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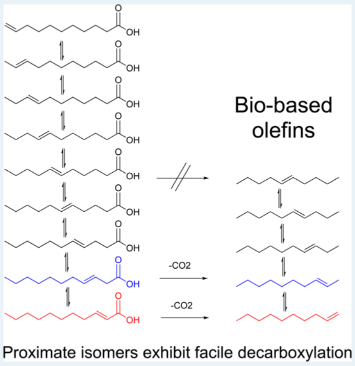
# Tandem Isomerization-Decarboxylation for Converting Alkenoic Fatty Acids into Alkenes

Rex E. Murray,[†,‡] Erin L. Walter,[†] and Kenneth M. Doll*[,†]

[†]Bio-Oils Research Unit, United States Department of Agriculture (USDA), Agricultural Research Service (ARS), National Center for Agricultural Utilization Research, 1815 North University Street, Peoria, Illinois 61604, United States

[‡]Department of Natural and Social Sciences, Wayne State College, 1111 Main Street, Wayne, Nebraska 68787, United States

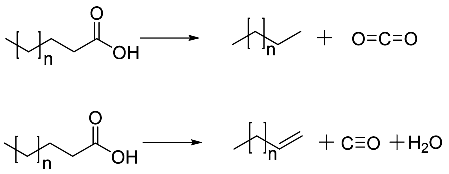
**ABSTRACT:** We report a facile Ru-catalyzed route to alkenes from unsaturated fatty acids (alkenoic fatty acids) via readily accessible catalyst precursors, $[Ru(CO)2RCO2]_n$ and $Ru_3(CO)_{12}$. The catalyst apparently functions in a tandem mode by dynamically isomerizing the positions of double bonds in an aliphatic chain and, subsequently, decarboxylating specific isomers with lower activation barriers. Substrates capable of tandem isomerization-decarboxylation processes (oleic acid, undecylenic acid) are readily converted to mixtures of alkenes. A catalytic cycle is proposed that relies on isomerization positioning double bonds proximate to the acid function to enable facile decarboxylation. To elucidate the proposed mechanistic pathway, substrates that do not undergo decarboxylation under these catalytic conditions (methyl oleate) are compared with those that cannot isomerize the position of unsaturation (cinnamic acid). Both were shown to be operational under these catalytic reaction conditions. Another illustrative comparison shows that the saturated octadecanoic acid is 28 times less reactive than the unsaturated counterpart when reacted using this precatalyst.



**KEYWORDS:** *unsaturated fatty acid, decarboxylation, isomerization, octadecenoic acid, ruthenium carbonyl carboxylate, triruthenuium dodecacarbonyl*

Reactions that convert fatty acids to hydrocarbons have been a topic of investigation for decades.[1] The conversion of biobased fatty acids into hydrocarbons useful for industrial applications is a key to the futuristic biorefinery platform which would enable biobased hydrocarbons, such as olefins, to efficiently drop into the already extensive infrastructure of the petrochemical industry. A significant thrust has been focused on catalytic reactions that accomplish efficient removal of oxygen species from fatty acid derivatives. There are two main deoxygenation pathways involving the elimination of carbon oxides from fatty acids (Scheme 1) and their derivatives. These pathways are commonly referred to as decarboxylation, carbon dioxide elimination (Scheme 1, top) and decarbonylation, carbon monoxide elimination (Scheme 1, bottom). Some recent reviews discuss these important reactions.[2,3] Both of these pathways have been extensively studied, and both are thermodynamically favorable at high temperature.[4−6] However, there are important differences in reaction rate, reagent and catalyst requirements, and overall mechanism.

**Scheme 1. Two Distinct Pathways To Remove Oxygen-Containing Species from a Fatty Acid[a]**



[a]Decarboxylation (top) and decarbonylation (bottom) both yield a hydrocarbon, but the product's level of unsaturation and the co-products are different in each case.

