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Reactions of fatty acids in superacid media: Identification of equilibrium products

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Abstract

Acid-catalyzed cracking reactions of model compounds, palmitic acid and oleic acid, using trifluoromethanesulfonic acid were investigated to determine the extent of products from a Bronsted superacid. No reaction was found with the saturated palmitic acid at neither 25 °C nor 100 °C. However, oleic acid, an unsaturated acid, reacted at 0 °C forming linear and branched saturated fatty acids that were of smaller molecular weight than the starting material. These results suggest the potential of using lipids and fatty acids as feedstocks for the manufacture of transportation fuels.

Keywords: Superacid; Oleic; Palmitic; Cracking; Bronsted acid

1. Introduction

Limited petroleum supplies and global warming concerns caused by the significant increase in fossil fuel utilization have prompted researchers to explore renewable raw materials for producing fuels and chemicals. Lipids, such as vegetable oils and animal fats, are being used for producing diesel-like fuels. One example is biodiesel, a mixture of methyl esters usually produced from the reaction of methanol and vegetable oils, catalyzed by a strong base, such as sodium methoxide. Biodiesel is considered a "green fuel" since it does not introduce new carbon into the biosphere unlike petroleum diesel, and it blends well with petroleum diesel and enhances the lubricity of ultra low sulfur diesel. These positive aspects of biodiesel have contributed to a production increase from 500,000 gallons in 1999 to 75 million gallons in 2005 [1].

Several disadvantages of the biodiesel production process could limit its growth in the near future. When biodiesel is produced from vegetable oils and animal fats, the primary reaction by-product is glycerine. The growth of the biodiesel industry has caused glycerine prices to plummet, eliminating any potential profits from this by-product stream. Another disadvantage is the transesterification processes require refined vegetable oils to comply with biodiesel quality standards. The inventory of refined vegetable oils is limited and the prices are higher than non-food quality related lipids. The use of raw materials with a high content of free fatty acids, such as brown grease and tall oil, require either a two-step process of acid-catalyzed esterification followed by base-catalyzed transesterification of triglycerides or a much slower one-step acid-catalyzed esterification. Both processes require higher capital cost compared to the basic transesterification, because of the additional unit operations and the expensive materials of construction needed to resist more corrosive raw materials. More robust conversion technologies are necessary to expand the feedstock inventory for producing biofuels and minimize the generation of low value, side products. Production of biofuels *via* catalytic cracking of lipids similar to petroleum refining for producing gasoline and diesel may offer a commercially attractive alternative to biodiesel technology.

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Past studies have examined the potential of using vegetable oils to produce gasoline range organics (GRO) and diesel range organics (DRO) *via* catalytic cracking [2–7]. Idem et al. [5] used canola oil as a model to determine the effect of different catalytic properties such as acidity, basicity, crystalline structure, and pore size on cracking reactions. They determined that the important factors for producing a high yield of oil from catalytic cracking of canola oil to liquid product were the catalyst crystalline structure and pore sizes. Their experimental design could not determine the effect of acidity on product distribution.

In other studies, a mixture of fatty acids was converted into gasoline, kerosene, diesel, and gaseous products using microporous, mesoporous, or composite catalysts [6]. For composite catalysts, conversion of the fatty acid mixture increased as alumina was added to the mesoporous mixture. Relatively large pore mesoporous catalysts resulted in higher selectivity toward diesel. In contrast, the liquid product generated using relatively small pore catalysts showed higher selectivity toward gasoline.

