Thermal Alteration of Oleic Acid in the Presence of Clay Catalysts with Co-Catalysts

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ABSTRACT

The effects of added co-catalysts on the clay catalyzed polymerization of oleic acid have been investigated. Heating oleic acid at 230 C for 3 hr with a clay catalyst gave a polymer fraction (dimer and trimer acids, 35% yield) and a monomer fraction (branched chain isomers of oleic acid, 27% yield) as the major products. The variation in yield between the polymer and monomer products was found to be dependent upon the co-catalyst used with the clay catalyst. For example, with both acidic and basic clays, polymer formation is favored (55% yield) in the presence of water and/or metal ions. In contrast, when Bronsted acids such as methanesulfonic or phosphoric acid are used as co-catalysts, the yield of branched monomer increased significantly (50%). Studies on the adsorption of oleic and Bronsted acids onto the clay surface showed that isomer formation is favored when both the oleic acid and the Bronsted acids are adsorbed onto the clay surface at selected molar ratios.

INTRODUCTION

The dimerization of polyunsaturated fatty acids or their esters using activated clays was first reported in patents by Johnston (1) and DeGroote (2). The clay catalyzed dimerization of monounsaturated fatty acids was described later by Barrett et al. (3). Subsequent to these reports, a number of articles have appeared describing possible improvements or modifications of the polymerization process which either increase the polymer yield or improve the dimer/trimer acid ratio (4-7). In practice, however, even under the most favorable conditions employed for the dimerization of monounsaturated fatty acids, a portion of the starting fatty acid does not polymerize. These unpolymerized fatty acids, commonly referred to as the monomeric fraction, are produced by a secondary reaction wherein the starting fatty acid is structurally modified and in this form is not polymerizable. Such structurally modified acids are formed as co-products in all methods of polymerizing unsaturated fatty acids.

In a series of detailed articles on the thermal polymerization of oleic acid in the presence of a montmorillonite clay, Den Otter (8-11) carried out a structure study on both the dimer and monomer acid fractions. For the dimer fraction a cyclic structure was proposed, whereas the monomer fraction was claimed to be comprised predominantly of normal and branched chain saturated acids. To account for these structures it was stated that disproportionation and chain branching were the major steps leading to dimer and monomer acid formation. In a later study by McMahon et al. (12), it was shown by GC-MS that the dimer acids obtained from the clay catalyzed polymerization of oleic acid had both cyclic and acyclic structures. The monomer fraction was found to be composed of stearic, octadecenoic and midchain monomethyl branched acids, both saturated and unsaturated.

Previous work from this laboratory (13) also demonstrated that the monomer fraction obtained from the clay catalyzed isomerization of methyl oleate and oleic acid retained a substantial portion of the original double bond content. The presence of chain branching and unsaturation in this monomer fraction also was established by means of a reductive ozonolysis-oxidation procedure. More recently we have shown (14) how changes in process parameters can alter the yields of the dimer and monomer fractions in the clay catalyzed polymerization of oleic acid. Aside from these latter studies, little attention has been directed toward improving the yields of the monomer fraction formed in the clay isomerization of oleic acid. This is surprising, because a facile method of preparation of these structurally modified fatty acids would be extremely important from both a practical and fundamental standpoint. Accordingly, this paper describes how co-catalysts can affect the yield distribution of the dimer and branched chain monomer fractions when oleic acid is heated in the presence of clay catalyst. The paper also covers an adsorption study of oleic acid onto the clay catalyst surface both in the presence and absence of co-catalysts to clarify and understand the results of the polymerization studies reported herein.

EXPERIMENTAL

Materials

Oleic acid (98%) was obtained from Applied Science Laboratories (State College, Pennsylvania). The clay catalysts used in this study were Clarolite T-300, Georgia Kaolin Company (Elizabeth, New Jersey), which is obtained by the acid leaching of subbentonite and Alabama Blue Clay, Union Camp Corporation (Princeton, New Jersey), a montmorillonite clay classified under the smectite mineral group. The acidity of the clays was determined by dispersing 1 g of clay in 5 ml of H_2O and measuring the pH of the supernatant: Alabama Blue Clay, pH = 7.86; Clarolite clay pH = 4.3. Moisture content of the clays was determined by heating the clay in a vacuum oven for 4 hr at 120 C and calculating % weight loss: Alabama Blue Clay, 12.5% moisture; the Clarolite clay, 11.5% moisture. Phosphoric acid (85%) and methanesulfonic acid were obtained from Fisher Chemical Company (King of Prussia, Pennsylvania). The methanesulfonic acid was distilled prior to use. Methyl esters were prepared by the boron trifluoride method (15).