Although ruthenium and rhodium metals abstract carbonyls from carboxylic acids and aldehydes,[7] catalytic decarbonylation was first employed in palladium systems[8] where much of the literature has focused on decarbonylation of saturated fatty acid substrates to form alkenes.[9−18] One highly interesting study shows that the activity of palladium in deoxygenation is affected by the polarity of the catalyst support.[19] In each of these catalytic systems of varied metals, it is necessary to have either in situ formation of an anhydride[20] or an added one as a coreactant. The stoichiometric amount of anhydride (Scheme 2) is converted into two moles of carboxylic acid coproduct. A simpler technology would enhance the viability of a fatty acid to alkenes biorefinery.

Catalytic oxidative decarboxylation is a different approach in which $Ag^{1+}$ is oxidized in situ to $Ag^{2+}$ by half of an equivalent of an oxidant, peroxydisulfate, which generates a sulfate coproduct. The $Ag^{2+}$ interacts with the fatty acid to give an oxygen-centered radical, regenerating $Ag^{1+}$ and a proton which is trapped by the sulfate formed in the initial step. The oxygen-centered radical then spontaneously decarboxylates to a carbon-

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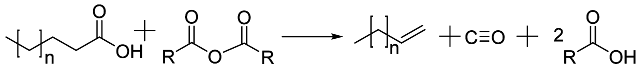
**Scheme 2. Balanced Reaction for Decarbonylation of a Fatty Acid Facilitated by an Anhydride Coreactant**[a]



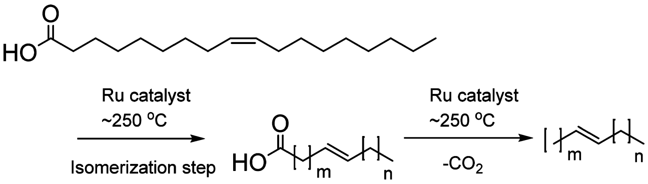
[a]This reaction produces an alkene, carbon monoxide, and 2 equiv of carboxylic acid.

centered radical. Abstraction of a hydrogen atom from a solvent gives the final deoxygenated alkane product. In an interesting twist, copper can also be added, which will catalyze an oxidative elimination to give a terminal alkene instead of an alkane.[21−23]

While this chemistry is interesting, it does have a lot of requirements making it difficult to implement in a biorefinery scenario. First, stoichiometric peroxydisulfate is consumed and a sulfate is produced. Next, a solvent with an easily abstractable hydrogen is required to produce an alkane, which is transformed to yet another coproduct. If an alkene is desired, additional reagents and metal catalysts are needed. Finally, unproductive reactions may occur on both the oxygen- and carbon-centered radicals, thus generating disproportionation, addition, and rearrangement side products. Direct decarboxylation without all of these drawbacks is possible at temperatures over 300 °C using palladium catalysts supported on carbon[2] or alumina.[24,25] However, a modified approach was needed to achieve higher conversion at lower temperatures.

The rate of thermal decarboxylation of unsaturated carboxylic acids is significantly affected by the position of unsaturation relative to the carboxylic acid moiety. Alpha-beta or beta-gamma unsaturated acids react the fastest.[26−28] There are many examples of isomerization catalysts in the literature,[29−33] some of which describe the use of metal carbonyls.[34−37] Specifically, ruthenium carbonyl in the presence of a carboxylic acid forms a complex[38] that will readily isomerize alkenes in the presence[39] or absence[40] of a phosphine ligand. The approach used herein (Scheme 3) is to take advantage of this phenomenon by using a catalyst that is capable of first isomerizing the substrate and then also facilitating decarboxylation. This tandem approach does not require additional coreagents, works at temperatures considerably below 300 °C, and has been demonstrated to work on unsaturated fatty acids of 11 to 18 carbons in length.

