Polymerization of Dehydrated Castor Acids Using an Acid Earth Catalyst

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Abstract

The atmospheric pressure polymerization of a commercial dehydrated castor oil fatty acid mixture, by using as catalyst the acid clay Filtrol 13, has been studied under different conditions of temperature, catalyst concentration, reaction time, and concentration of conjugated linoleic acid in the starting material. At 180C or above, extremely rapid polymerization of the conjugated fatty acids occurred (50% complete in about 4 min at 66% concentration). This was accompanied by *trans* isomerization and some hydrogen transfer to form oleic (or *iso*-oleic) acids. The ratio of dimer/polymer in the product was approximately 2 to 2.5 and was only slightly affected by variation in the reaction conditions.

Introduction

THE USE OF CLAY CATALYSTS, either acid or alkaline, is well established for commercial production of polymerized fatty acids which are rich in the dimer species, and many patents have been filed (3,4,6,8–10, 13,20,24–28). Modifications, such as the addition of water (26), basic materials (10,26), or lithium salts (27), have been made to suppress the polymer and enhance yields of the dimer; differences between acid and alkaline clays and natural clays from different sources have been noted (8). Although monounsaturated acids may be polymerized under vigorous conditions, *cis* to *trans* isomerization of oleic acid (together with bond migration), under milder conditions, has been induced by Filtrol clay (7).

Yield and type of product vary with the starting material, and comparison of the dimer produced by clays or other ionic catalysts with the purely thermal dimer which was extensively studied by Paschke and his co-workers (17–19) suggests that the products of the two reactions have structural differences. This is exemplified by an apparently higher degree of unsaturation in the products from the catalyzed reactions.

Little interest has been shown in this reaction outside the patent field. Turke and Boone examined activated alumina and metal oxides as conjugation catalysts but without estimating any polymer formation (22). Model experiments by Ney (15), using oleic and linoleic acids, showed that, at 100C in the absence of oxygen or prior oxidation, bleaching clays had no effect. Pre-oxidized linoleic showed clear changes but not isomerization, which occurred only above 150C (14,15). The ionic nature of this reaction relates it to the work of Baltes, who used clays to activate fatty acid double bonds in co-oligomer formation (2,23).

This study is concerned with the production of polymerized linoleic acid by the action of the clay catalyst Filtrol 13 on one particular fatty acid mixture which was rich in conjugated linoleic isomers.

Experimental Section

Materials

Filtrol 13. A product of the Filtrol Corporation, this contained 17% of free water estimated by drying at 150C. Material dried at this temperature for several hours was used unless otherwise stated. Titration of a sample of undried catalyst suspended in water showed an apparent AV of 43.7. Sulphate ions were detected in an aqueous suspension, suggesting that the clay was sulphuric acid-activated.

Dehydrated Castor Oil Fatty Acid. Commercial material (DEDICO, a registered trade mark of Victor Wolf Ltd.) with the following characteristics was used: AV 197.2; SV 199.1; hydroxyl value 3.2; peroxide value 4 milliequivalents per kilogram, SG 0.89, N_D^{25} 1.4761. Analysis of methyl esters by GLC is shown in Table I. In the same table is shown the analysis of the safflower fatty acids, which were used in one experiment.

Analysis

Analytical procedures were as follows: hydroxyl value according to British Standard Spec. 684 (1958), Method 1, p. 58; peroxide value according to AOCS Test Method Cd8–53; iodine values according to British Standard 684 (1958) but with the addition of 2½% mercuric acetate solution (10 ml) and reaction time of 3–5 min (1).

The GLC results in Table I are according to Reference 5; later results were obtained on a Pye Series 104 Dual Flame Ionization Detector instrument by using 5-ft glass columns, packed with 10% Reoplex 400 on Embacel. The conditions were temperature (isothermal), 183C; carrier gas, oxygen-free nitrogen at 30 ml/min; hydrogen, 40 ml/min; air, 400 ml/min; attenuation, 2000X; sample size, 0.06 microliters of methyl ester undiluted; and chart speed (Kent Mark 3 Recorder), 15 in./hr.