The present work seeks to establish fundamental information on the cracking of plant, animal, and microbial oils by reacting model compounds over a model, Bronsted acid catalyst. This paper focuses on the homogeneous catalytic cracking of oleic and palmitic acids, major components of plant and animal oils, using the superacid trifluoromethanesulfonic acid (triflic acid). These two organic acids were chosen as models of the major components in plant and animal oils. For example, oleic acid, or *cis*-9-octadecenoic acid, is an 18-carbon fatty acid with a symmetrically placed double bond. Palmitic acid, or hexadecanoic acid, is a 16-carbon saturated fatty acid. The free fatty acid content of olive oil is 83 and 8% [8], canola oil is 60 and 5% [9], oleaginous yeasts 52 and 24% [10], soybean oil 23 and 8% [11], and sewage sludge oils 30 and 36% [12], of oleic acid and palmitic acid, respectively. The choice of model catalyst is dictated by the need to examine the effect of Bronsted acidity alone on the cracking of the organic acids in the absence of thermal cracking. Thus, we chose an acid that could be used at sufficiently low temperatures so as to suppress thermal cracking. Triflic acid is 100 times more acidic than fuming sulfuric acid with a Hammett acidity of −14.1 [13]. Superacids are capable of catalyzing a host of organic chemical reactions, such as isomerization, cracking, alkylation, acylation, and carboxylation at temperatures near room temperature [14,15]. The use of a liquid acid as a model catalyst eliminates the effects of pore sizes and solid crystallinity upon the reactivity results.

The objective of this research was to determine if the Bronsted acidity of triflic acid was capable of cracking and decarboxylating oleic and palmitic acid. In most experiments, evidence of fatty acid cracking was collected by determining equilibrium products. Positive results from triflic acid reactions do not assure cracking and decarboxylation of oleic acid *via* the Bronsted and Lewis acid sites present in zeolites. However, negative results with the super acid would suggest that the intrinsic acidity of zeolites may not be capable of achieving cracking and/or decarboxylation. To our knowledge, the effect of acidity on the product distribution of cracking oxygenated feedstocks using zeolites has not been isolated from thermal cracking, crystalline structure, and pore size.

2. Experimental section

2.1. Chemicals

All chemicals (oleic acid, palmitic acid, triflic acid, and solvents) were obtained from Sigma–Aldrich at their highest available purity and were used without further purification. All gasses (argon, hydrogen, air, and helium) were of ultra high purity grade.

2.2. Reactions

Extreme care was taken to avoid skin contact or inhalation of triflic acid. All reactions were completed in a VAC glove box under an atmosphere of argon to reduce hazardous exposure and to exclude oxygen and water as unwanted reactants. The reaction vessels were 60 ml vials that could be capped with a mini-inert valve for gas sampling. Reactions for this study were conducted at 25 °C and 100 °C for palmitic acid and 0 °C for oleic acid. Reaction completion was ensured by conducting reactions overnight, which yielded the same results as those ran for 6 h. Triflic acid was first added to a stirred vial followed by oleic acid or palmitic acid. A 10:1 molar ratio of triflic acid to fatty acid was needed to obtain a homogenous mixture between the two components. The reactions were quenched with sodium bicarbonate water (5%, m/v) that was added until bubbling stopped, indicating complete neutralization of protonated species.

After quenching of the reactions, the vials were removed from the glove box and prepared for analysis. Sample preparation included extraction with methylene chloride of the products and removal of solvent using a rotary evaporator. Methylation, required for GC analysis, was conducted by reacting a 6:1 molar ratio of methanol to initial oleic acid content using 375 mM sulfuric acid in methanol at 60 °C for a minimum of 6 h. All other analytical procedures were conducted using non-methylated samples.

2.3. Analytical

2.3.1. NMR spectroscopy

Proton and carbon NMR spectroscopy were conducted on the methylene chloride extract (organic phase) of reaction mixtures and the aqueous material collected from the aqueous quenching step. The NMR instruments used in this study are located in the NMR Facility at Mississippi State University. The proton NMR samples were analyzed on an AMX 600 (MHz) Bruker system. The carbon NMR samples were analyzed on an AMX 300 (MHz) Bruker system. Methylene chloride was removed from the organic phase using a rotary evaporator. The solvent-free sample was then diluted using deuterated chloroform with 0.05% (v/v) TMS (tetramethylsilane) as internal standard. Deuterium oxide with 1.0% (v/v) DSS (2,2-dimethyl-2-silapentane-5-sulfonate) internal standard was added to the aqueous samples for NMR testing. All NMR spectra were collected at room temperature and

ambient pressure. Spectral analysis was made using MestRec software.