Gas liquid chromatography (GLC) was conducted with a Hewlett Packard Model 7620 chromatograph equipped with dual flame ionization detectors. Methyl esters were separated on 8-ft × 1/8-in. silanized stainless steel columns packed with 7.5% EGA + 2% H_3PO_4 on 90/100 mesh Anakron ABS. Thin layer chromatography (TLC) was performed on Silica gel G plates (250 micron) obtained from Analtech (Newark, Delaware). Plates were developed with toluene: ether (95:5) and visualized by spraying with 50% H_2SO_4 and charring. A Perkin-Elmer model 720-B infrared spectrophotometer was used for IR analyses.

Methods

Oleic acid (120 g, 0.425 mole), clay catalyst (8 wt % of oleic acid), and co-catalyst (Table I) were placed into a l-liter stainless steel autoclave (Parr Instrument Company, Moline, Illinois) equipped with a stirrer and sampling tube. The vessel was evacuated and pressurized with nitrogen (30 psi) and heated to 230 C by means of an electric heating mantle equipped with a Versatronic potentiometer controller. The temperature was held at 230 ± 5 C and sampled (~15 g) hourly over the course of the reaction (Table I). At the end of the reaction (Table I) the reactor was cooled to ambient temperature, vented, methylene chloride (200 ml) was added and the reaction product filtered through Celite to remove the clay catalyst. The filtrate was washed with water (50 ml)

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TABLE I

Distribution of Products after Clay Treatment of Oleic Acid

Clay[a]	A		B		A		B		B		B	A		B		A		A		A[d]		A[d]	
Co-catalyst[b,c]	–		–		4.0 wt% H_2O		4.0 wt% H_2O		4.0 wt% H_2O 1.0 mol% LiOH		4.0 wt% H_2O 1.0 mol% LiCl	3.3 mol% H_3PO_4		3.3 mol% H_3PO_4		6.0 mol% CH_3SO_3H		4.0 wt% H_2O 3.3 mol% H_3PO_4		3.3 mol% H_3PO_4		16.5 mol% H_3PO_4	
time (hr)	2	3	2	3	2	3	2	3	2	3	2	3	5	3	5	3	5	1	2	4	6	4	6
Distillate (wt%)	66.0	64.9	74.9	71.0	44.0	43.9	44.7	45.4	39.8	41.5	41.7	69.9	67.7	88.1	79.4	71.8	68.7	70.5	65.7	81.9	80.0	~100%	
Straight chain	37.4	32.3	55.5	42.1	15.2	15.2	13.8	13.7	14.4	14.3	15.1	23.1	13.1	64.5	37.2	19.5	14.0	37.0	27.9	58.1	52.0	~100%	
C16:0 + C18:0	9.6	10.1	10.2	10.2	15.2	15.2	13.8	13.7	14.4	14.3	15.1	11.4	12.2	7.0	9.1	13.5	14.0	9.5	11.1				
C18:1	27.8	22.1	45.3	31.9	–	–	–	–	–	–	–	11.7	0.9	57.5	28.1	6.0	–	27.5	16.8				
Branched chain	24.6	28.4	18.0	26.9	27.8	27.7	29.4	30.2	23.9	25.7	25.1	39.8	47.5	19.6	36.2	45.3	47.6	29.5	32.6	16.8	20.9	trace	
γ-Lactone	4.0	4.3	1.4	2.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5	7.0	7.1	4.0	6.0	7.0	7.1	4.0	5.2	7.0	7.1	–	
Residue (wt%)	34.0	35.1	25.1	29.0	56.0	56.1	55.3	54.6	60.2	58.5	58.3	30.1	32.3	11.9	20.6	28.2	31.3	29.5	34.3	18.1	20.0	trace	

[a] A–Clarolite T-300 (moisture 12.5%) (pH = 4.30, g/5 ml H_2O). B–Alabama Blue clay (moisture 11.5%) (pH = 7.86, g/5 ml H_2O).

[b] Wt% against the weight of oleic acid employed.

[c] Mol% against the moles of oleic acid employed.

[d] Results are for dried clay. (Dried clays were obtained by heating in a vacuum oven for 4 hr at 120 C).

repeatedly until the pH of the water wash was neutral. The organic phase was dried over anhydrous Na_2SO_4, filtered, and the crude reaction product was isolated by removal of solvent in vacuo (Table I).