Procedure

The fatty acid was charged to a 5-necked, 1,000-ml flask, fitted with a stirrer, thermometer, nitrogen inlet, and air condenser (in a typical experiment 700 g of acids were used). A nitrogen atmosphere was maintained above the fatty acids while the flask was heated by means of an electric mantle to 5–10C below the required temperature. Dried catalyst was added with

TABLE I
Percentage Composition of the Fatty Acids Used (GLC)

		DCO acids	Safflower acids
Unknown		0.1	0.1
Palmitic		0.9	6.6
Stearic		0.7	2.3
Oleic		2.8	11.6
Nonconjugated linoleic		29.2	79.5
Conjugated Linoleic	*cis/trans*	50.1	Traces only
	cis/cis	8.7	
	trans/trans	7.8	
Linolenic		0.0	Trace

rapid stirring over 2–3 min, during which a temperature rise of 5–10C occurred. The stirred mixture was maintained at the reaction temperature under nitrogen, and samples were withdrawn at intervals by means of a dip leg which was connected to a Buchner flask. It was assumed that, with continuous stirring, a homogeneous sample of acids and catalyst was being removed.

Samples were cooled rapidly and filtered under suction to remove the Filtrol before distillation at 0.2 mm of mercury pressure until the still residue was at 270C. Polymeric residue was analyzed for monomer and dimer content by the method of Paschke et al. (16).

Residue from the distillation always contained some monomer, and corrected yields are expressed as weight percentage of residue after subtraction of the amount of monomer obtained from the above analysis.

It was possible to follow the reaction qualitatively by TLC of the free acids (10–15 microliters of a 2% solution in 60–80° petroleum ether) on 200-micron thickness of Kieselguhr-G. The plates were developed with ether/cyclohexane/acetic acid: 25/75/1 and sprayed with phosphomolybdic acid (5%) in ethanol to locate the spots. This showed good separation of monomer, dimer, and polymer.

Discussion

The conversion of nonconjugated linoleic acid to dimer and polymer by clay catalysts requires prolonged heating and elevated temperatures, and at temperatures below 200C the difference in behavior between conjugated and nonconjugated dienoic acids in contact with ionic catalysts becomes very marked. This work is concerned with the reaction below 270C, particularly around 180C, and the following variables are briefly examined separately: a) variation of concentration of conjugated linoleic acid, b) time, c) temperature, d) weight of catalyst used, e) miscellaneous variables, such as use of steam in place of nitrogen to blanket the reaction and use of a solvent.

Effect of Conjugated Linoleic Acid Content (variation of the starting material)

Direct comparison of Dedico containing 66.2% of conjugated isomers and of safflower fatty acid, containing none when treated with 5% of catalyst at 180°, is shown in Figure 1.

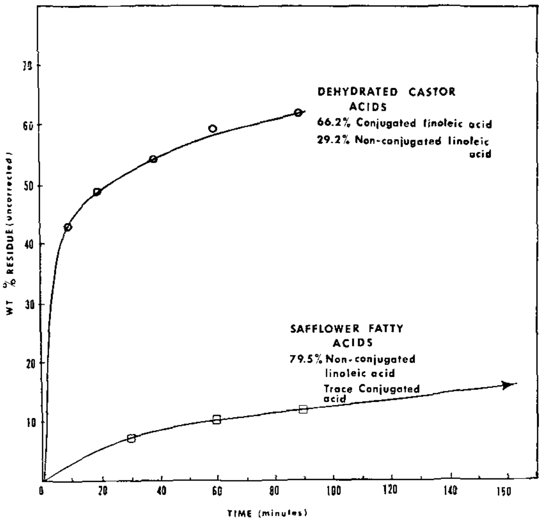

FIG. 1. Polymer formation (uncorrected) vs. time (5% catalyst at 180C).

Under these conditions the effect on nonconjugated material is much less than that on the conjugated dienes. Infrared examination of samples of monomer recovered from the safflower experiment after 30, 60, and 90 min showed an increase in absorption because of *trans* unsaturation, but no quantitative estimate was made of this.

Comparison of the reaction rate of the Dedico with that of a 50/50 mixture of Dedico plus stearic acid (commercial 90% material) having 33.1% concentration of conjugated linoleic confirmed that the reaction rate is initially dependent upon the concentration of this species. At 50% dilution a marked reduction in reaction rate was observed (cf. Table II, No. 5, and Table III; see also below).

In the sections which follow, the DCO fatty acid "Dedico" is the only material used.

