Super Acid Catalyzed Dimerization of Fatty Acids Derived From Safflower Oil and Dehydrated Castor Oil

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Dimerization of fatty acids derived from dehydrated castor oil and safflower oil was carried out on the recently described sulphate-treated zirconia catalyst and trifluoromethane sulphonic acid (triflic acid) under autogeneous pressure in the temperature range of 160-240 C. Triflic acid was observed to be highly active; however, the product obtained was deeply colored. Zirconia exhibited high activity for the reaction. The important features of this catalyst were the high selectivity for dimer (low yields of trimer) and no significant coloration of the products. The zirconia catalyst shows promise for industrial use.

Dimerization of unsaturated straight chain aliphatic acids and their esters is an industrially important reaction. The commercial dimer acids which are mixtures of 36-carbon dibasic acids contain some amount of 54-carbon trimer acids and traces of the monomer. The fatty acid-derived dimers (C36) are the highest molecular weight dibasic acids available commercially. Their derivatives possess unusual properties by virtue of the long chain part in the molecule. The most important commercial use of dimer acids is in the production of polyamide resins (1). They also have been used as corrosion inhibitors in petroleum processing equipment (2) and as stabilizers in winterized vegetable oils (3). Traditionally, dimer acids were produced by thermal polymerization under steam pressure (4). However, the current practice involves use of clay catalysts at a temperature of 220-260 C under pressure for several hours (5,6). Other catalysts investigated for this reaction include peroxides (7), hydrofluoric acid (8) and sulphonic ion exchange resin (9). The reaction also has been investigated under corona discharge (10). None of these methods has succeeded commercially.

Catalysis by super acids has received considerable attention in recent years (11-15). The difficulty in the industrial use of several super acids is their chemical instability, which precludes the possibility of their reuse. The soluble super acids also pose corrosion problems. The recently described (15) sulphate-treated zirconia catalyst offers several advantages in this respect. This super acid catalyst has high chemical stability, and being a solid does not pose any corrosion problems. It costs considerably less than some other super acids like Nafion-H or trifluoromethane sulfonic acid. Further, it has high structural stability and hence can be used at temperatures much higher than those permissible for polymer resin catalysts.

In this light this catalyst was considered very promising for dimerization of fatty acids. The present work, therefore, was carried out to investigate the suitability of the catalyst for this reaction using fatty acids derived from safflower oil and dehydrated castor oil (DCO) as feedstocks. For comparison, the reaction also was carried out using trifluoromethane sulfonic acid, one of the strongest acids known. This acid is also chemically stable and reusable.

EXPERIMENTAL PROCEDURE

Materials. Safflower oil fatty acids (75% linoleic acid, 15% oleic acid, 6.0% palmitic acid and 2% stearic acid with AV 200-201) and dehydrated castor oil fatty acids (conjugated dienoic acid 48-50% and AV 198-200) were obtained commercially. Zirconyl chloride, hexane, ethyl acetate and isooctane were of A.R. grade.

Catalysts. The recently reported solid superacid, sulphate-treated zirconia was prepared by treating zirconium hydroxide with 1N sulphuric acid followed by drying and calcination at 650 C for three hr. Zirconium hydroxide was in turn prepared by the hydrolysis of zirconyl chloride with liquor ammonia followed by washing it free of alkali and subsequent drying at 100 C (15).

Triflic acid (CF_3SO_3H) was obtained from Fluka.

Reactions with zirconia. Reactions were conducted in a stainless steel high pressure Parr autoclave of 2-1 capacity. A feed solution consisting of measured quantities of fatty acids and catalyst (which was dried at 110 C for one hr just before use) along with 2% (v/v) water was charged in the autoclave. The air above the reaction mixture was purged with nitrogen. The reaction mixture was heated to the desired reaction temperature under stirring (600 rpm) and autogeneous pressure. Small amounts of samples were withdrawn from time to time through a sampling valve.

