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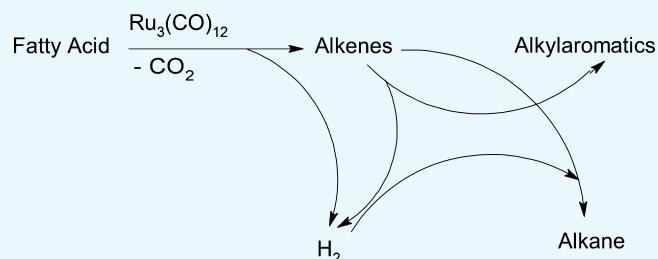
Decarboxylation of Fatty Acids with Triruthenium Dodecacarbonyl: Influence of the Compound Structure and Analysis of the Product Mixtures

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ABSTRACT: Recently, the decarboxylation of oleic acid (9(Z)-octadecenoic acid) catalyzed by triruthenium dodecacarbonyl, $\text{Ru}_3(\text{CO})_{12}$, to give a mixture of heptadecenes with concomitant formation of other hydrocarbons, heptadecane and C17 alkylbenzenes, was reported. The product mixture, consisting of about 77% heptadecene isomers, 18% heptadecane, and slightly >4% C17 alkylbenzenes, possesses acceptable diesel fuel properties. This reaction is now applied to other fatty acids of varying chain length and degree of saturation as well as double-bond configuration and position.

Acids beyond oleic acid included in the present study are lauric (dodecanoic), myristic (tetradecanoic), palmitic (hexadecanoic), stearic (octadecanoic), petroselinic (6(Z)-octadecenoic), elaidic (9(E)-octadecenoic), asclepic (11(Z)-octadecenoic), and linoleic (9(Z),12(Z)-octadecadienoic) acids. Regardless of the chain length and degree of unsaturation, a similar product mixture was obtained in all cases with a mixture of alkenes predominating. Monounsaturated fatty acids, however, afforded the alkane with one carbon less than the parent fatty acid as the most prominent component in the mixture. Alkylbenzenes with one carbon atom less than the parent fatty acid were also present in all product mixtures. The number of isomeric alkenes and alkylbenzenes depends on the number of carbons in the chain of the parent fatty acid. With linoleic acid as the starting material, the amount of alkane was reduced significantly with alkenes and alkylaromatics enhanced compared to the monounsaturated fatty acids. Two alkenes, 9(E)-tetradecene and 1-hexadecene, were also studied as starting materials. A similar product mixture was observed but with comparatively minor amount of alkane formed and alkene isomers dominating at almost 90%. The double-bond position and configuration in the starting material do not influence the pattern of alkene isomers in the product mixture. The results underscore the multifunctionality of the $\text{Ru}_3(\text{CO})_{12}$ catalyst, which promotes a reaction sequence including decarboxylation, isomerization, desaturation, hydrogenation, and cyclization (aromatization) to give a mixture of hydrocarbons simulating petrodiesel fuels. A reaction pathway is proposed to explain the existence of these products, in which alkenes are dehydrogenated to alkadienes and then, under cyclization, to the observed alkylaromatics. The liberated hydrogen can then saturate alkenes to the corresponding alkane.



INTRODUCTION

The production of fuels from renewable resources continues to be a major focus on reducing the dependence on petroleum, lessening carbonization of energy sources, and reducing exhaust emissions. Among these, fuels are those derived from vegetable oils or, more generally, plant oils. Several types of fuels can be produced from plant oils. One is biodiesel^{1,2} which is the (mono)alkyl esters of vegetable oils, animal fats, or other triacylglycerol-based oils or fats and obtained by a transesterification reaction. Another is a fuel best termed renewable diesel which consists of a mixture of hydrocarbons obtained by a hydrodeoxygenation reaction^{3–12} which usually involves decarboxylation and hydrogenation of oleochemical materials by adding H_2 in the presence of sulfided NiMo– Al_2O_3 , CoMo– Al_2O_3 , Ni/SiO₂, Pd/C, Raney nickel, or similar catalysts.^{13–21} Renewable diesel, which is also known by other terms, such as hydrotreated vegetable oils, consists of straight-chain and branched alkanes. Straight-chain alkanes are

the straightforward products of this reaction, for example, heptadecane is the “ideal” hydrocarbon obtained from C18 fatty acids but lesser amounts of side products such as alkenes and aromatics may also arise. Jet fuels^{22,23} can be obtained via a subsequent isomerization reaction of the product mixture to give branched alkanes with improved cold flow properties.