**Scheme 3. Tandem Isomerization-Decarboxylation Pathway for the Conversion of Unsaturated Fatty Acids to Alkenes, Using 9-*cis*-Octadecenoic Acid As an Example**



The isomerization-decarboxylation catalyst precursor complex, $[Ru(CO)_2(EtCO_2)]_n$, was synthesized according to a modified literature method.[38] An inert atmosphere glovebox (nitrogen) was used for manipulation of reagents, where 0.2384 g of $Ru_3(CO)_{12}$ (99%, Acros, Pittsburgh, PA) was placed in a 50 mL Schlenk flask that was connected to a Vigreux column capped with a vacuum adapter. The apparatus was removed from the glovebox, and an argon flow from a Schlenk line was connected to the vacuum adapter. At this time, 20 mL of propanoic acid (99.5%, Sigma-Aldrich, St. Louis, MO) was added to the Schlenk flask through the side arm while maintaining an inert (argon) atmosphere. Heating to reflux gave an orange solution within 1 h. After 7 h of reaction, excess propionic acid was removed by vacuum while ensuring that the reaction was not exposed to oxygen. Finally, an orange product was collected, washed with ethyl ether (99.5%, Sigma-Aldrich), and dried under vacuum again to afford 0.1215 g (51% of theoretical) of catalyst. Its identity was confirmed by FT-IR spectroscopy. In all of the examples, conversion was determined using an Agilent (Santa Clara, CA) model 7890A GC-FID with a DB35-MS (30 m × 320 um, 0.25 $\mu$m film) column. Relative response factors for alkanes, methyl esters, and carboxylic acids were calculated by comparison of authentic samples. Identities of products were also verified by injection into a similar GC that was equipped with an MS detector.

The efficacy of the catalyst complex in isomerization reactions was demonstrated on 1-octadecene (90%, Sigma-Aldrich) and 7-*trans*-tetradecene (98%, Sigma-Aldrich). Additionally, because methyl esters are not decarboxylated under these catalytic conditions, methyl 10-undecenoate (96%, Sigma-Aldrich) and methyl 9-*cis*-octadecenoate (methyl oleate; >99%, Nu-Check Prep, Elysyian, MN) were also used. As an example, methyl 10-undecenoate (2.0521 g) was isomerized using 0.0021 g of $[Ru(CO)_2(EtCO_2)]_n$ at 250 °C for 4 h in a 16 × 150 mm culture tube that was sealed with a septa-capped lid. The reaction was prepared in an inert-atmosphere glovebox and was connected to a Schlenk line through a 22 gauge needle. In each of these systems, distribution of positional isomers was obtained (Table 1). In another example, 2-methyl-1-decene (90%, Acros) was isomerized solely to 2-methyl-2-decene (14% of theoretical yield).

There was also no observable fragmentation of the isomerized materials. Additionally, NMR spectroscopy shows that the isomerized material does not have a change in the integration values of the alkane/alkene protons. For example, in 7-*trans*-tetradecene, the starting material value was 13.7, whereas it was essentially the same, 13.9, in the isomerized tetradecene.

The efficacy of decarboxylation using the same precatalyst (Scheme 4) was demonstrated on a proximate isomer, *trans*-cinnamic acid (99%, Sigma-Aldrich). Positional isomerization was not possible because of the relative positions of the ring and the unsaturation in this material. In an example reaction, 0.0023 g of $Ru_3(CO)_{12}$ and 2.0734 g of *trans*-cinnamic acid were prepared as in the prior example, and the reaction was run at 200 °C for 4 h. GC analysis revealed that ~29% of the starting material was converted to styrene, which increased to >70% when the catalyst amount was increased to 0.2105 g. Under these same conditions, but without $Ru_3(CO)_{12}$, less than 1% conversion to product was observed, thus clearly demonstrating the dramatic acceleration of the reaction by the precatalyst (Table 1). From these results the demonstrated total turnovers and turnover frequency can be calculated. In the 4 h experiment, 0.0041 mol of substrate was converted by only $3.6 \times 10^{-6}$ mols of the catalyst which is a demonstration of 1130 total turnovers (377 $Ru^{-1}$) and a turnover frequency of 280 $h^{-1}$ (93 $h^{-1}$ $Ru^{-1}$).