Reactions with triflic acid. A reaction mixture consisting of 10 ml fatty acids, the required quantity of catalyst and 2% (v/v) water was taken in a 25-ml capacity glass tube and was sealed. Four glass tubes containing the same quantity of feed solution were heated to the desired temperature. The tubes were withdrawn periodically and the contents were analyzed.

Analysis. An Iatroscan TH10 TLC-FID analyzer, coupled with a Perkin Elmer Sigma 15 data station, was used for analysis. Chromarods Type S II were used for separations. Aliquots of a 10% (v/v) solution of reaction mixture in hexane were used for spotting. Sample (0.5 μl) was applied to the Chromarods. The rods were placed in a presaturated solvent tank containing mobile phase of isooctane:ethyl acetate (9:1, v/v) for elution for about one hr (16). The rods were dried for two or three min and scanned at a speed of 30 sec/rod. Blank scanning of the rods was carried out to check the contamination of any foreign bodies before spotting. The peaks were identified by spotting

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authentic samples obtained from Emery Industries Inc.

The product was also analyzed on a Perkin Elmer 8320 capillary gas chromatograph by converting the product into methyl esters (17,18). The analysis was carried out with a SGE BP1 (12 meters) capillary column using a flame ionization detector.

Acid value was determined by the standard method (18).

Conversions given in the paper are based on polymerizable acids only.

RESULTS AND DISCUSSION

Dimerization of DCO fatty acids. The reaction was first studied at various loadings of the zirconia catalyst at 240 C. Figure 1 shows conversions obtained at various loadings after different time intervals. The activity increased to 13% (w/w) loading; however, further loading increases did not result in any additional conversion. This may be due to a decrease in turbulence in the system and hence finite solid-liquid diffusional influence at higher loading of solids. Table 1 shows the product distribution at the end of four hours. It is also observed that the selectivity for the dimer decreases with an increase in catalyst loading from 13% to 19%. The subsequent experiments therefore were carried out at 13% w/w loading of zirconia.

To investigate the effect of temperature, the reaction was carried-out at varying temperatures between 180 and 240 C. The typical variation of the composition of reaction mixture with time is shown in Figure 2. The product distribution obtained at the different temperatures at the end of two and four hr is compared in Table 2. The data could be fitted with simple first order kinetic expression. Figure 3 shows the Arrhenius plot for the reaction, which gives activation energy of 7.72 kcal/gmol. The selectivity, however, does not seem to be affected by temperature.

TABLE 1

Dimerization of DCO Fatty Acids[a]

Zirconia loading %(w/w) of monomer	Monomer (wt % in product)	Dimer (wt % in product)	Trimer (wt % in product)
2.0	79.5	19.0	1.5
6.5	50.0	46.0	4.0
13.0	28.0	65.0	7.0
19.5	26.0	58.0	16.0

[a] Product distribution after 4 hr at 240 C.

To examine the possibility of reuse of the catalyst, the zirconia catalyst was filtered, washed with acetone and reused. The dotted curves in Figure 2 show the results obtained in this experiment. The progress of the reaction was almost identical with that on the fresh catalyst. This demonstrates the reusability of the catalyst, an important consideration for industrial use.

Table 3 presents results obtained using triflic acid as catalyst at different temperatures. Triflic acid at the loading of 1% (w/w) gave almost the same rates as those obtained with 13% (w/w) loading of zirconia. The selectivity to dimer at a given conversion was, however, lower in the case of triflic acid. At the same time, the use of triflic acid always resulted in deeply-colored products, which would be very unsatisfactory for industrial practice.

In all the above experiments there was no decarboxylation as confirmed by the measurement of acid value before and after the reaction.