Effect of Reaction Temperature

At 100C, reaction was slow with a yield of only 17.8% polymer after 90 min compared with 57.7% at 180C. The reaction rate continues to increase up to 248C though at a slower rate since conjugated material is rapidly consumed and nonconjugated linoleic is reacting to a greater extent. This is shown by an increase in dimer/polymer ratio although this remained below 3 under these conditions. (The commercial processes in which nonconjugated dienoic acids are polymerized by clays during several hours of reaction time give dimer/polymer ratios of 4 or 5/1.)

TABLE II

Polymerization of Dehydrated Castor Oil Acids at Various Temperatures, Using Filtrol 13 as Catalyst

Expmt. No.	% Catalyst w/w	Temp. (°C)	Time (min)	% Residue	AV	SV	IV	Analysis of residue[1]				% Corrected yield[2]
								M	D	P	D/P	
1	2.5	180	10	36.6	188.0	193.3	....	10.0	63.5	26.5	2.4	32.9
			20	39.2	188.1	195.4	....	5.6	65.0	29.4	2.2	37.0
			40	46.0	186.5	196.5	....	5.4	66.5	28.1	2.4	43.5
			60	51.4	187.5	196.1	....	7.7	61.1	31.2	2.0	47.4
2	2.5	244	10	47.8	183.7	190.9	119.8	8.9	66.0	25.1	2.6	43.5
			40	63.9	184.6	191.4	118.9	9.1	67.5	23.4	2.9	58.1
3	2.5	270	10	47.2	183.4	188.5	125.1	12.7	63.4	23.9	2.7	41.8
4	5.0	100	90	20.3	....	....	110.5	12.4	60.7	26.9	2.3	17.8
5[3]	5.0	180	10	43.1	187.2	193.5	119.4	8.3	65.7	26.0	2.5	39.5
			20	49.1	189.1	193.1	....	9.8	61.7	28.5	2.2	44.3
			40	54.3	186.5	194.1	....	9.4	59.9	30.7	1.95	49.2
			60	59.5	186.5	194.2	....	10.7	60.9	28.4	2.2	53.1
			90	61.5	189.4	200	125.3	6.2	57.0	36.8	1.5	57.7
6	5.0	248	10	67.2	187.5	191.5	134.0	8.4	63.7	27.2	2.3	62.3
			40	76.2	188.1	191.7	120.4	11.2	66.2	22.6	2.9	67.7
			90	77.4	....	....	....	9.2	65.9	26.9	2.5	71.8
7	7.5	180	10	46.5	187.2	194.1	....	7.9	60.7	31.4	1.9	42.9

[1] M = monomer, D = dimer, P = polymer higher than dimer.

[2] Corrected yield = % residue after subtraction of monomer present.

[3] $t_{0.5}$ = time for disappearance of half initial conjugated linoleic acid. Taken as time for appearance of polymer based on this (corrected yield = 33.1%). In Experiment 5 this was 4.5 min by extrapolation.

TABLE III

Effect on Rate of Polymerization of DCO Acids of Dilution by an Equal Weight of Stearic Acid

% Catalyst w/w	Monomer	Temp. °C	Time[1] (min)	% Residue	AV	SV	Analysis of Residue M	D	P	D/P	% Corrected yield
5	50/50 Dedico/stearic acids	180	10	19.1	184.8	197.6	15.0	58.0	27.0	2.1	16.2
			20	21.9	187.0	196.0	6.6	60.7	32.7	1.9	20.4
			40	24.3	183.0	19[illegible].7	8.9	60.2	30.9	1.95	22.1
			60	27.2	181.6	193.0	9.5	60.3	30.2	2.0	24.6

[1] $t_{0.5}$ taken as time to produce 16.5% polymer, was 11 min.

At higher temperatures (270C) some cracking occurred, and the yield of polymer fell slightly even with short reaction time (Table II, cf. 2 and 3).

Effect of Reaction Time

Sampling at 10, 20, 40, 60, and, in some cases, 90 min (Table II) established that an initial reaction of great rapidity occurred (180C/5% catalyst gave 39.5% of polymerized material in 10 min). The reaction rate slowed as conjugated isomers were consumed. This same pattern was followed in all experiments where the time factor was considered. No significant variation in acid value of the distillation residues was noted and this remained steady around 188 with saponification values of about 190 so that anhydride or inner ester formation was little different from that in purely thermal polymerization. Anhydride determination (method of Reference 12) on one or two random samples showed negligible anhydride content.

Dimer and higher polymer appear to be formed at approximately the same rate, and the value of D/P remained near 2, being only slightly higher after 10 min than after 60 min (at 180C it fell from about 2.5 to 2.2), i.e., prolonged reaction increased the polymer content.