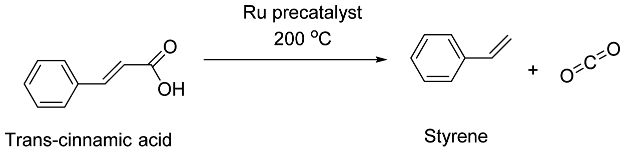
The efficacy of the decarboxylation, as measured by turnover frequency (Table 1), shows that *trans*-cinnamic acid is readily converted. Much higher loading of catalyst increased the observed conversion. However, lower observed turnover

Table 1. Yield and Products from the Decarboxylation-Isomerization of Unsaturated Substrates and Isomerization of Ester and Alkene Substrates Which Do Not Undergo Decarboxylation under These Conditions[a]

| substrate | conditions | conversion to alkene (GC %) | turnover frequency ($h^{-1}$ $Ru^{-1}$) | observed product |
|---|---|---|---|---|
| *trans*-cinnamic acid | no precatalyst 200 °C, 4 h | 1 | NA | styrene |
| | 0.11 wt % $Ru_3(CO)_{12}$ 200 °C, 4 h | 29 | 93 | |
| | 10.0 wt % $Ru_3(CO)_{12}$ 200 °C, 4 h | 74 | 3 | |
| 9-*cis*-octadecenoic acid | no precatalyst 250 °C, 24 h | 0 | NA | heptadecene, multiple isomers |
| | 0.10 wt % $Ru_3(CO)_{12}$ 250 °C, 4 h | 20 | 39 | |
| | 0.10 wt % $Ru_3(CO)_{12}$ 250 °C, 24 h | 36 | 12 | |
| 10-undecenoic acid | 0.89 wt % $Ru_3(CO)_{12}$ 250 °C, 4 h | 60 (GC-MS) | 20 | decene, multiple isomers |
| methyl 10-undecenoate | 0.10 wt % $[Ru(CO)_2(EtCO_2)]_n$ 250 °C, 4 h | NA | NA | isomerized ester (apparent steady state of isomers) |
| | 0.14 wt % $[Ru(CO)_2(EtCO_2)]_n$ 150 °C, 4 h | NA | NA | starting material (minor amount of isomerization) |
| methyl 9-*cis*-octadecenoate | 0.13 wt % $[Ru(CO)_2(EtCO_2)]_n$ 250 °C, 4 h | NA | NA | isomerized ester (apparent steady state of isomers) |
| methyl 9-*cis*-octadecenoate | 0.12 wt % $[Ru(CO)_2(EtCO_2)]_n$ 150 °C, 4 h | NA | NA | starting material (minor amount of isomerization) |
| 7-*trans*-tetradecene | 0.015 wt % $[Ru(CO)_2(EtCO_2)]_n$ 150 °C, 4 h | NA | NA | isomerized alkenes (apparent steady state of isomers) |

[a] Under reaction conditions where a carboxylic acid substrate is used, the catalyst forms in situ. When non-carboxylic acid substrates are utilized, a precatalyst with carboxylate ligands must be used to give efficacy.

Scheme 4. Catalyzed Decarboxylation of *trans*-Cinnamic Acid



frequency is evident, caused by the lower number of possible turnovers in the experiment.

As with both of the steps in the process, the tandem reaction was greatly accelerated in the presence of the precatalyst. Both a large carboxylic acid, 9-*cis*-octadecenoic acid (oleic acid), and a smaller terminal acid, 10-undecenoic acid (98%, Sigma-Aldrich), demonstrated significant conversion. Using the same methods as described above, 0.0021 g of $[Ru(CO)_2(EtCO_2)]_n$ and 2.0055 g of oleic acid (>99%, Nu-Check Prep) reacted at 250 °C for 4 h afforded nearly 20% conversion to a mixture of alkene isomers. The same results were achieved using $Ru_3(CO)_{12}$ as well, thus indicating similar behavior between the catalyst precursors (Table 1). In the 9-*cis*-octadecenoic acid decarboxylation, using equal catalyst loading, the 4 h experiment has lower conversion but average higher turnover frequency than the 24 h experiment. This is probably due to the reaction slowing down as conversion increases due to less substrate availability, along with inhibition of the decarboxylation reaction caused by the buildup of product. In each of the systems, both the product and the starting material showed an apparent steady state of isomers, with no observed fragmentation. Control experiments demonstrated that, even at higher temperatures, catalyst-free systems did not undergo decarboxylation. Experiments which were run for longer times showed that the amount of decarboxylation continues to increase with time, albeit at a slower rate. The time required for complete conversions were studied and compared and are expected to be highly dependent on substrate, temperature, and catalyst concentration.