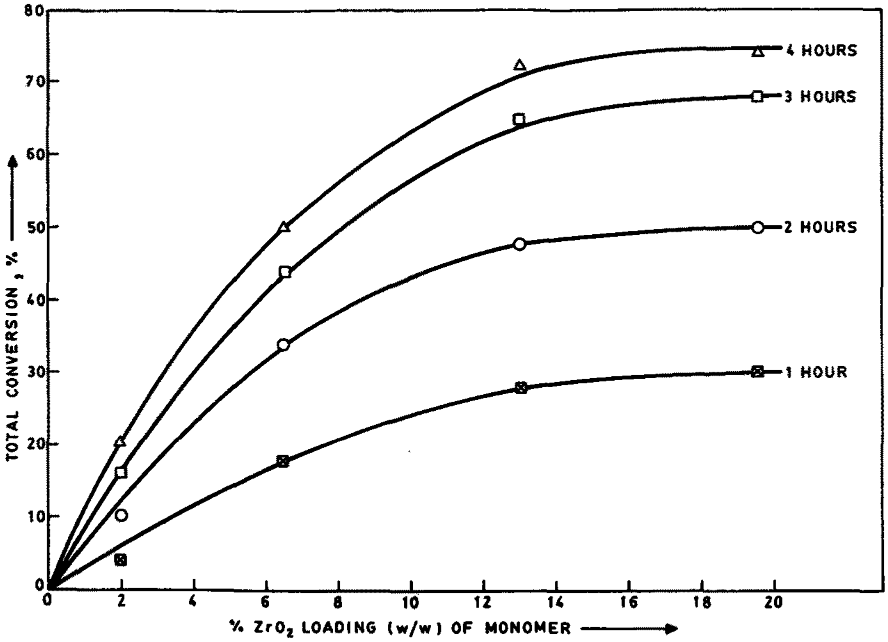

FIG. 1. Effect of zirconia catalyst loading on conversion of DCO fatty acids at 240 C.

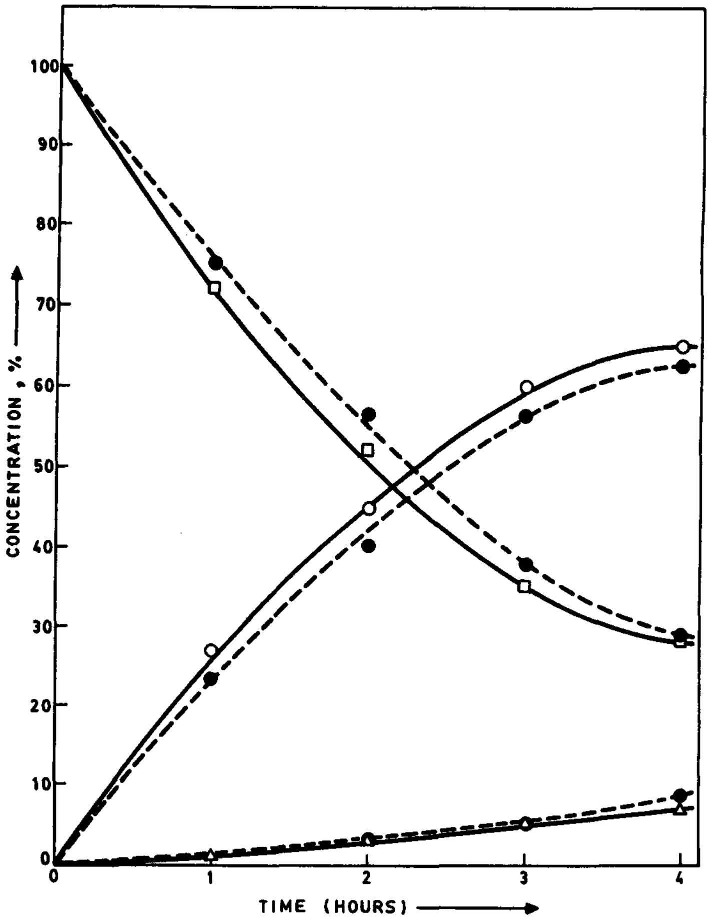

FIG. 2. Dimerization of DCO fatty acids using zirconia [13% (w/w) of monomer] catalyst at 240 C. Typical variation of product composition: □, monomer; ○, dimer; △, trimer.