Besides the energy-related materials mentioned above, 1-alkenes (also known as α -olefins) are of considerable interest as starting materials for a variety of commercially valuable derivatives. These compounds have been synthesized from long-chain fatty acids and their related compounds via dehydrating decarbonylation/decarboxylation by catalytic approaches^{24,25} using mainly Pd-, Pt-, Rh-, Ir-, or Ru-based organometallic catalysts and, in a more recent development,

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Table 1. Alkanes Formed and Number of Possible Isomers of Alkenes and Alkylaromatics Arising from the Different Starting Materials in the Reaction with $\text{Ru}_3(\text{CO})_{12}$

starting material ^a	alkane	number of possible products	
		alkenes	alkylaromatics (combinations of $s + t$) ^b
Alkenes			
7(<i>E</i>)-tetradecene	tetradecane	13 (tetradecenes)	5 (0 + 8; 1 + 7, 2 + 6; 3 + 5, 4 + 4) MW = 190
1-hexadecene	hexadecane	15 (hexadecanes)	6 (0 + 10, 1 + 9, 2 + 8, 3 + 7; 4 + 6; 5 + 5) MW = 218
Fatty Acids			
lauric acid	undecane	9 (undecenes)	3 (0 + 5; 1 + 4, 2 + 3) MW = 148
myristic acid	tridecane	11 (tridecenes)	4 (0 + 7; 1 + 6; 2 + 5; 3 + 4) MW = 176
palmitic acid	pentadecane	13 (pentadecenes)	5 (0 + 9; 1 + 8; 2 + 7; 3 + 6; 4 + 5) MW = 204
stearic acid, oleic acid, elaidic acid, petroselinic acid, asclepic acid, and linoleic acid	heptadecane	15 (heptadecenes)	6 (0 + 11; 1 + 10; 2 + 9; 3 + 8; 4 + 7; 5 + 6) MW = 232
oleic acid	heptadecane	15 (heptadecenes)	6
elaidic acid	heptadecane	15 (heptadecenes)	6
petroselinic acid	heptadecane	15 (heptadecenes)	6
vaccenic acid	heptadecane	15 (heptadecenes)	6
linoleic acid	heptadecane	15 (heptadecenes)	6

^aSystematic names of the fatty acids used here: dodecanoic acid (lauric acid), tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), 9(*Z*)-octadecenoic acid (oleic acid), 9(*E*)-octadecenoic acid (elaidic acid), 6(*Z*)-octadecenoic acid (petroselinic acid), 11(*Z*)-octadecenoic acid (asclepic acid), and 9(*Z*),12(*Z*)-octadecadienoic acid (linoleic acid). ^bSee Figure 3 for the definition of s and t .

enzymatic catalysts. The formation of mixtures of alkenes in such reactions has also been reported. Similar to long, straight-chain alkanes that are ideal constituents of petrodiesel, the mixtures of alkenes (and side products) may also be of interest as fuels as their high cetane numbers show that, although resulting from the presence of double bonds, their oxidative stability is reduced compared to the saturated alkanes. Examples in the literature describing decarboxylation/decarbonylation with dehydration reactions include using lead tetraacetate in the presence of Cu(II) to give α -olefins,²⁶ stearic acid to a mixture of heptadecenes using rhodium trichloride and triphenylphosphine,²⁷ Ni- and Pd-based catalysts for decarboxylating heptanoic and octanoic acids,²⁸ conversion of carboxylic acids to mixed anhydrides which add to a PdCl_2 -DPE-Phos catalyst,²⁹ various iridium-based catalysts,³⁰ linear olefins by decarboxylation of unsaturated fatty acids with Ag(II)/ NaS_2O_8 ,³¹ FeCl_2/KI , or FeI_2/KI ,³² and linear olefins and α,ω -dienes from saturated fatty acids with $\text{PdCl}_2/\text{Ph}_3\text{P}$ or $\text{Pd}(\text{PP}_3)_4/\text{Ph}_3\text{P}$,³³ $\text{PdCl}_2(\text{PPh}_3)_2$,^{34,35} and $\text{Pd}/\text{Al}_2\text{O}_3$.³⁶ A different example is the formation of alkanes or saturated fatty acids from saturated and unsaturated fatty acids with Pt/C or PtSn_x/C in water.^{37,38}