Effect of Weight of Catalyst

Since large amounts of catalyst would begin to affect the nonconjugated linoleic acid, the effect of Filtrol 13 at 2.5%, 5%, and 7.5% level by weight only was examined. In the absence of a catalyst at 180C, change of the refractive index suggests that up to 2% of polymer might be formed in 10 min from Dedico. A comparison of the 10-min figures from Table II, Experiments 1, 5, and 7 shows a diminishing effect as the catalyst weight is increased from 5% to 7½% as compared with the 2½% and 5% and the 0 and 2½% levels.

Effect of Miscellaneous Variables

An experiment, using 5% of catalyst with wet steam in place of nitrogen at 170–175C (temperature control proved more difficult in this experiment), and sampling after 10 min and 20 min gave results comparable with those obtained from the other experiments which used nitrogen as the inert blanket. No change in dimer/polymer ratio was observed.

At 180C, undried Filtrol (the weight was corrected for water content) gave results identical with those from dried material.

Dedico, refluxed at 180C in half its weight of xylene (no nitrogen) on treatment with 5% of catalyst for 10 and 20 min, showed a slight increase in dimer/polymer ratio (3.1 in 10 min) but with reduced yield (22.6%).

Side Reactions: Isomerization and Hydrogen Transfer

The principal reactions (polymerization of conjugated and some polymerization of nonconjugated diene) are accompanied by *trans* isomerization and hydrogen transfer reactions to produce oleic or *iso*-oleic acid. This latter effect is manifested by an increase in the weight of oleic (or *iso*-oleic) acid in monomer recovered from polymerizations. This is especially noticeable if the ratio of palmitic to oleic acid is measured by GLC of the esters and compared with that of the feedstock. The palmitic, taking no part in the reaction, serves as an internal standard.

A materials balance for two experiments is shown in Table IV, and the extent of the changes (rate of disappearance of the conjugated and nonconjugated linoleic, rate of formation of iso-oleic) can be seen.

In order to measure the effect of the reaction on *cis/trans* isomerization of the diene, a separate experiment was done and the results are shown in Table V. This experiment used a different batch of Dedico, also a newer batch of catalyst from that used in the earlier experiments. As it was desired to take a sample of the mixture after 5 min, the catalyst was added to the reaction more rapidly than in the earlier runs. This is believed to account for the apparently higher rate of reaction in this experiment compared with Table II, No. 5. Monomer samples were analyzed by GLC of the methyl esters, and the weight of recovered isomers was calculated.

From the figures in Table V it can be seen that the *cis/trans* conjugated isomer disappears most rapidly, *cis/cis* at a lower rate and *trans/trans* isomer actually increases in quantity during the initial stages of the reaction. (The three configurations would tend toward an equilibrium in favor of *trans/trans.*) Nonconjugated material shows a slow decrease and "oleic" a regular increase in weight.

TABLE IV

Materials Balance, Showing Weight Changes and Formation of Iso-oleic During Polymerization[1]

Reference	Table II, No. 7		Table II, No. 5	
Expmtl. conditions	7.5% Cat. 180C 10 min		5% Cat. 180C 90 min	
Weight of sample	400 g		73.7 g	
Feedstock anal.	%	Act. wt. (g)		Act. wt. (g)
Linoleic	29.2	116.8		21.5
Conj. linoleic	66.2	264.8		48.8
Oleic	2.8	11.2		2.1
Saturated	1.8	7.2		1.3
Product monomer anal.	%	Act. wt. (g)	%	Act. wt. (g)
Linoleic	45.8	104.6	54.4	17.0
Conj. linoleic	43.2	98.7	22.9	7.1
Oleic + *iso* oleic	7.6	17.3	14.6	4.6
Satd. and lower MW materials	3.4	7.8	8.1	2.5
Weight of recovered monomer		228.5		31.2
Wt. change linoleic		− 12.2		− 4.5
Wt. change conj. linoleic		−166.1		−41.7
Wt. change oleic		+ 6.1		+ 2.5
Wt. change other constit.		+ 0.6		+ 1.2
Total		−171.6		−42.5
Weight of polymer		171.6		42.5

[1] The figures are corrected for mechanical losses.