TABLE 2

Dimerization of DCO Fatty Acids Using Zirconia Catalyst[a]

Temperature (°C)	Time (hours)	Monomer	Dimer	Trimer
		(wt % in product)		
240	2	50.5	46.6	3.5
	4	27.0	66.5	6.5
220	2	60.0	38.0	2.0
	4	38.0	57.0	5.0
200	2	71.0	28.0	1.0
	4	55.0	43.0	2.0
180	2	80.0	20.0	0.0
	4	61.5	37.5	1.0

[a]Variation of product composition at various temperatures.

TABLE 3

Dimerization of DCO Fatty Acids[a]

Temperature (°C)	Time (hours)	Monomer	Dimer	Trimer
		(wt % in product)		
240	1	72.0	25.5	2.5
	2	52.0	43.0	5.0
	3	41.0	51.0	8.0
	4	34.0	56.0	10.0
200	1	81.0	17.5	1.5
	2	66.0	31.0	3.0
	3	55.0	41.0	4.0
	4	50.0	44.0	6.0
160	1	88.0	11.5	0.5
	2	78.0	20.5	1.5
	3	70.0	28.0	2.0
	4	66.0	31.5	2.5

[a]Progress of reaction using triflic acid [1% (w/w) of monomer] as catalyst.

Dimerization of safflower oil fatty acids. Figure 4 shows the effect of zirconia catalyst loading on the extent of reaction. Unlike the case of DCO fatty acids, in this case there was an almost linear increase in conversion with an increase in catalyst loading. This reaction is slower than that of DCO fatty acids and hence may not be influenced to the same extent by diffusional limitations. Product distribution at the end of four hr is given in Table 4. It can be seen that the selectivity for dimer is not impaired greatly with an increase in catalyst loading for this reaction.

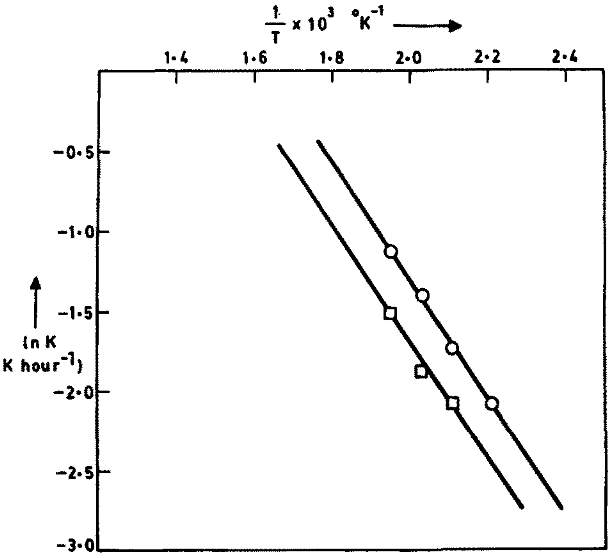

FIG. 3. Arrhenius plots, dimerization of fatty acids derived from DCO and safflower oil. ○, DCO fatty acids; □, safflower oil fatty acids.