In connection with the synthesis of alkenes from fatty acids, we recently reported that oleic acid, which is probably the most common fatty acid in plant oils, can be decarboxylated in the presence of triruthenium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$) to a mixture of isomeric heptadecenes and heptadecanes, accompanied by a lesser amount of isomeric C17 alkylaromatics.^{39–41} The heptadecene isomers comprises about 77% of the mixture, whereas heptadecane is the single most prominent component at about 18% with alkylaromatics at approximately 4%. To the best of our knowledge, this is probably the first time that decarboxylation was reported with $\text{Ru}_3(\text{CO})_{12}$ as a catalyst, although $\text{Ru}_3(\text{CO})_{12}$ has found its use in numerous other reactions, including isomerizations, alkylations, and arylations.⁴² Here, we report an expansion of that work and the compositional analysis of the products to other fatty acids of different chain lengths (C12–C18) and saturation including saturated and diunsaturated fatty acids while keeping other reaction parameters constant. To the best of our knowledge,

there are also only few reports^{37,38} on the decarboxylation of a neat polyunsaturated fatty acid such as linoleic acid. Two alkenes were also selected as starting materials to investigate if aromatization and hydrogenation also occur with hydrocarbons, providing insight into the reaction pathways.

RESULTS AND DISCUSSION

Analyses by gas chromatography-flame ionization detection and gas chromatography–mass spectrometry (GC–MS) of the product mixtures and their dimethyl disulfide (DMDS) derivatives for the determination of double positions showed that several classes of compounds are formed in the reaction of fatty acids and alkenes with catalytic $\text{Ru}_3(\text{CO})_{12}$. All products from the reaction of fatty acids with $\text{Ru}_3(\text{CO})_{12}$, regardless of saturation or double-bond position and configuration, possess one carbon atom less than the starting material, showing that nearly quantitative decarboxylation occurs. In the case of alkenes as starting materials, of course, the number of carbons remains the same as that of the starting material. Summarily, the classes of compounds formed are an alkane, all possible isomers of the corresponding alkenes, a mixture of alkadienes, and a mixture of alkylaromatics. Although the overall pattern of the classes of compounds formed remains the same, the ratios, however, in which they are formed strongly depend on the starting material. The number of possible isomers of alkenes and alkylaromatics decreases systematically with decreasing chain length of the fatty acid used as the starting material. Table 1 contains information on the nature of the compounds formed, and these compounds are discussed below, whereas Table 2 presents the yields of the different classes of compounds. As an example, Figure 1 depicts a GC–MS total ion chromatogram of the products of the reaction of palmitic acid with $\text{Ru}_3(\text{CO})_{12}$. Figure 2 contains information on the evaluation of the mass spectra corresponding to the peaks in the GC–MS run shown in Figure 1. A pathway to the products is proposed in Figure 3.

Alkane Products. The reaction of alkenes with $\text{Ru}_3(\text{CO})_{12}$ leads to the corresponding saturated alkane of the same chain length. The alkane derived from fatty acids with n carbon atoms (in Figure 3: $n = x + 2$) is $\text{C}_{n-1}\text{H}_{2(n-1)+2}$ ($=\text{C}_{n-1}\text{H}_{2n}$).

Table 2. Relative Yields (As Determined by GC) of the Different Product Classes in the Reaction of Fatty Acids and Alkenes as well as Methyl Oleate with $\text{Ru}_3(\text{CO})_{12}$ ^a

starting material	relative yields (%)			
	alkane	alkenes	alkadienes	alkylaromatics
Alkenes				
7(<i>E</i>)-tetradecene	9.3	87.5	1.3	0.5
1-hexadecene	8	89.1	1	0.7
Fatty Acids				
lauric acid	52.4	41.1	1.5	4.7
myristic acid	56.1	36.5	0.8	6.2
palmitic acid	54.5	38.7	0.3	5.7
stearic acid	78.2	12.2	0.7	7.1
oleic acid	25.7	65.7	0.3	6.2
elaidic acid	19.6	73.5	0.7	5.3
petroselinic acid	17.6	74.5	0.7	5.2
asclepnic acid	14.1	77.5	0.6	4.2
linoleic acid	2.7	81.4	1.3	13.5

^aYields after product washing are given by setting the total of alkane, alkene, alkadiene, alkylaromatics, and minor amounts of unidentified products to 100%. Unreacted fatty acid in the mixture is typically 1–3%.

