Ketonization kinetics of stearic acid

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On ketonization kinetics of stearic acid

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Abstract

Ketonization of stearic acid was investigated in a stainless steel reactor under catalyst-free conditions. The reaction was selective towards formation of 18-pentatriacontanone following quasi-zero kinetics. A reaction mechanism explaining such behaviour is discussed.

Key-words: ketonization, thermal, kinetics, stearic acid

1. **INTRODUCTION**

There is a growing interest in the recent years in biomass as a source of chemicals and fuels [1-5] having a potential to replace at least partially the fossil fuel consumption. One of the interesting feedstock, are derivatives of fatty acids (ca. C_{16}-C_{22}), for example, esters or triglycerides [6]. The non-branched structure of the fatty acid chain being close to diesel fuel components is an advantage, which has been exploited commercially for production of rather low- value added products – fuels. Another option for the transformation of this feedstock into more valuable products is connected to increasing the chain length by ketonization or ketonic decarboxyltion [7] of fatty acids with a release of CO_2 and water forming a corresponding ketone. Figure 1 displays the reaction scheme for ketonization for stearic acid as an example.
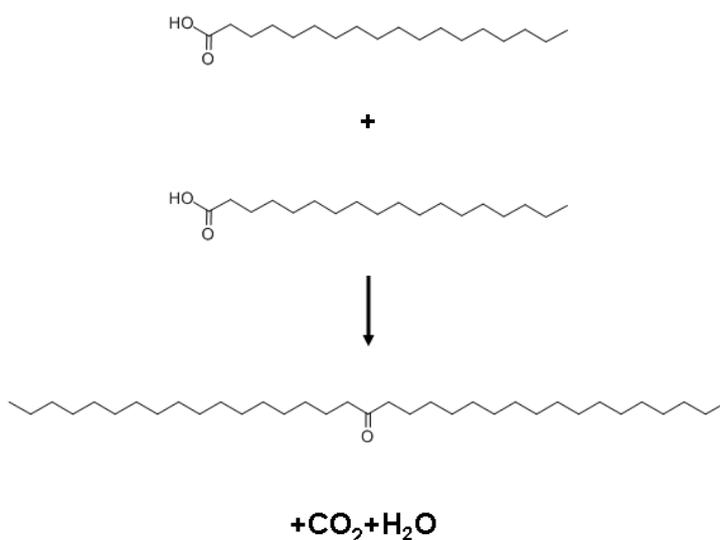
FIGURE 1. Ketonization of stearic acid for production of 18-pentatriacontanone.

The formed ketone can be further hydrogenated giving a hydrocarbon which is in the range of lube base oils [8]. The paraffinic structure of triglycerides and their low sulphur content could allow their utilization for production of Group II and Group III lube base oils [9].

Ketonization has been mainly studied using shorter cartboxylic acids, such as for example pentanoic acid [7]. Various metal oxides as catalysts have been utilized giving first by

abstraction of an α-hydrogen enolate species on the basic sites followed by further reaction with another molecule of the acid [7] on the Lewis acid sites. Finally β-ketoacids formed by these steps are decomposed giving the final products.

Ketonization of fatty acids is less studied compared to the shorter chain counterparts [10-16]. Application of various catalysts such as iron, nickel and manganese oxides with subsequent hydrogenation of the formed ketone was described in the patent literature as early as in 1939 [10]. Magnesia was also applied for the same purpose of ketonization with higher fatty acids in the 1940s [11]. MgO was utilized more lately with lauric acid as a substrate resulting in high yields [12]. Recently sunflower oil and stearic acid methyl ester were used as starting materials in the presence of zirconia [13]. The reactions are typically performed in the liquid phase at 350-400°C [10-16].

Interestingly enough, decarboxylation of fatty acids can proceed not only over Fe, Ni or Mn oxides, but even thermally or more correctly on the walls of metallic reaction vessels acting as catalysts [10]. In order to access the role of this background reaction which is often omitted in the literature on ketonic decarboxylation of fatty acids, the current work the liquid-phase ketonization of C18 carboxylic acid (stearic acid) was applied in a stainless steel batch reactor.

2. EXPERIMENTAL

Reagent grade stearic acid of 95% purity, dodecane solvent of over 99% purity, and 18-pentatriacontanone were purchased from Sigma-Aldrich.