Analytical Procedure

A portion of the crude product (1 g) was esterified with BF_3-CH_3OH reagent. The γ-stearolactone content in the methyl ester products was measured by IR spectroscopy using a standard curve obtained from measurements of standard solutions containing 0 to 10% pure γ-stearolactone dissolved in pure methyl oleate.

The total reaction product was distilled in vacuo (0.3 Torr) until no further distillate fraction was obtained. The distillate (monomer fraction) and the residue (dimer fraction) were esterified with BF_3-CH_3OH reagent and analyzed by either TLC or GLC. The yield data for the monomer (distillate) and dimer (residue) fractions are reported in Table I as wt % of total product. The straight chain, branched chain monomer and γ-stearolactone content were calculated from the product of area % by GLC × wt of distillate.

Adsorption of Oleic Acid or Bronsted Acid onto Clay

Into a 100-ml Erlenmeyer flask equipped with a magnetic stirring bar were placed oleic acid (2 g) and methylene chloride (40 ml). The solution was stirred for 5 min and the initial acid concentration determined by titration of an aliquot with N/20 NaOH in methanol. The clay (2 g) was added to the flask, and the mixture was stirred for 1 hr at room temperature. After standing for 10 min, the final acid concentration in the clear supernatant was measured by titration. Oleic acid adsorption onto the clay was calculated as the difference between the initial and final acid concentration. Methanesulfonic acid adsorption onto the clay surface was determined by the procedure used for oleic acid. However, phosphoric acid adsorption onto the clay could not be measured by this method because of its limited solubility in methylene chloride. The adsorption of oleic acid and methanesulfonic acid onto the clay is shown in Figure 2.

The adsorption of oleic acid onto the clay in the presence of Bronsted acids was studied as follows: into a 100-ml Erlenmeyer flask was placed methanesulfonic acid or phosphoric acid in methylene chloride (40 ml) along with the clay (2 g). The mixture was stirred for 1 hr at which time oleic acid (4 g) was added, and the initial acid concentration was measured by titration. The mixture was stirred for an additional hour, and the final acid concentration was measured by titration. Oleic acid adsorption onto the clay was calculated as the difference between the initial and final acid concentration. The adsorption of oleic acid onto the clay in the presence of Bronsted acids is shown in Figure 3.

RESULTS AND DISCUSSION

Among the many papers which have reported improved methods for the polymerization of unsaturated fatty acids, it is stated that any type of clay can be used as the polymerization catalyst, provided that certain amounts of water and/or base are used as co-catalyst (3,8-11). In the present work we used two types of clay as catalyst, namely: a bentonite clay, an acidic 1:1 clay mineral, and a montmorillonite clay, a basic 2:1 clay mineral (16). Even though both clays contained a similar amount of water of hydration, we found that the conversion of oleic acid to isomer (branched monomer) and polymer products proceeded faster with the bentonite clay than with the montmorillonite clay without

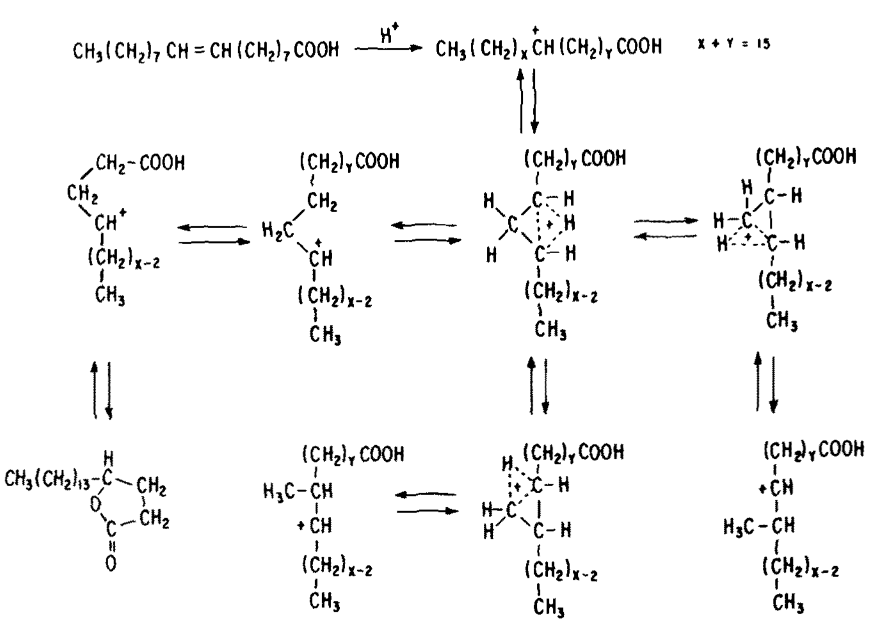

FIG. 1. Pathway for chain branching and γ-stearolactone formation.