Alkene Products. The number of all positional and geometric (*E* and *Z*) alkene isomers that can be formed from fatty acids with an even number of n carbon atoms in the chain is $n - 3$. For fatty acids with odd n , the number of possible alkene isomers is $n - 2$. In the case of alkenes as starting materials, the number of isomers is $n - 1$ if n is even and the number of alkene isomers is $n - 2$ for odd n . The presence of all possible alkene isomers was ascertained by the derivatization of the product mixture with DMDS⁴⁰ which afforded the corresponding bis(methylthio) alkanes. In all cases, both diastereomers of each bis(methylthio) alkane positional isomer were identified by GC–MS.⁴⁰ The number of possible alkenes (accounting for *Z* and *E* double-bond configurations) in the product mixture is given in Table 1. The products with *Z* configuration dominate over those with *E* configuration. Additionally, a thermodynamic (or near) distribution of alkene products was obtained, as indicated by lesser amounts (around 1–2%) of individual terminally unsaturated (and thus less

thermodynamically favored) alkenes relative to higher amounts of individual internal (i.e., more stable) alkenes.

Alkyl aromatic Products. The alkylaromatics formed are of the type $\text{H}(\text{CH}_2)_s-\text{C}_6\text{H}_4-(\text{CH}_2)_t\text{H}$ with $s + t = n - 7$. Accordingly, the number of isomeric alkylaromatics that can be formed from fatty acids with even n is $(n - 6)/2$, giving, for example, six alkyl aromatic compounds from fatty acids with $n = 18$, and for fatty acids with odd n , it is $(n - 5)/2$. In the case of alkenes with even n , $(n - 4)/2$ alkylaromatics of this type can arise and with odd n , it is $(n - 5)/2$. Table 1 lists the possible isomers (with the combination of $s + t$) of the alkyl aromatic compounds that are observed in the product mixtures. One compound in each mixture is unambiguously identified as the monoalkylbenzene with $s = n - 7$ ($x - 5$ in Figure 3). This evaluation resembles that given in the literature for alkylbenzenes found in some crude oil.⁴³ It may be noted that the formation of minor amount of aromatics was also observed,^{15,17} but the presence of hydrogen in these reactions may reduce the amount of aromatics.¹⁵

The nuclear magnetic resonance (NMR) spectra also confirm the existence of compounds with aromatic moieties. An integration ratio of about 8.7:1 of alkene to aromatic protons (unresolved peak at 7.1–7.2 ppm) was observed. Assuming that four protons ($-\text{C}_6\text{H}_4-$) are responsible for the aromatic signals (regardless of the number of isomers) with two protons ($-\text{CH}=\text{CH}-$) causing the olefinic signals, a ratio of alkenes to aromatics of about 17:1 is obtained. This result agrees well with the evaluation by GC. The NMR spectra also agree well with previous data.⁴⁰

Alkadiene Products. This class of compounds is the least prominent in the product mixture, consistently constituting 1.5% or less. The number of possible isomers exceeds the number of discrete peaks observed which may be due to overlap and the very minor amounts of individual alkadiene isomers that are formed. No assignments to individual compounds were made. It appears likely, however, that the alkadienes are precursors to the alkylaromatics as further dehydrogenation would lead to alkatrienes which may spontaneously cyclize to the stable alkylaromatics under the influence of the $\text{Ru}_3(\text{CO})_{12}$ catalyst (shown in Figure 3). A detailed mechanistic investigation of this proposed pathway would need to be the subject of a further study.