The ketonization experiments were carried out under argon (99.999%, AGA) in a pressurized 500 ml stainless steel reactor from Autoclave Engineers, which was equipped with an electrical heating jacket, a cooling coil, an inlet line containing a 5 μm filter, and an impeller.

The temperature was measured via a thermocouple and the heating jacket surrounding the reactor was automatically controlled with a Brooks instrument. The reactor outlet was equipped with a spring valve to prevent the pressure from rising because of CO_2 and H_2O formation. The reactor had a sampling line for measuring the concentration versus time dependence. Temperature and pressure data were registered by a PC. After the solvent (dodecane) was introduced into the reactor, the system was flushed with argon under stirring at 1000 rpm by increasing the argon pressure up to 5 bar and emptying the reactor from the gas in order to remove all remaining oxygen. This procedure was repeated three times. The reaction time was set-up to zero as soon as the reaction temperature was reached and the stirring was turned on. The stirring was kept at 1000 rpm in the experiments.

The course of the reaction was followed by withdrawing samples of negligible volume for gas chromatography (GC) analysis. A measured amount of tetradecane (99%, Aldrich) was added to each sample as the GC standard. Prior to the analysis, calibration was done by calculation of the response factors for tetradecane, stearic and 18-pentatriacontanone.

The samples from the reactor were silylated with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS), both supplied by Acros Organics, and analyzed by a gas chromatograph (GC, Hewlett Packard 5890 Series 2) equipped a 30 meter HP-5 column (inner diameter: 0.20 mm, film thickness: 0.11 μm), flame ionization detector (FID) unit, and an autosampler injector. Helium was used as a carrier gas. The column temperature was initially 80°C for 2 min after the injection, and thereafter, the temperature was increased from 80°C to 270°C with a rate of 7 °C/min, from 270°C to 290°C with a rate of 10 °C/min, and from 290°C to 320°C with a rate of 15 °C/min. Thereafter, the column temperature was held at 320°C for 40 min. The retention times for stearic acid and 18-pentatriacontanone were respectively 27.7 min and 60.2 min.

3. RESULTS AND DISCUSSION

The ketonization of stearic acid was investigated by conducting experiments at 350°C with different reactant masses. Figure 2 demonstrates the concentration versus time dependence in the ketonization of stearic acid to 18-pentatriacontanone under 10 bar argon pressure (Figure 2).

a)

b)
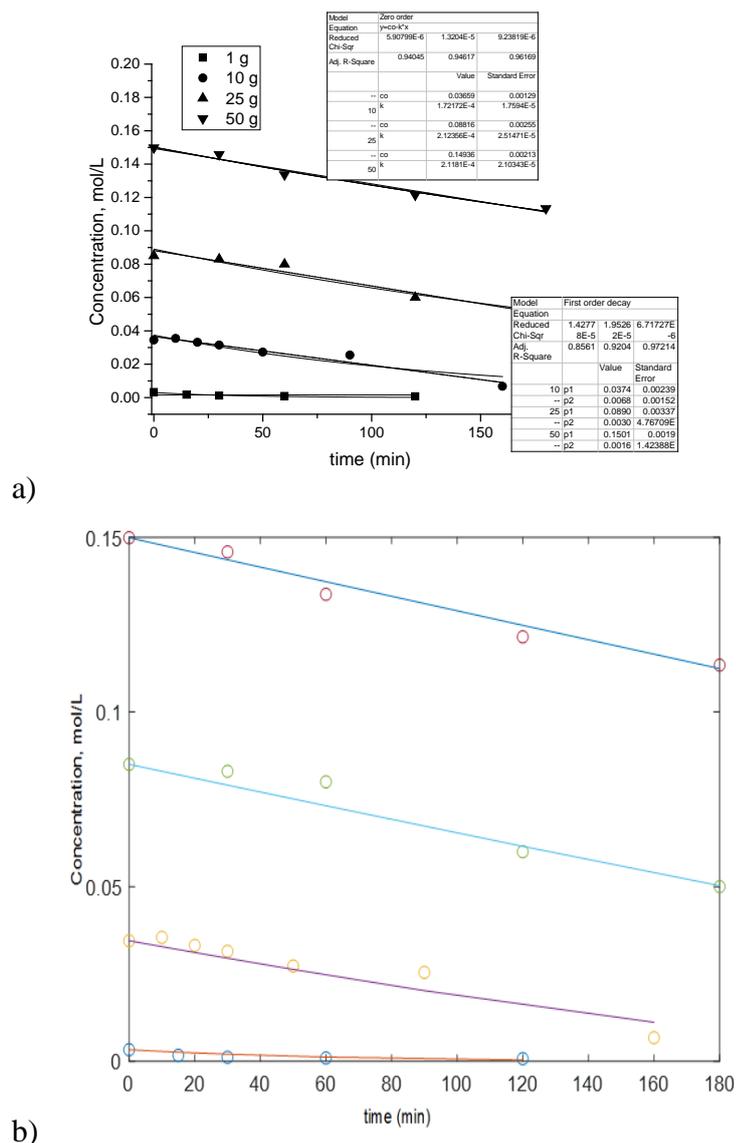
FIGURE 2. Ketonization of stearic acid with different reactant masses. Conditions: 300 ml dodecane, reaction temperature 350°C, 0 bar of argon, stirring rate: 1000 rpm. a) experiments with separate fitting using zero and first order kinetics, b) modelling for all data sets together using eq. (3).