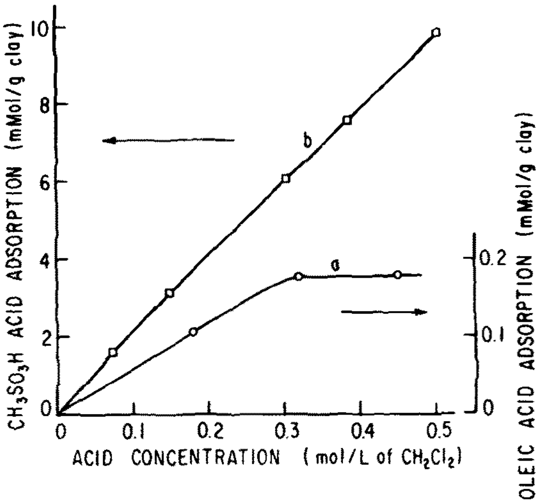

FIG. 2. a) Oleic acid adsorption onto bentonite clay ○. b) Methanesulfonic acid adsorption onto bentonite clay □.

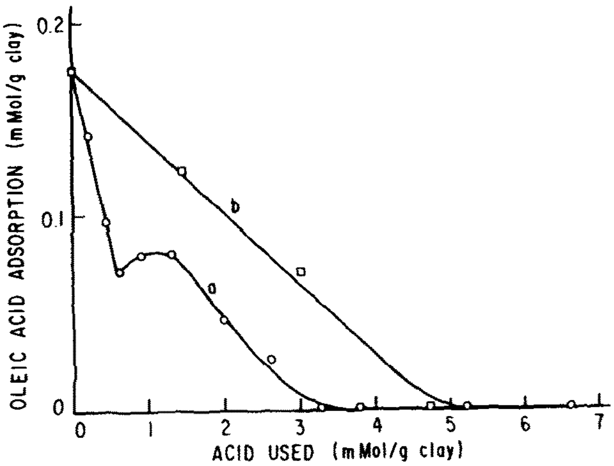

FIG. 3. Oleic acid adsorption onto bentonite clay in presence of Bronsted acids. a, Phosphoric acid; b, methanesulfonic acid.

any added co-catalysts. The final distributions of isomer and polymer products using the two clays are shown in Table I. As noted previously, the addition of water as a co-catalyst increased the rate of oleic acid disappearance for both the acidic and basic clays. More importantly, the yield of oleic acid dimer increased significantly with both clays from 35 to 55%, whereas the isomer product (branched-chain monomer) stayed constant at 28-30% (Table I). There was no significant difference in the distribution of other products between the acid and base clay catalyzed reactions. The addition of a small amount of base (LiOH) with the water also seemed to increase the yield of dimer product from the montmorillonite clay catalyzed reaction. However, the addition of LiCl with water also gave a similar increase in dimer yield (Table I). In both cases, the increase in dimer product resulted in a decrease of the isomer product (25% vs 30%). From these results it was unclear whether the base had an effect on the dimer yield or if the effect observed was due to the interpolation of lithium ion between the clay surfaces. The latter instance may be correct on the evidence that intercalation of tetraalkylammonium salts into the clay lattice structure also has resulted in excellent yields of oleic acid dimer (17). Further evidence for this was obtained when we employed $ZnCl_2$ as co-catalyst and obtained the same product distribution as with LiCl. As expected, the use of lithium hydroxide or lithium chloride with the acidic bentonite clay resulted in a decrease in the rate of oleic acid consumption. In these instances, the reaction required almost 8 hr to attain the product distribution shown in Table I, when just water alone was used as the co-catalyst.

On the other hand, Bronsted acid addition resulted in a significant improvement of the isomer yield together with increased amounts of γ-lactone formation when the acid clay was used as the catalyst. For example, with phosphoric acid as a co-catalyst with the acid clay, the isomer, polymer and γ-lactone yields were 39.8%, 30.1% and 7.0%, respectively, after 3 hr reaction time, whereas the yields were 28.4%, 35.1% and 4.3% in the same order in the absence of a co-catalyst. Since the isomer and γ-lactone products are most probably formed through migration of carbocation ions along the aliphatic chain followed by an intramolecular cyclization, and/or chain branching as depicted in Figure 1, it is assumed that Bronsted acids accelerated these reactions and that the intermolecular reaction leading to the polymer product was inhibited.