2.3.2. Infrared spectroscopy

Liquid aliquots of both the organic extract and aqueous samples were scanned using a Perkin Elmer (Spectrum 100) Fourier transform spectrometer with a deuterated triglycine sulphate detector. Spectral resolution was 4 cm^{-1}. The organic extract was first concentrated to dryness using a rotary evaporator before droplet-sized aliquots were placed onto the diamond window of the spectrometer. The aqueous samples, obtained from the reaction quenching step, were brought to a pH ~7 using sodium bicarbonate to prevent damage to spectrometer from highly acidic samples.

2.3.3. Gas chromatography/mass spectrometry

Extracts were analyzed by GC/MS using a Varian 3600 GC equipped with a Varian 2000 ion trap mass spectrometer. The extracts were derivatized with H_2SO_4 in methanol, as described above, to produce methyl esters for chromatographic analysis. Both electron impact ionization (EI) and chemical ionization (CI)) were used for product characterization. A splitless injector operated at 280 °C was used. The separations were obtained using an Rtx-5MS column (30 m × 0.25 mm, with a 0.25 μm film) manufactured by Restek. The oven was programmed with an initial temperature of 50 °C, held for 3 min and was then ramped to 150 °C at 10 °C/min, then ramped to 190 °C at 1°/min, and finally ramped to 280 °C at 10°/min and held for 2 min. The carrier gas was helium utilizing the Built in Purifier, BIP® (Air-Gas, Radnor, PA), and the chromatographic system utilized the NIST library to aid in compound identification. The multiple peaks from the total ion chromatograms were identified using CI spectra to determine molecular weight. Quantitation of fatty acid isomers was performed while in EI mode using calibration curves for straight-chain saturated fatty acids obtained from standard compounds. Quantitation of compounds was achieved using the Supelco FAME-37 mix, which contains saturated and unsaturated straight-chain fatty acid methyl ester compounds. It was assumed that the peak observed in the product at the retention time of each saturated straight-chain standard was the straight-chain fatty acid. Estimation of branched-chain fatty acid isomers was made by assuming the response of the branched isomers was the same as the corresponding straight-chain fatty acids.

3. Results and discussion

In the case of palmitic acid, there appears to be no change upon reaction with triflic acid at either 25 °C or 100 °C reaction temperatures. None of the analytical techniques employed indicated otherwise.

Reactions for NMR and FTIR analysis were allowed to run to completion. Proton NMR analysis of oleic acid indicated vinyl protons (5.34 ppm chemical shift) and allylic protons (2.01 ppm). Analysis of the extract of the organic phase, post-reaction (Fig. 1) indicated a loss of both vinyl and allylic protons; thereby, indicating saturation of the double bond. The absence