No by-products were detected and the selectivity to the desired product was almost 100%. The gas chromatogram of the final sample for the reactant mass of 1 g is shown in Figure 3a. These results were confirmed by the spiking method when solutions of commercial sample of 18-pentatriacontanone and samples from the experiments in Figure 2 with 1 and 10 g were mixed with the mixtures analyzed by GC. Such analysis confirmed that just one product with a high molecular weight exists, which can be identified as 18-pentatriacontanone. Moreover, the GC-MS analysis and NMR (not shown) confirmed that the product is 18-pentatriacontanone.
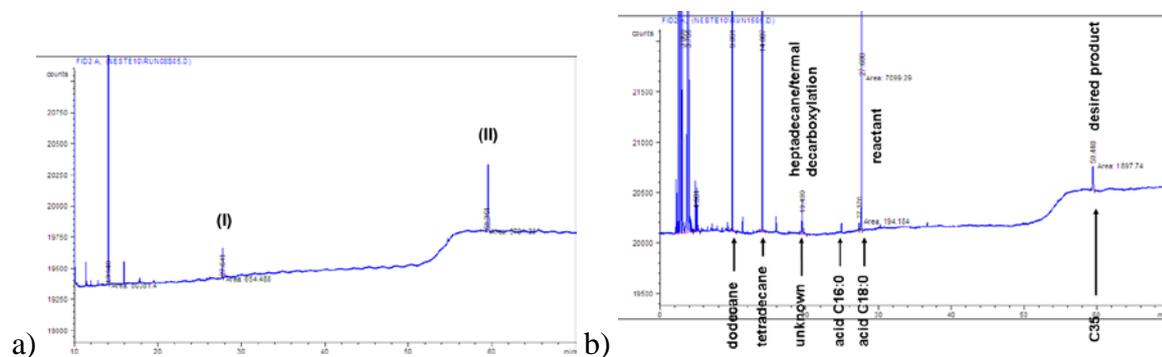

FIGURE 3. Gas chromatogram of product mixture in ketonization of stearic acid (I): Stearic acid; (II) 18-pentatriacontanone. Conditions: dodecane: 300 ml, reaction temperature: 350°C, pressure: 10 bar of argon, stirring rate: 1000 rpm, stearic acid mass: a) 1 g, b) 25 g.

On the contrary, from the gas chromatogram of the last sample from the experiment with the reactant mass 25 gram shown in Figure 3b it can be concluded that besides ketonization to a certain extent also decarboxylation of stearic acid to heptadecane occurred.