TABLE V

Experiment at 180C/5% Filtrol 13 Catalyst for Monomer Examination

	Calculated percentage composition of the product[2]					
				Conj. linoleic		
Time (min)[1]	Polymer	"Oleic"	Non-conj. linoleic	c/t	c/c	t/t
0	0	4.3	27	41.9	11.4	10.2
5	41.1	5.8	25	7.2	3.3	12.5
10	44.1	6.8	23.8	6.8	2.6	11.5
20	54.3	6.8	21.8	4.3	1.4	7.7
40	57.4	7.0	19.8	3.6	1.0	6.4
90	59.7	10.6	17.4	2.14	0.7	4.8

[1] A sample was taken at 60 min, but, owing to incomplete distillation during removal of monomer, results were obtained which were clearly in error so these have been disregarded.

[2] The C_{18} acids were determined by GLC of the recovered monomer. The 4–5% difference between the sum of these six columns and 100% is made up of saturated acids and traces of unidentified material. Slight discrepancies are attributable to errors inherent in the methods of analysis.

The distilled monomer which was recovered generally shows an increase in low MW constituents produced by pyrolysis, particularly if the reaction conditions have been severe.

Kinetics of the Reaction

Consideration of the above data indicates that the following reactions are occurring.

1. *cis/trans*) conj. linoleic ⟶ *trans/trans* conj. linoleic
   cis/cis) (rapid)
2. *cis/trans*) conj. linoleic ⟶ polymer
   trans/trans) (rapid, but slower than 1)
3. Nonconj. linoleic ⟶ polymer
   (very much slower than 2 below 200C)
4. Hydrogen transfer ⟶ *iso*-oleic acid
   (parallels other reactions but slower)
5. Pyrolytic breakdown ⟶ low MW fragments
   (slight at 180C with short contact time)

The small variation of the dimer/polymer ratio with time shows that trimer and higher MW material are also formed rapidly; this reaction keeps pace with dimer formation.

No attempt has been made at a complete kinetic study, but the results from Table V may be plotted in the familiar form of $\log_{10}$ [conj. Diene] vs. time. This plot shows an initial steep fall and thereafter the straight-line plot characteristic of a first-order reaction (Figure 2).

It has also been noted that the effect of dilution by stearic acid was to slow down the reaction in the initial stages and, since in the first 10 minutes or so polymer arises mainly from conjugated diene, the rate of formation of polymer can be taken as the rate of disappearance of conjugated linoleic acid. The time for disappearance of half the conjugated linoleic at 66.2% initial concentration (Table II) was, by extrapolation, 4.5 min and, at 33.1% concentration (Table III), 11 min; hence the apparent order of reaction is given by

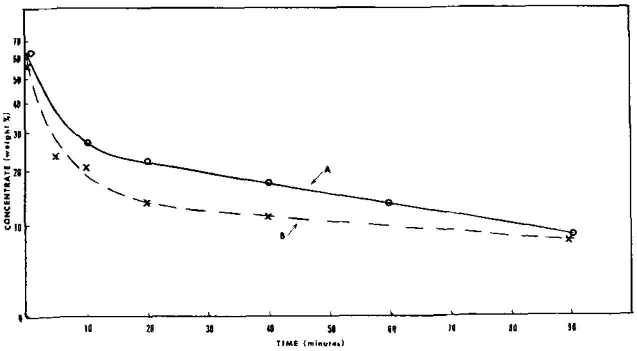

FIG. 2. Variation of diene concentration with time (concentration shown logarithmically). A is (total diene—polymer) vs. time from Table II, Expmt. 5. B is conjugated diene (by GLC) from Table V.

$$n = 1 + \frac{(\log 11 \; - \log \; 4.5)}{(\log 66.2 - \log 33.1)} = 2.29$$

i.e., at 180C and while the rate-determining step is the disappearance of *cis/trans* conjugated linoleic acid, the reaction order averages about 2.29 over the first 10 min. Thereafter, when a new balance of isomers has been set up and conjugated material is diluted by other constituents, the rate of disappearance of the conjugated isomer follows a first-order law. At higher temperatures and with prolonged reaction time, new reactions, such as polymerization of nonconjugated linoleic (which may not take place via conjugation), become the rate-controlling steps (21).

That *cis/trans* material should disappear more rapidly than *trans/trans* is, of course, not surprising in view of the less stable nature of the *cis* bond and its lower energy requirement for activation, but it should be noted that under the conditions reported *cis/cis* material never entirely disappeared.

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