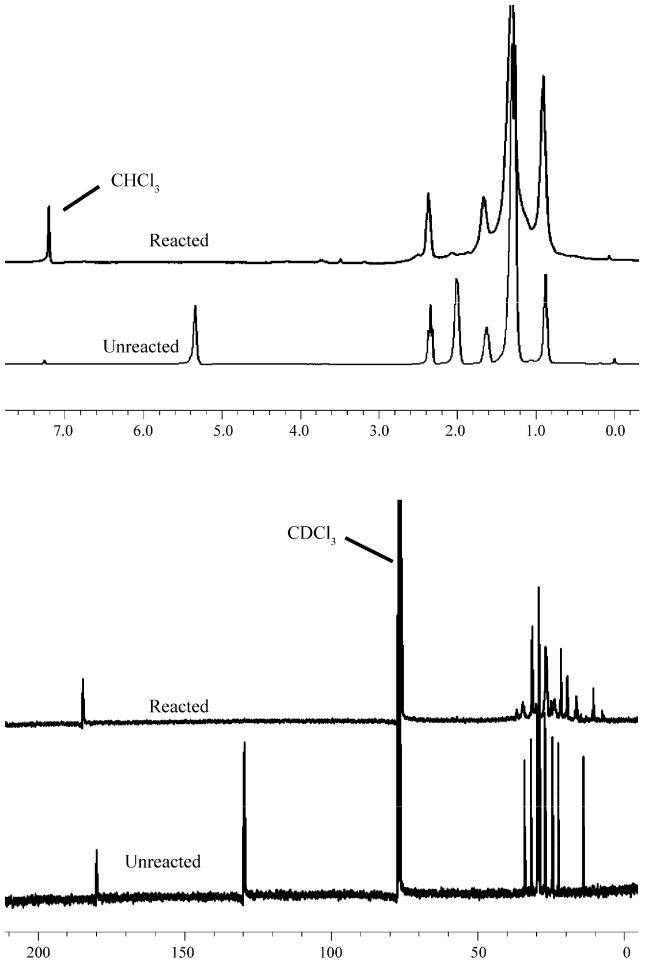

Fig. 1. (Top) ^{1}H NMR of oleic acid; (bottom) ^{13}C NMR of oleic acid. Reactions for NMR analysis were allowed to run to completion.

of vinyl carbons was confirmed with ^{13}C NMR analysis. The peak at 180 ppm indicates the presence of the carbonyl group of the carboxylic acid in both the starting material and the products. GC/MS results show that a multitude of fatty acid methyl esters of varying molecular weights were produced. This is also supported by ^{1}H NMR (Fig. 1) data where the relative ratio of the CH_3 band at 0.87 ppm of the proton spectra is about 2:1 for reacted versus unreacted oleic acid, which suggests an increase

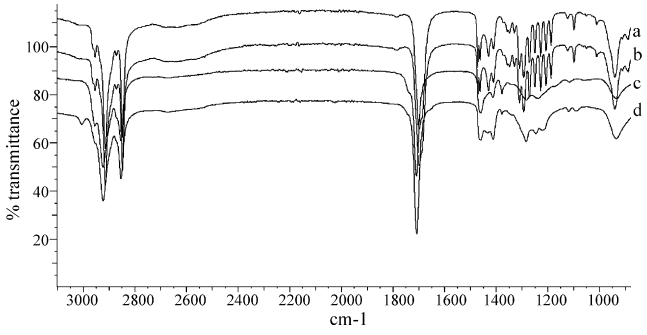

Fig. 2. FTIR analysis of unreacted/reacted fatty acids: (a) palmitic acid reacted to completion at 25 °C; (b) unreacted palmitic acid; (c) oleic acid reacted to completion at 0 °C; (d) unreacted oleic acid.

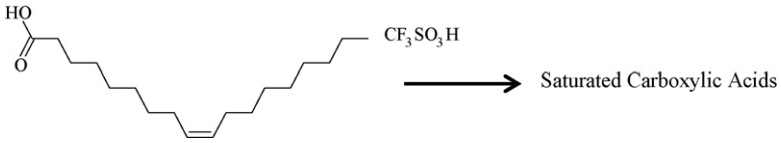

Fig. 3. Reaction of oleic acid with triflic acid as suggested from the NMR and FTIR analysis (reaction temperature 0 °C).

in the number of methyl groups, probably due to branching along the carbon chain. In the FTIR spectrum (organic phase), the band at 1710 cm^{-1} (Fig. 2) is consistent with the carbonyl bond of a carboxylic acid. The well-defined bands between 2800 and 3100 cm^{-1} are due to C–H stretching within the aliphatic molecule with weak O–H absorption from the carboxylic acid, which is consistent to the spectra for hexadecanoic acid [16]. An interesting feature of the NMR spectra is the lack of aromatic resonances between 6 and 8.5 ppm in the ^{1}H NMR spectra and between 120 and 160 ppm in the ^{13}C spectra.

These results suggest that the Bronsted acid reacts with long chain unsaturated fatty acids at the double bonds (Fig. 3). Aqueous samples from the aqueous, quenching step showed no evidence for compounds other than inorganics, as confirmed by NMR and FTIR analysis of these samples.

