Group 10 Metal Complexes: Role of the Metal in Reactivity and Selectivity. *Organometallics* **2020**, *39*, 4027–4036. [CrossRef]
- Janssen-Müller, D.; Sahoo, B.; Sun, S.Z.; Martin, R. Tackling Remote sp3 C H Functionalization via Ni-Catalyzed "chain-walking" Reactions. Isr. J. Chem. 2020, 60, 195–206. [CrossRef]
- 19. O'Hair, R.A.J. The 3D quadrupole ion trap mass spectrometer as a complete chemical laboratory for fundamental gas-phase studies of metal mediated chemistry. *Chem. Commun.* **2006**, *14*, 1469–1481. [CrossRef] [PubMed]
- 20. O'Hair, R.A.J. Organometallic Gas-Phase Ion Chemistry and Catalysis: Insights Into the Use of Metal Catalysts to Promote Selectivity in the Reactions of Carboxylic Acids and Their Derivatives. *Mass Spectrom. Rev.* **2020**. [CrossRef]
- 21. O'Hair, R.A.J.; Rijs, N.J. Gas Phase Studies of the Pesci Decarboxylation Reaction: Synthesis, Structure, and Unimolecular and Bimolecular Reactivity of Organometallic Ions. *Acc. Chem. Res.* **2015**, *48*, 329–340. [CrossRef]
- Conroy-Lewis, F.M.; Mole, L.; Redhouse, A.D.; Litster, S.A.; Spencer, J.L. Chemical Communications, Synthesis of coordinatively unsaturated diphosphine nickel (II) and palladium (II) β-agostic ethyl cations: X-ray crystal structure of [Ni [1](C 2 H 5)][BF 4]. J. Chem. Soc. 1991, 22, 1601–1603.
- 23. Takeuchi, D. Olefin Polymerization with Non-metallocene Catalysts (Late Transition Metals). In *Organometallic Reactions and Polymerization;* Springer: Berlin/Heidelberg, Germany, 2014; pp. 119–167.
- 24. Guo, L.; Dai, S.; Sui, X.; Chen, C. Palladium and Nickel Catalyzed Chain Walking Olefin Polymerization and Copolymerization. *ACS Catal.* **2016**, *6*, 428–441. [CrossRef]
- 25. Parker, K.; Geethika Weragoda, R.A.J.O.H.; Ryzhov, V. Work currently being readied for submission describing activation and cracking of cyclohexane by ternary metal complexes. Unpublished work. 2021.
- 26. Choi, J.-C.; Shiraishi, K.; Takenaka, Y.; Yasuda, H.; Sakakura, T. Synthesis and Reactivity of Five-Membered Palladalactones from Arylallenes and Carbon Dioxide: Relevance to Catalytic Lactone Synthesis. *Organometallics* **2013**, *32*, 3411–3414. [CrossRef]
- 27. McMillen, D.F.; Golden, D.M. Hydrocarbon Bond Dissociation Energies. Annu. Rev. Phys. Chem. 1982, 33, 493–532. [CrossRef]
- 28. Santillan-Jimenez, E.; Morgan, T.; Lacny, J.; Mohapatra, S.; Crocker, M. Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel. *Fuel* **2013**, *103*, 1010–1017. [CrossRef]
- 29. Léonard, N.G.; Chirik, P.J. Air-Stable α-Diimine Nickel Precatalysts for the Hydrogenation of Hindered, Unactivated Alkenes. *ACS Catal.* **2017**, *8*, 342–348. [CrossRef]
- 30. Stanković, M.; Krstić, J.; Gabrovska, M.; Radonjić, V.; Nikolova, D.; Lončarević, D.; Jovanović, D. Supported nickel-based catalysts for partial hydrogenation of edible oils. In *New Advances in Hydrogenation Processes—Fundamentals and Applications*; IntechOpen: London, UK, 2017; Volume 131.
- 31. Bridier, B.; López, N.; Pérez-Ramírez, J. Partial hydrogenation of propyne over copper-based catalysts and comparison with nickel-based analogues. *J. Catal.* 2010, 269, 80–92. [CrossRef]
- 32. Sakintuna, B.; Lamari-Darkrim, F.; Hirscher, M. Metal hydride materials for solid hydrogen storage: A review. *Int. J. Hydrogen Energy* 2007, 32, 1121–1140. [CrossRef]
- 33. Fukuzumi, S.; Suenobu, T. Hydrogen storage and evolution catalysed by metal hydride complexes. *Dalton Trans.* **2013**, *42*, 18–28. [CrossRef]