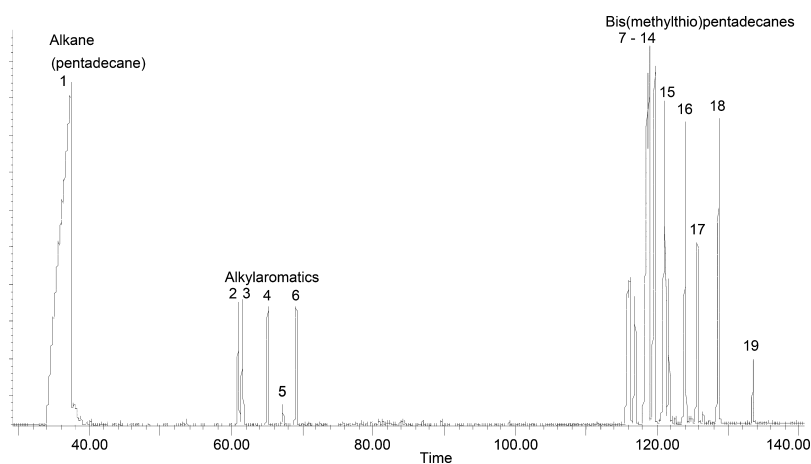


Figure 1. Total ion chromatogram (GC–MS trace) of the reaction products of palmitic acid with $\text{Ru}_3(\text{CO})_{12}$ after derivatization with DMDS. The inscribed numbers identifying specific peaks correspond to those in Figure 2 which contains information on their evaluation.