Results obtained from GC/MS (Figs. 4 and 5) are consistent with those from NMR and FTIR indicating the presence of a multiplicity of saturated fatty acids. CI mass spectral data (Fig. 6) yielded molecular weight information. Reaction products were characterized using mass spectrometry according to molecular weight and structural type using standards from Sigma–Aldrich and with the aid of the MS software. Samples were prepared for mass spectral analysis by quenching the reaction after only 10 min so as to minimize secondary reactions. The only qualitative difference between the shorter term reaction and longer runs was the absence of the unreacted oleic acid at longer reaction times. The peak distributions for the remaining peaks were very similar (Figs. 4 and 5).

The cracking products from oleic acid (Figs. 4 and 5) yielded a complex mixture, mostly fatty acids, that has been identified within the liquid organic product. The compounds identified were C9, C10, C11, C12, C13, C14, C16, and C18 fatty acids. As indicated from the NMR and FTIR data, the fatty acids present in the product were saturated, and according to the NMR and GC/MS, many branched-chain isomers were present in the products (Fig. 7).

It appears that in all cases that the carboxylic acid group was unchanged by the reaction, and the logical first step in the reaction is protonation of the oleic acid by the triflic acid at the carbon–carbon double bond. Then, the position of the charge on this protonated intermediate probably migrates away from the carboxylic acid end of the molecule. This migration trend is supported by the lack of fatty acid compounds less than nine carbons length indicating that the smallest fatty acid (i.e. C9:0) results from cracking while the double bond is in its initial position. Longer chain fatty acids result as the intermediate charge migrates away from the carboxylic acidic end before cracking.

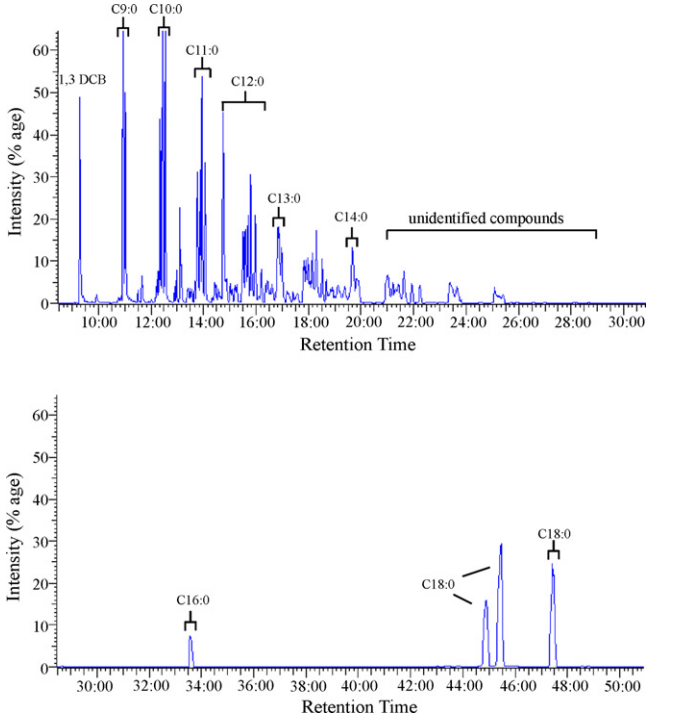

Fig. 4. GC/MS total ion chromatogram (chemical ionization) for oleic acid subjected to 10 min triflic acid reaction. Chromatograms are shown for retention times 8–30 min (top) and out to 48 min (bottom).