In contrast, the reaction rate decreased when phosphoric acid was used as a co-catalyst with the base clay. It is assumed that the basic sites of the clay were neutralized by phosphoric acid and minimized its catalytic activity. Despite the slower reaction, both the isomer and γ-lactone products were favored (monomer 36.2%, γ-lactone 6.0%, polymer 20.6% in 5 hr reaction) over the dimer product.

The isomer (32.6%) and polymer (34.3%) products were formed in comparable amounts when water and phosphoric acid were used together as co-catalysts. This result was not unexpected because water favored polymer formation, whereas phosphoric acid favored isomer formation.

A slow reaction and relatively low isomer yield were obtained if phosphoric acid was used with the dried acid catalyst, although a high yield of γ-lactone product was formed. It seemed that not only phosphoric acid but also a certain amount of water contributed to the catalyst activity of the clay in the formation of the isomer product. The use of a large amount of phosphoric acid with either dried or undried clay catalyst, however, gave no reaction. These results suggested that the surface of the clay catalyst should be studied both in the presence and absence of a Bronsted acid in order to understand the reaction pathways. It is difficult to study the surface of a clay mineral at high temperature and under pressure. Accordingly, we examined the adsorption of oleic acid onto the clay surface at room temperature under atmospheric conditions. Oleic acid adsorption onto the clay surface was studied by varying the oleic acid concentration in CH_2Cl_2 in the presence of a constant weight of clay. As shown in Figure 2a, the clay adsorbed oleic acid up to the extent of 0.177 mmol/g of clay, above which no increase of adsorption was noted. On the other hand, the clay adsorbed almost all the methanesulfonic acid present in the methylene chloride solution (Fig. 2b). This would seem to indicate that methanesulfonic acid adsorption onto the clay surface is most probably chemisorption, whereas for oleic acid it is physical adsorption. This adsorption difference between the two acids is probably the result of their different acid strengths. The change of oleic acid adsorption onto the clay surface also was studied using various concentrations of either phosphoric acid or methanesulfonic acid in the CH_2Cl_2 solution.

A significant change of oleic acid adsorption onto the clay was observed when even a small amount of phosphoric acid was added (Fig. 3a), whereas addition of methanesulfonic acid caused oleic acid adsorption to decrease gradually (Fig. 3b). The differences noted between phosphoric acid and methanesulfonic acid may be the result of their mode of absorption onto the clay surface. It may be assumed that phosphoric acid makes the clay surface more hydrophilic than does methanesulfonic acid, or that H_3PO_4, being a polyprotic acid, may interact with a larger number of active sites on the clay surface. In any event, the data in Figure 3 demonstrate how the amount of Bronsted acid used as a co-catalyst can affect the clay catalyzed isomerization and/or polymerization of oleic acid. From Table I, it is seen that the best yields of isomer products are obtained when 3.3 mole % phosphoric acid per mole of oleic acid is used as co-catalyst. This amount of acid is equivalent to 1.3 mmole of phosphoric acid per gram of clay. Accordingly, as seen in Figure 3a, at this ratio both the oleic and phosphoric acid can be adsorbed onto the clay, and the observed reactions proceed readily. On the other hand, when 16.5 mole % phosphoric acid per mole of oleic acid is used, this is equivalent to 6.5 mmole of phosphoric acid per gram of clay. At this ratio no oleic acid can be adsorbed onto the clay, and the expected reactions are not observed.

Similarly, a high yield of isomer was obtained when 6.0 moles of methanesulfonic acid per mole of oleic acid was used as the co-catalyst in the reaction. This amount, equivalent to 2.3 mmole of methanesulfonic acid per 1 g of clay employed, indicates that both the methanesulfonic acid and oleic acid could be adsorbed onto the clay surface as shown in Figure 3b. Even though the adsorption conditions are not the same, namely room temperature and atmospheric pressure for Figure 3 vs high temperature and pressure for the reactions, it is likely that even under the latter conditions adsorption plots similar to those shown in Figure 3 would be obtained.

It is concluded, therefore, that the isomer is formed in high yield when both oleic acid and Bronsted acid are adsorbed onto the clay surface at certain ratios, and that no reaction occurred when only the Bronsted acid occupied the active sites of the clay surface.

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