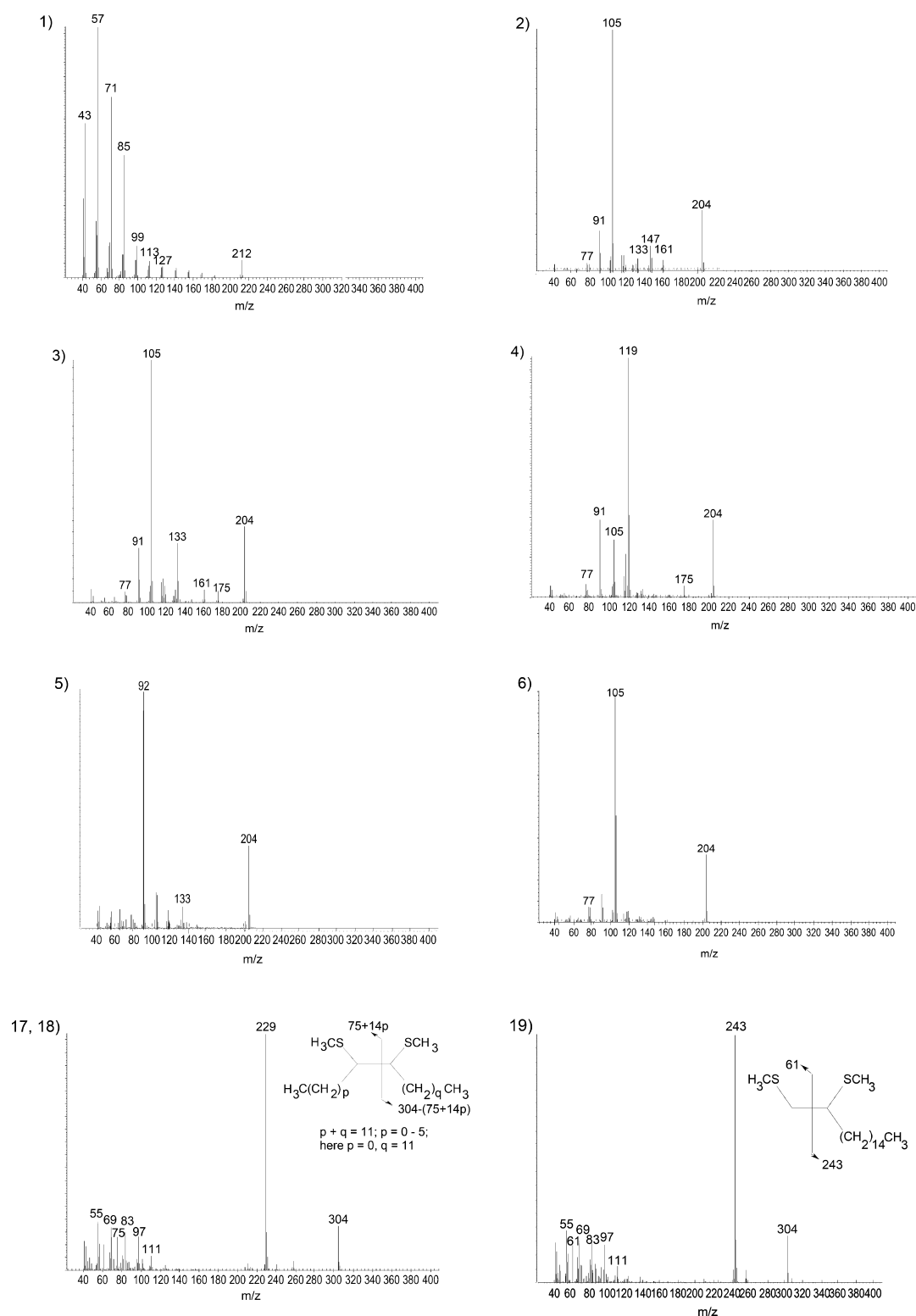


Figure 2. Mass spectra of the products of the reaction of palmitic acid with $\text{Ru}_3(\text{CO})_{12}$ after derivatization with DMS. The subscripts p and q correspond to those in this figure. The peaks labeled 1–19 are assigned as follows: (1) pentadecane, (2–6) aromatics with peak 5 assigned to nonylbenzene (for further details see text), and (7–19) DMS derivatives of pentadecene isomers. As examples only the mass spectra corresponding to peaks 17–19 are shown which are (17,18) the erythro and threo diastereomers of 2,3-bis(methylthio)pentadecane and (19) 1,2-bis(methylthio)pentadecane, respectively. Similar to peaks 17 and 18, peaks 7–16 are caused by the erythro and threo diastereomers of the other bis(methylthio)pentadecanes derived from (*E*)- and (*Z*)-pentadecenes, respectively.

Product Mixture from Alkenes (7(E)-Tetradecene and 1-Hexadecene) as a Starting Material. As mentioned above, when using alkenes as starting materials, the product mixture

consists of compounds with the same number of carbons. Although alkenes predominate in the mixture, the overall composition is more complex than previously reported.³⁹ The

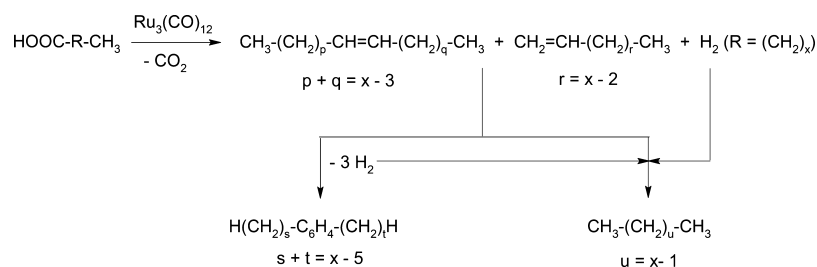


Figure 3. Possible pathway to various products found in the reaction of fatty acids with $\text{Ru}_3(\text{CO})_{12}$. Note that $x = n - 2$ as n is the total number of carbons in a fatty acid chain (see text). Also, $\text{R} = (\text{CH}_2)_x$ with $x = 10, 12, 14,$ and 16 ; $(\text{CH}_2)_y\text{CH}=\text{CH}(\text{CH}_2)_z$ with $y + z = x - 2$; $(\text{CH}_2)_7\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_2$.

corresponding saturated hydrocarbon, tetradecane or hexadecane, is the single most prominent compound because the mixture of alkenes is composed of all possible isomers. The amount of alkane formed is minor, compared to that observed with the fatty acids as starting materials (Table 2). Alkenes with double bonds located toward the middle of the chain predominate regardless of the position of the double bond in the two starting materials (7(*E*)-tetradecene and 1-hexadecene) used, although the amounts of individual isomers were not determined. The amount of alkylaromatics formed is low, less than 1%, whereas alkadienes were formed in slightly greater amounts of 1–1.5%. Overall, the amount of alkylaromatics was the lowest with alkenes as the starting materials.

Product Mixture from Fatty Acids as Starting Materials.