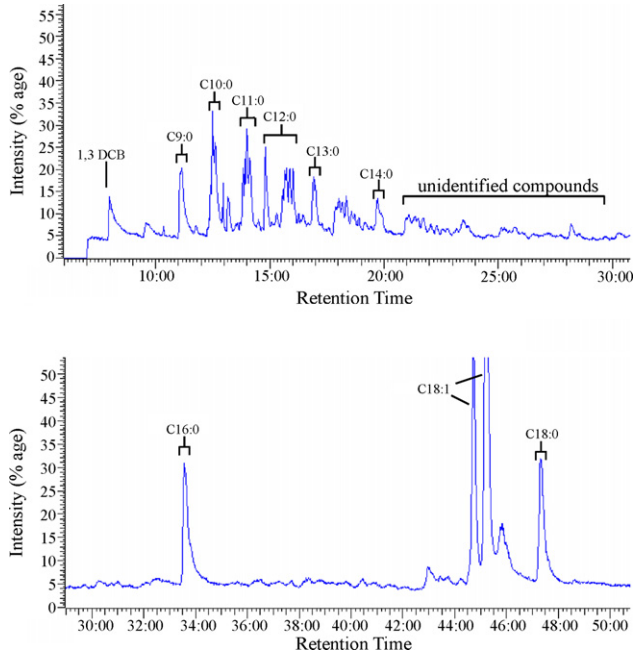

Fig. 5. GC/MS total ion chromatogram (electron impact ionization) for oleic acid subjected to 10 min triflic acid reaction. Chromatograms are shown for retention times 8–30 min (top) and out to 48 min (bottom).

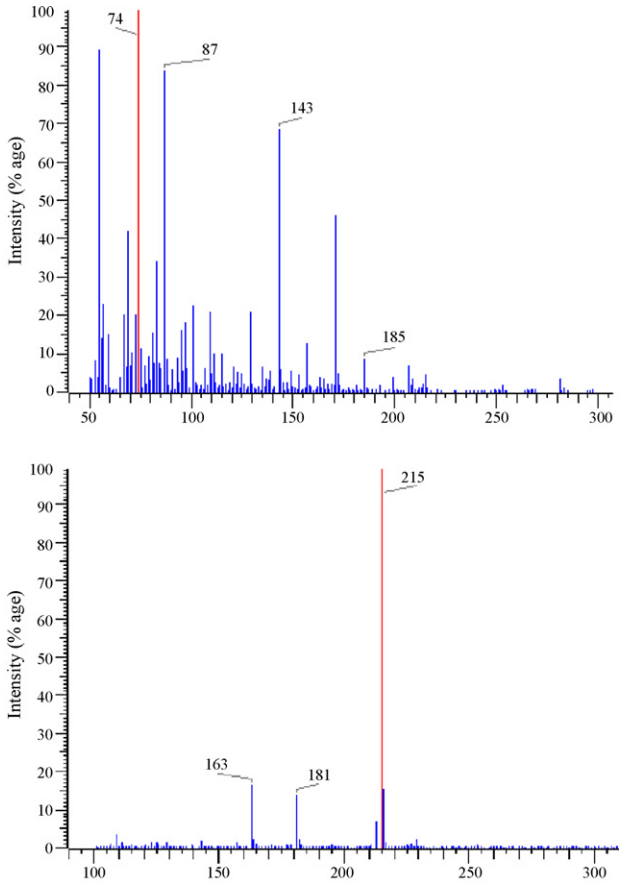

Fig. 6. Example of mass spectral data: electron impact ionization (top) and chemical ionization (bottom) for C12:0. The $(m+1)$ ion from CI is 215, corresponding with that of dodecanoic acid methyl ester.

Table 1 shows the fatty acids quantified using standards and the total fatty acids for each molecular weight group (Fig. 7) that have been identified using mass spectral analysis. To quantitate the branched compounds, peak areas were compared to that of

Table 1
Product distribution for oleic acid reacted to completion based on 15 mg/ml of methylated products dissolved in hexane

Compound name (scientific)	Compound shorthand	Straight-chain concentration (mg/ml)	Total isomeric concentration (mg/ml)
Nonanoic acid	C9:0	3.073	3.073
Decanoic acid	C10:0	0.361	1.115
Undecanoic acid	C11:0	0.238	1.991
Dodecanoic acid	C12:0	0.480	3.354
Tridecanoic acid	C13:0	0.307	1.572
Tetradecanoic acid	C14:0	0.452	0.412
Hexadecanoic acid	C16:0	0.876	0.876
Octadecanoic acid	C18:0	0.193	0.713
Total			13.106

Concentrations were derived from EI spectra with identifications made from CI spectra.

the corresponding fatty acid straight-chain compound. The mass of organic liquid product accounts for 83% of the original mass of the oleic acid, and the total identified products were 87% of the methylene chloride extractable mass.