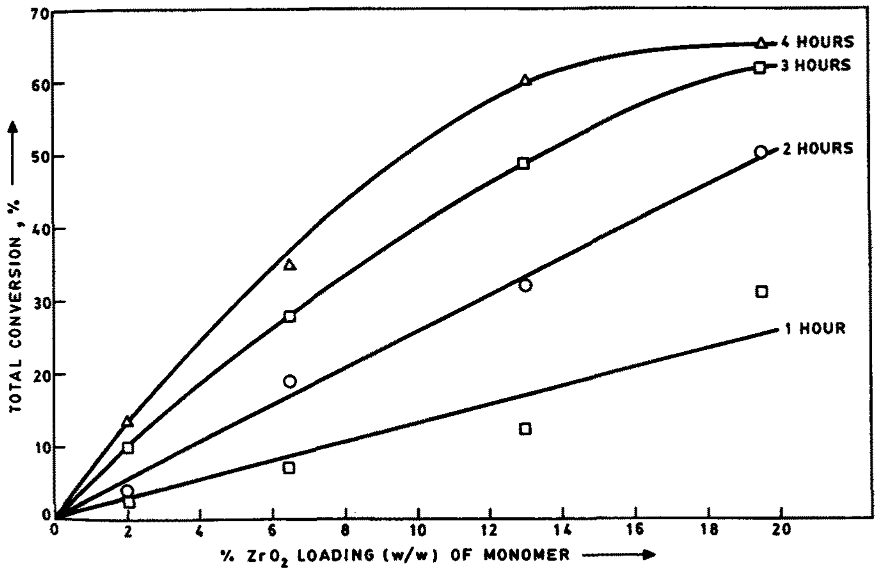

FIG. 4. Effect of zirconia catalyst loading on conversion of safflower oil fatty acids at 240 C.

The reaction was studied at various temperatures in the range 200-240 C. The product distribution obtained at the end of two and four hr is shown in Table 5. The selectivity is not affected by temperature. The data could be fitted by first order kinetic expression. The Arrhenius plot which gives an activation energy of 7.45 kcal/gmol is included in Figure 3.

Table 6 shows the results of dimerization using triflic acid as catalyst. The rate of dimerization is lower than that for DCO fatty acids under identical conditions. This may be due to a lower content of diunsaturated acids (which are nonconjugated) and higher proportions of monounsaturated acids in this case. The selectivity for dimer is also lower. The product obtained was deeply colored. No change in acid value was observed during the reaction.

The results demonstrate the promise of a novel catalyst for dimerization of fatty acids. Most of the information on the clay catalysts which are com-

TABLE 4

Dimerization of Safflower Oil Fatty Acids

Zirconia loading %(w/w) of monomer	Monomer	Dimer	Trimer
	(wt % in product)		
2.0	86.5	12.0	1.5
6.5	65.0	30.0	5.0
13.0	40.0	48.5	11.5
19.5	35.0	50.0	15.0

[a] Product distribution after 4 hr at 240 C.

TABLE 5

Dimerization of Safflower Oil Fatty Acids Using Zirconia Catalyst[a]

Temperature (°C)	Time (hours)	Monomer	Dimer	Trimer
		(wt % in product)		
240	2	68.0	30.5	1.5
	4	40.0	49.5	10.5
220	2	78.0	21.5	0.5
	4	51.0	42.0	7.0
200	2	82.0	17.5	0.5
	4	60.0	34.5	5.5

[a] Variation of product composition at various temperatures.

TABLE 6

Dimerization of Safflower Oil Fatty Acids[a]

Temperature (°C)	Time (hours)	Monomer	Dimer	Trimer
		(wt % in product)		
240	1	74.0	24.0	2.0
	2	61.0	34.0	5.0
	3	54.0	38.0	8.0
	4	48.0	42.0	10.0
200	1	82.0	16.5	1.5
	2	71.0	26.0	3.0
	3	62.0	33.0	5.0
	4	59.0	35.0	6.0

[a] Progress of reaction using triflic acid [1% (w/w) of monomer] as catalyst.

monly used in industry is in the form of patents. Hence, a detailed comparison of zirconia and these catalysts cannot be presented. However, one of the significant differences appears to be with respect to the selectivity to the dimer. Formation of trimer, which is one of the undesirable side reactions, is required to be controlled during dimerization, because subsequent separation of dimer and trimer is very difficult. The results of the present study indicate that conversions of dimerizable acids of 75% can be achieved with only 10% concurrent trimer formation with zirconia catalyst. This selectivity is decidedly superior to that reported on clay catalysts. Another important consideration is the color of the dimerized product. Very marginal color deepening could be observed at the end of the reaction. The reaction product at the end of 75% conversion was pale yellow with Gardner color 9. This can perhaps be further improved by using appropriate additives such as antioxidants. Triflic acid, however, does not appear suitable for industrial use because it yields deeply colored products.

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