The GC–MS analyses (see Figure 1 for a typical chromatogram with the products formed from palmitic acid as example) revealed that the same classes of compounds, an alkane, all possible alkene isomers, alkadienes, and alkylaromatics, observed previously in work on decarboxylation of oleic acid in the presence of $\text{Ru}_3(\text{CO})_{12}$ ⁴⁰ are formed in all reactions. The pattern of the reaction products appears to depend on neither the chain length, similar to the results regarding hydrothermal deoxygenation with Pt/C,³⁷ nor the number of double bonds and their position and configuration. The saturated acids, monounsaturated C18:1 acids [oleic acid (9(*Z*)-octadecenoic acid), elaidic acid (9(*E*)-octadecenoic acid), asclepic acid (11(*Z*)-octadecenoic acid), petroselinic acid (6(*Z*)-octadecenoic acid)], and the diunsaturated linoleic acid give the same product pattern. The alkane with one less carbon atom in the chain ($\text{C}_{n-1}\text{H}_{2n}$) dominates in the case of saturated fatty acids with the formation of the alkane decreasing with increasing unsaturation of the starting material. Thus, a mixture of all possible alkene isomers with one less carbon atom in the chain as the parent fatty acid constitutes the bulk of the product mixture in the case of monounsaturated fatty acids as well as linoleic acid as the starting material. Taken individually, each alkene isomer is present in lesser amounts than the alkane with monounsaturated fatty acid substrates. In the case of linoleic acid as the starting material, however, the alkane is a minor product. For a given degree of unsaturation of C18:1 fatty acids, the relative amounts of the products vary only in a minor to moderate fashion. Thus, position and configuration of the double bonds have only minor influence on the product pattern. The amount of alkylaromatics formed in cases of the saturated and monounsaturated fatty acids (range of about 4–7%) well exceeds that produced with alkenes as the starting material. In the case of linoleic acid as the starting material, however, the amount of alkylaromatics exceeds that of the other fatty acids as the starting material likely because of the already

present higher degree of unsaturation and therefore less need for dehydrogenation. Furthermore, in the case of linoleic acid as the starting material, the peak caused by what is likely ethylonylbenzene (last eluting peak in the series of aromatics) was by far the strongest of all alkylaromatics, accounting for about 5.75% of the total of 13.5% alkylaromatics observed. Other authors³⁷ found “heavy” products in their Pt/C in water-based decarboxylation together with some unidentified aromatics.

Reaction Pathway. The above discussion shows that the reaction of fatty acids with $\text{Ru}_3(\text{CO})_{12}$ proceeds with several processes occurring sequentially and/or simultaneously. These processes include decarboxylation (shortening of the chain length), isomerization (all positional and geometric isomers formed from unsaturated fatty acids and alkenes), dehydrogenation (formation of alkadienes and alkylaromatics), cyclization (aromatization; formation of alkylaromatics), and hydrogenation (formation of alkanes). The ratios of the products differ depending on the starting material as some of the possible reactions are already “built-in” into the structure of the starting materials. It appears that decarboxylation is an independent reaction as isomerization can also occur with alkenes and methyl esters. Furthermore, it could be assumed that the reaction consists of decarbonylation and dehydration instead of decarboxylation and dehydrogenation, but this is probably not the dominant path, considering that the same classes of compounds are formed from fatty acids and alkenes (which can be viewed as fatty acids already decarboxylated), as well as that hydrogenation is observed in the formation of alkanes from unsaturated starting materials. While some other reactions in which alkanes with $n - 1$ carbons are formed from monounsaturated fatty acids such as oleic acid employ external hydrogen,^{3–21} that is not the case here. Thus, the hydrogen needed for forming the alkane must arise in situ from other reactions, which, as the product mixture indicates, are dehydrogenation to alkenes (in the case of saturated fatty acids) and alkadienes as well as further dehydrogenation with concomitant aromatization. The formation of various alkylaromatics implies that cyclization can occur at any location in the heptadecene chain, although the predominance of ethylonylbenzene with linoleic acid as a starting material may indicate some preference toward specific products and thus double-bond locations. The fact that no alkatrienes were identified in any of the product mixtures regardless of the starting material indicates that aromatization likely occurs spontaneously upon dehydrogenation of the alkadienes, likely because of the stability of the aromatic ring. In the case of saturated fatty acids, this may be a cyclic process. The alkane dehydrogenates to alkene and further to alkadiene and then forms alkyl aromatic, with the hydrogen liberated in this

sequence then in turn hydrogenating some of the alkene to the alkane. It would be of interest to investigate in detail the mechanism of this obviously complex reaction sequence as the subject of a subsequent study. The deoxygenation of stearic anhydride under H₂-free conditions at 250 °C using Pd/Al₂O₃ has been proposed to proceed via stearic anhydride as an intermediate giving a multitude of C17 hydrocarbons.³⁶ Another question that arises is if the reaction could eventually be tailored, which may include other cocatalyst(s) or coreagent(s), to favor a specific compound or class of compounds as product(s). This aspect could render the reaction of considerable interest if the products may not be easily accessible in high yields or purity otherwise and uses for these products would be forthcoming. Other aspects to study could include catalyst separation and potential for reuse at a larger scale.