Next, the necessity of the unsaturation in the substrate was evaluated by the reaction of octadecanoic acid (99%, Sigma-Aldrich), a saturated analogue of oleic acid. When the decarboxylation was conducted at 250 °C, only a small amount of hydrocarbon was produced, ~7 times less than (Figure 1) that from oleic acid. This effect was even more pronounced when the reactions were performed at 225 °C. The conversions in 24 h under those conditions were 11.1% for the unsaturated substrate and 0.4% for the saturated species, yielding a ratio of 28:1.

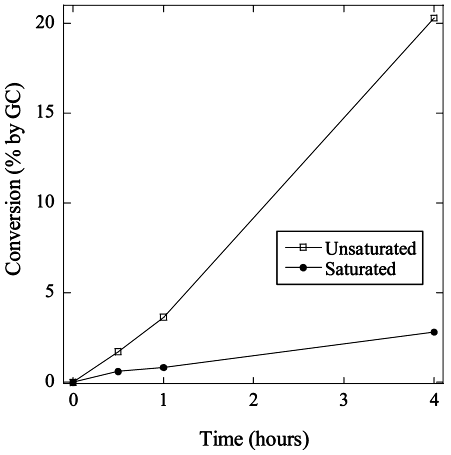


**Figure 1.** A comparison of the decarboxylation of 9-*cis*-octadecenoic acid (□) with the saturated octadecanoic acid (●). The reactions both contained 0.11 wt % of $Ru_3(CO)_{12}$ (4 h point) or $[Ru(CO)EtCO_2)]_n$ (shorter time points) and were run at 250 °C. In the shorter time experiments, the catalyst which already contained carboxylate groups was used to avoid an induction period which would have convoluted the resulting conversions. In the longer experiment, the induction period is not a substantial factor.

Finally, a reaction system was assembled, where the product could be removed as the reaction progressed. The substrate used was 10-undecenoic acid, which when decarboxylated by this system yields isomers of decene as the product. Because decene boils at ~170 °C, an appropriate collector and condenser can be used to obtain nearly pure product straight from the reaction. Additionally, more substrate was added without the addition of more catalyst, showing further activity. Initially, 11.8 g of 10-undecenoic acid was subjected to tandem isomerization-decarboxylation using 0.273 g of $Ru_3(CO)_{12}$, under an argon atmosphere. Later, 6.1 g of decene was removed from the system, and an additional 4.9 g of substrate was added. Overall, 4 aliquots of substrate, 26.5 g were used resulting and 10.7 g of product was collected, a 53% yield. The total turnovers of this catalyst were 178 (59 per Ru). Unfortunately, it was not feasible to quantitatively capture the carbon dioxide in order to achieve 100% mass balance.

The triruthenium dodecacarbonyl and $[Ru(CO)RCO_2]_n$ are effective *in situ* precatalysts for producing unsaturated hydrocarbons from a large carboxylic acid such as oleic acid. The utility of this method differs from that in the literature. Our method is catalytic, does not require coreagents, and can be conducted under 300 °C, and the only apparent coproduct is $CO_2$. Key to this surprising and useful reactivity is the tandem effect, i.e. the presumably faster isomerization reaction allows access to configurations where decarboxylation is favored.

The most important practical aspect of this work is that it can convert materials derived from agriculture into higher-value industrial products similar to those produced via conventional petrochemical means. The hydrocarbons obtained from this process can be used in fuels, polymers, lubricants, or other applications where a biobased source of large alkenes is desirable. The new approach gives industries direct drop-in replacements for petroleum-based products and also benefits the agricultural industry.

## AUTHOR INFORMATION

### Corresponding Author

*Phone: 309-681-6103. Fax: 309-681-6524. E-mail: Kenneth.Doll@ars.usda.gov.

### Notes

Disclosure: Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

The authors declare no competing financial interest.

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