Formation of the by- products was even more visible for an experiment conducted with 100 gram of stearic acid as a reactant in 200 ml of dodecane at 365°C under 10 bar of argon for 96 hours in order to test a higher reactant concentration, longer reaction time, and elevated temperature. Besides the desired product 18-pentatriacontanone with the mass yield of 10.3 wt-% (calculated excluding solvent) and unconverted stearic acid (14.2 wt%), also heptadecane resulting from thermal decarboxylation of stearic acid was present in substantial

quantities (47.8 wt-% heptadecane). Some other products could be also visible (Figure 4) confirming that higher temperatures and longer reaction times gave a broader product distribution.
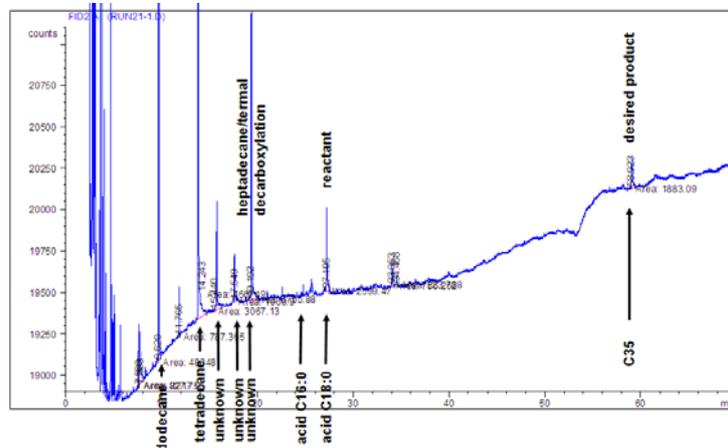
FIGURE 4. GC of the final mixture from ketonization of stearic acid. Conditions: Stearic acid: 100 g, dodecane: 200 ml, reaction temperature: 365°C, pressure: 10 bar of argon, reaction time: 96 h, stirring rate: 600 rpm.

To further explore the influence of the temperature, ketonization of stearic acid was tested at 400°C. Figure 5 displays the concentration dependences of stearic acid *vs* time for the lowest reactant amount (1 g) at 400°C and for comparison at 350°C showing that there was no influence of the reaction temperature.
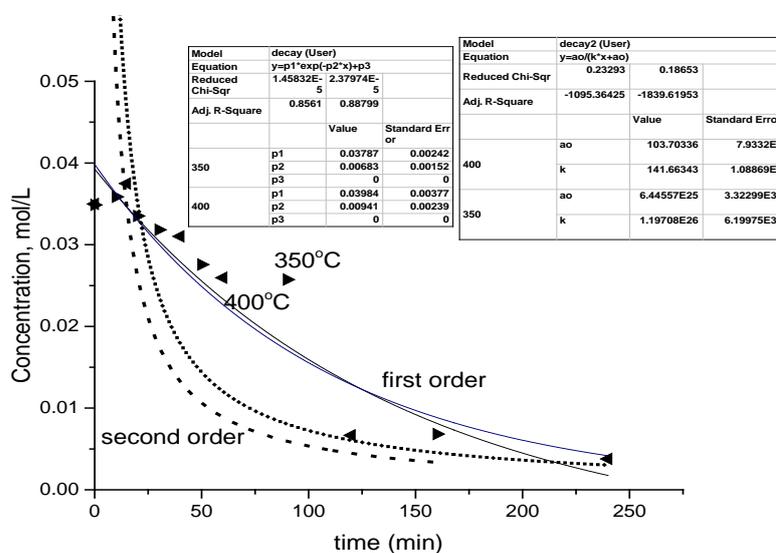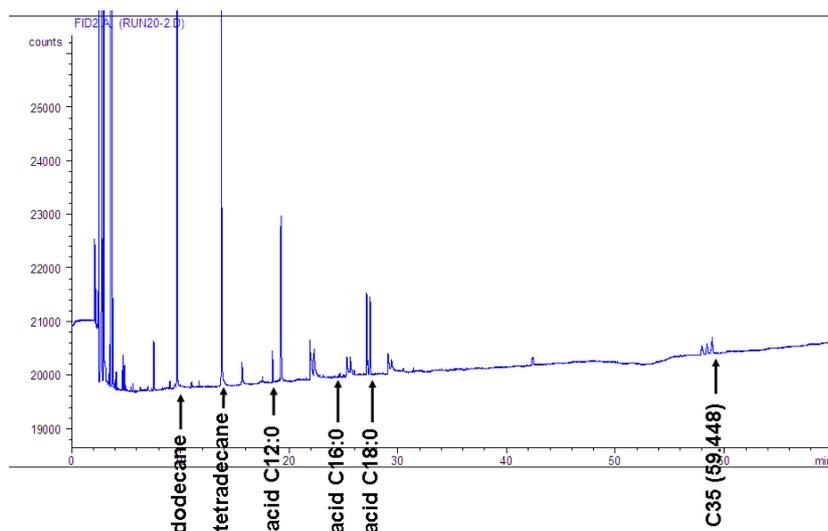
FIGURE 5. Thermal ketonization of stearic acid. Conditions: stearic acid mass: 1 g, dodecane: 300 ml, reaction temperature: 350°C and 400°C, pressure: 10 bar of argon, stirring rate: 1000 rpm.