Properties. Essential fuel properties of the product mixture obtained from oleic acid were determined previously.⁴⁰ The cetane number was 86.9, the kinematic viscosity at 40 °C was 3.14 mm²/s, the cloud point (CP) was -1 °C, the pour point (PP) was -4 °C, the oxidative stability by the so-called Rancimat test was 3.4 h, the density at 15 °C is 791 kg/m³, and the wear scar in the high-frequency reciprocating rig lubricity test is 299 μm. Although no properties were determined here for the products derived from the other fatty acids and alkenes, it can be observed that the products with high amounts of alkane and lower amounts of alkenes would likely have more problematic cold flow properties (higher CP and PP) but improved oxidative stability, whereas the converse would hold for the products with reduced amounts of alkane but therefore greater amounts of alkenes. This generalization also depends on the chain length of the starting material and thus the products, with cetane numbers decreasing with the chain length⁴⁴ and cold flow improving because of the lower melting points of shorter-chain compounds.⁴⁵

SUMMARY AND CONCLUSIONS

The catalyst Ru₃(CO)₁₂ reacts with fatty acids irrespective of the saturation level and chain length to give the same product pattern. The most prominent single product is the alkane with one carbon less than the parent fatty acid, whereas alkenes with one carbon less make up the major part of the product mixture. The alkene mixture consists of all possible positional and geometric isomers for a given chain length. A mixture of alkyl aromatic compounds with the number of components depending on the chain length of the fatty acid starting material also arises and the greatest amount formed with linoleic acid as the starting material. The degree of saturation of the fatty acids appears to have a little to no influence on the pattern of the products obtained but influences their relative amounts significantly. Thus, in the presence of Ru₃(CO)₁₂, fatty acids and subsequent intermediates undergo a variety of reactions which include decarboxylation, dehydrogenation, isomerization, hydrogenation, and cyclization/aromatization as shown by the present reaction sequence using oleic acid as the starting material. The reaction of alkenes with Ru₃(CO)₁₂ affords the same product pattern, albeit with the products containing the same number of carbons as the starting material and with differing amounts compared to the fatty acids as the starting material. The product mixtures likely possess properties rendering them acceptable as diesel fuels, although the properties likely vary in the starting material and resulting product pattern. A further direction of research indicated by the

present work would be to define and optimize reaction conditions using Ru₃(CO)₁₂ as a catalyst to steer the reaction toward certain desired products as well as exploring additional issues such as the nature of the catalyst in the reaction and catalyst separation at a larger scale. Thus, varying the starting material, also depending on the fatty acid profile, offers the possibility of tailoring the reaction toward products with specific properties.

EXPERIMENTAL SECTION

Materials and Methods. All fatty acids were purchased from Nu-Chek Prep, Inc. (Elysian, MN) and were of purity >99% as confirmed by random checks using NMR spectroscopy, Bruker (Billerica, MA) Avance 500 spectrometer operating at 500 MHz for ¹H NMR with CDCl₃ as a solvent, and/or gas chromatography-mass spectrometry, Agilent Technologies (Palo Alto, CA) 6890 gas chromatograph equipped with an HP-88 capillary column and coupled to Agilent Technologies (S973 mass selective detector at 70 eV) of some materials. Alkenes were obtained from Sigma-Aldrich (St. Louis, MO) and also randomly checked for advertised purity (≥98%, in most cases ≥99%; verified by the GC-MS analysis). DMDS was also acquired from Sigma-Aldrich, and Ru₃(CO)₁₂ (99%) was obtained from Strem Chemicals, Newburyport, MA. All reagents were used as received. Derivatization of the samples with DMDS was carried out as described previously.^{46,47}

Reaction Procedure. The catalyst, stored under inert atmosphere, was used as received. The reactions were carried out under inert atmosphere as described previously,⁴⁰ albeit on a scale of 2 g (for oleic acid; 0.007 mol) with 0.018 g (2.81 × 10⁻⁵ mol; 0.4 mol % relative to oleic acid) of Ru₃(CO)₁₂ under a nitrogen for 24 h at 250 °C. The reaction mixture was allowed to cool to room temperature with catalyst separation; the product was washed three times with water and then subjected to analyses by GC, GC-MS, and NMR, including analysis of their DMDS addition product, as well as yield determination by GC.

DISCLAIMER

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 US Department of Agriculture. USDA is an equal opportunity provider and employer.

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Notes

The authors declare no competing financial interest.

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