Fig. 7 shows one possible reaction scheme for the cracking of oleic acid. Step 1 is the protonation of the double bond. Step 2 is the migration of the charge by hydrogen transfer. Step 3 is the cracking of the molecule into shorter chain carboxylic acids and hydrocarbon gases. The reaction shown is the production of hexadecanoic acid (C16:0) and ethylene.

The chemical reaction that appears to be occurring is the loss of two carbons from the oleic acid molecule. This is seen from the formation of fatty acid carbon chain with an even number of carbon atoms. Odd numbered fatty acid chain lengths are probably formed from methyl shifts occurring before the β-scission. It is speculated that the formation of stearic acid (C18:0) comes from hydride abstractions.

The results presented for the cracking of oleic acid are consistent with the cracking of olefins in which the formation of

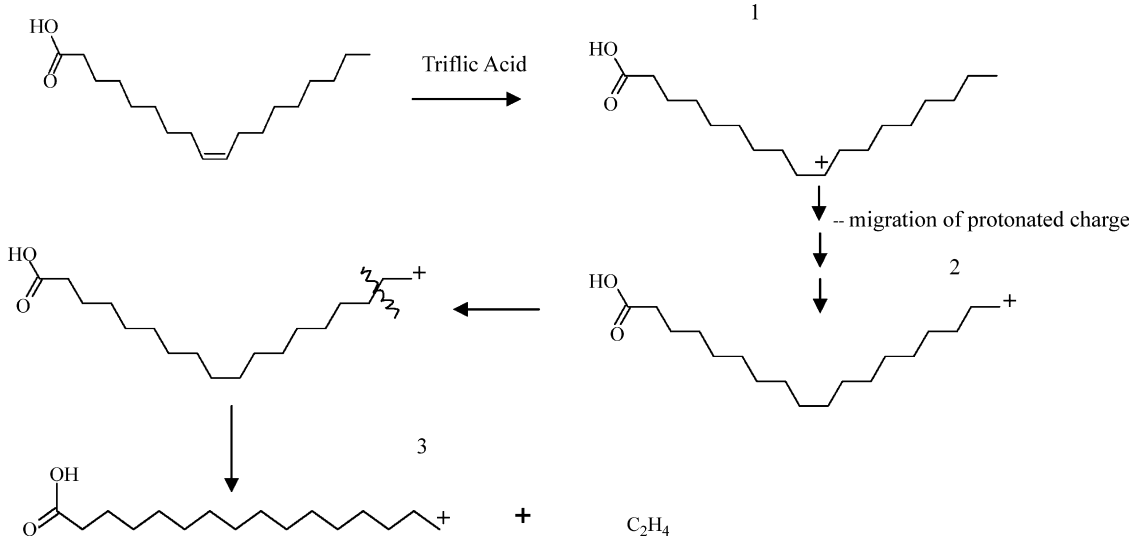

Fig. 7. Proposed reaction chemistry for the cracking of oleic acid into saturated, shorter chain carboxylic acids. This particular example shows the production of hexadecanoic acid and ethylene.

saturated products proceeds *via* hydrogen transfer [17]. Likewise, olefins undergo series of hydrogen and methyl shifts due to the formation of carbenium ions producing secondary and tertiary carbocations. These carbocations experience double bond migrations, controlled by thermodynamic stabilities, producing olefinic cations before undergoing β-scission. Similarly to our work, the source of hydrogen in olefinic cracking reactions is not fully understood. It is suggested that H^- is abstracted from aromatic compounds that are produced during the cracking reaction [17–19].

4. Conclusions

Strong Bronsted acids are capable of cracking unsaturated fatty acids into smaller carbon chain fatty acid molecules that can contain branched isomers. However, these strong acids did not crack saturated fatty acids. This suggests that acids with Bronsted activities attack the fatty acid molecule at the carbon–carbon double bond site. Protonation of the molecule results in a series of hydride shifts and methyl shifts along with β-scissions producing a series of branched-chain fatty acid molecules. Neither fatty acid, saturated or unsaturated, could be decarboxylated using triflic acid in the liquid phase.

Acknowledgements

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