In order to elucidate whether other fatty acids can undergo ketonization without any heterogeneous catalysts, an experiment was done using 5 gram of lauric acid and 20 gram of stearic acid as reactants at 350°C in 200 ml of dodecane solvent under 10 bar Ar for 24 hours reaction time. Clearly three peaks are visible in Figure 6 at the retention time of ca. 60 minutes. Some unassigned peaks in Figure 6 are related to impurities in the solvent and the reactants. For example, the reactant stearic acid contained some traces of palmitic acid and that reaction product thus contained some traces of 16-tritriacontanone.

FIGURE 6. Gas chromatogram of the final mixture from ketonization of stearic acid in the presence of lauric acid. Conditions: Lauric acid: 5 g, stearic acid: 20 g, dodecane: 200 ml, reaction temperature: 350°C, pressure: 10 bar of argon, reaction time: 24 h, stirring rate: 1000 rpm.

It is reasonable to speculate that they besides 18-pentatriacontanone also products of lauric acid homo-ketonization and a cross- ketonic decarboxylation of lauric and stearic acids were formed.

Heterogeneous catalytic ketonization of short-chain carboxylic acids is often considered as a reaction sequence comprising a second order reaction of adsorbed acids. It was interesting to check whether the second order kinetics *per se* can explain the observed concentration vs time dependencies. The data fitting results for the lowest reactant concentration are presented in Figure 5 clearly illustrating that the second order kinetics clearly fails to explain the experimental observations. The discrimination between the first and zero order kinetics is less apparent for experiments carried out with higher substrate concentrations. Figure 2 shows a comparison between data fitting for different reaction orders not allowing a direct discrimination between rival models based on just the quality of the fit. Interestingly enough for the zero order kinetics, the rate constant was independent on the initial substrate loading being close to 2×10^{-4} mol/l min. On the contrary, the first order rate constant displayed substantial deviations at different concentrations, which contradicts the basic notion of a rate constant.

Mechanistic aspects of ketonization have been addressed in the literature [15-19] and also discussed from the viewpoint of kinetics. For example, decarboxylative coupling of C5 acid into 5-nonanone was studied over CeO_2-ZrO_2 in an inert gas [19] showing changes in the reaction order from second to zero as the partial pressure was increasing.
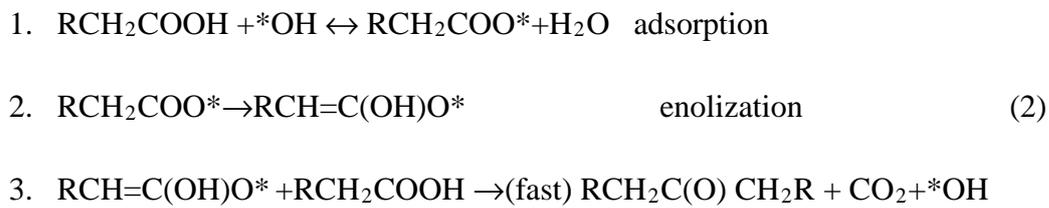
Such observations can be rationalized by assuming quasi-equilibrium adsorption of the acids on the basic sites and water and carbon dioxide on acidic sites with a bimolecular reaction of adsorbed acids as a rate-determining step. In ref. [19] the kinetic equation for the reaction rate was proposed

$$r = \frac{k \cdot P_{acid}^2}{(1 + K_{acid} \cdot P_{acid})^2 (1 + K_{H2O} \cdot P_{H2O} + K_{CO2} \cdot P_{CO2})^2} \qquad (1)$$

where r is the reaction rate, k is the rate constant, K_{acid}, K_{H2O}, K_{CO2}, P_{acid}, P_{H2O}, P_{CO2} – denote adsorption constants and partial pressures of carboxylic acid, carbon dioxide and water, respectively. The model obviously can account for changes in the reaction order from second

to zero order with an increasing acid concentration. At the same time, our experimental data do not comply with the second order kinetics at the lowest stearic acid concentration.

An alternative mechanism for the heterogeneous catalytic ketonization [16] involves first adsorption of the acid on hydroxylated surfaces eventually giving an adsorbed enolized carboxylate species. The latter can undergo a nucleophilic attack to another adjacent carboxylate forming a β-ketoacid, which then decomposes to a ketone and CO_2. The mechanism of this can pathway can be presented as

1. $RCH_2COOH + {}^*OH \leftrightarrow RCH_2COO^* + H_2O$ adsorption

2. $RCH_2COO^* \rightarrow RCH=C(OH)O^*$ enolization   (2)

3. $RCH=C(OH)O^* + RCH_2COOH \rightarrow (fast)\ RCH_2C(O)\,CH_2R + CO_2 + {}^*OH$

where ${}^*OH$ is a hydroxylated catalyst surface site or the walls of the reactor as in the current case. Apparently the last step is a complex one comprising several elementary steps. The kinetic expression for this reaction mechanism is well-known [20]

$$r = \frac{\omega_1 \omega_2}{\omega_1 + \omega_2 + \omega_{-1}} C_{cat} = \frac{k_{+1}k_{+2}C_{acid}}{k_{+1}C_{acid} + k_{+2} + k_{-1}C_W} C_{cat} =$$

$$= \frac{\dfrac{k_{+1}k_{+2}}{k_{+2} + k_{-1}C_W} C_{cat}C_{acid}}{\dfrac{k_{+1}}{k_{+2} + k_{-1}C_W} C_{acid} + 1} = \frac{k' C_{acid}}{k'' C_{acid} + 1} \tag{3}$$

where C_{cat} and C_W are the catalyst and water concentration respectively and ω_1, etc are frequencies of steps. It is apparently clear that eq. (3) can explain the shift of the reaction order in stearic acid from zero at high stearic acid concentrations to first when the stearic acid concentration is significantly low.

To confirm this modelling of the whole set of experimental data was performed using eq. (3) Kinetic modeling was performed using ModEst software [21]. The objective function (Q) for the residual sum of squares between the calculated and experimental data was minimized during the parameter estimation to search for the best-fit values using the

Levenberg−Marquardt algorithm implemented in the software. The error function is defined

as:

$$Q = \Sigma\left(C_{i,t\,(est)} - C_{i,t\,(exp)}\right)^2 \tag{4}$$

where i and t denote the components and the corresponding times, respectively.

The accuracy of the model description was determined with the R^2 – coefficient or degree of

explanation, which reflects comparison between the residuals given by the model with the

residuals of the simplest model, i.e. the average value of all data points. The R^2 value is given

by expression:

$$R^2 = 100 \frac{\left(y_{model} - y_{experiment}\right)^2}{\left(y_{model} - \bar{y}_{experiment}\right)^2} \tag{5}$$

The degree of explanation was 99.61%, the values of constants k' and k''were respectively

0.019 ± 0.0088 min^{-1} and 88 ± 45 l/mol. The results presented in Figure 2b clearly show that the

model is able to capture the experimental data in an excellent way.

4. CONCLUSIONS

Liquid- phase ketonization of stearic acid to 18-pentatriacontanone was studied in a 500 ml stainless steel reactor in the absence of of any catalyst. The desired product 18-pentatriacontanone was identified by several analytical techniques, such as GC, GC-MS and NMR of the end composition of the experiments and also by analysis of commercial 18-pentatriacontanone for comparison. Kinetic modelling was done, explaining the shift of the reaction order in stearic acid from zero at high stearic acid concentrations, when the sites on the reactor walls available for adsorption of stearic acid are mainly occupied, to the first one when the stearic acid concentration is significantly low and the fraction of available site is high.

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