Fluoride Catalysis at 175°C. of the Reaction: Glycerol Plus Fatty Acid

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ALTHOUGH synthetic glycerides of saturated acids have been widely prepared, the unsaturated substances have received little mention, probably because of the scarcity of the basic acids and their tendency toward thermal decomposition. Recent shortages in drying oils, however, have fostered a renewed investigation of tailor-made glycerides of unsaturated acids. A series of mixed glycerides containing elaidic acid was prepared by Bomer and Stather (2) in 1937. Kinetics of esterification of oleic and linoleic acids with pentaerythritol was reported in 1940 (1) and of the mixed fatty acids of peanut oil with glycerol in 1945 (3). In the latter synthesis Feuge used various inorganic chlorides as catalysts and found only zinc and stannous chlorides to have merit. Since the oxides of these metals and chlorides of others did not appreciably accelerate the reaction, a specificity of both metal and non-metal was postulated. In view of these conclusions the use of compounds of the more active halogen fluorine seemed interesting. There appear to be no reported instances in which solid metallic fluorides have been used as catalysts in esterification although boron trifluoride has received extensive attention, particularly by Nieuwland (4).

Experimental

The initial portion of the program involved the reaction between glycerol and stearic acid, the general purpose being the evaluation of 14 metallic fluorides as catalysts. A saturated acid was chosen to avoid oxidation and polymerization, possibly coincident with the use of unsaturated acids, and thus limit the reaction to one of esterification. Following determination of the better catalysts and optimum amounts the stearic acid was replaced by oleic acid and finally by linolenic acid.

Materials

The reactants were obtained from commercial supply and had the following properties:

Glycerol (Merck, C.P.-U.S.P.) water-white; neutral; moisture 5%.

Stearic acid (Baker, powdered) white; acid number 204.5, ester number 5.0, iodine value (Hanus) 0.0.

Oleic acid (Merck, U.S.P.) pale yellow; acid number 198.0, ester number 3.5, iodine value 87.5.

Linolenic acid (Pittsburgh Plate Glass Co.) light orange; acid number 201.0, ester number 3.8, iodine value 229. Approximate composition from iodine value: 50% linoleic acid, 50% linolenic acid.

Antimony trifluoride (Harshaw) sublimed.

The remaining fluorides were experimental research samples supplied by General Chemical Company.

TABLE I

Esterification of Stearic Acid With Glycerol Decrease of Acid Number With Time

Catalyst	0.5 Hr.	1.0 Hr.	1.5 Hr.	2.5 Hr.	4.0 Hr.	6.5 Hr.	9.0 Hr.	15.0 Hr.
ZnF_2	121.5	95.5	77.0	58.0	44.0	34.0	28.0	18.5
$CoF_2 \cdot 2H_2O$	142.5	117.5	98.0	75.5	58.0	43.5	36.0	28.0
KF	137.0	111.5	95.5	75.5	58.5	44.5	37.5	30.0
$CuF_2 \cdot 2H_2O$	127.0	111.5	100.0	87.0	70.5	55.0	46.0	33.5
BiF_3	136.5	110.5	93.5	76.0	64.0	53.5	49.0	36.0
PbF_2	135.5	109.0	94.5	79.0	66.5	54.0	45.0	37.0
KHF_2	141.0	117.0	100.0	85.5	69.5	54.0	47.0	39.5
$KFeF_4$	145.5	121.0	105.0	85.0	71.0	58.5	51.5	39.5
MnF_2	136.5	113.5	101.5	87.0	74.5	64.5	59.0	48.5
CaF_2	145.5	121.5	107.5	87.5	71.5	60.5	53.0	45.0
$AlF_3 \cdot H_2O$	142.0	119.0	104.0	86.0	73.0	62.0	54.0	49.0
NiF_2	139.5	118.5	105.0	87.5	74.0	62.5	56.0	50.0
$KTiF_4 \cdot H_2O$	141.5	120.0	107.0	91.5	78.5	67.5	63.0	55.0
CrF_3	128.0	114.0	102.5	89.5	78.5	69.5	65.0	61.0
Control	145.0	124.0	111.5	94.5	82.5	71.0	63.0	55.5
ZnF_2*	96.0	69.0	53.5	36.5	26.5	21.5	18.5	9.5
$CoF_2 \cdot 2H_2O$*	147.0	121.5	101.0	77.0	57.0	45.0	37.0	25.5

* 0.1 mole catalyst.

Esterification

The reaction flask was a 500-ml. round bottom two-necked flask equipped with a mercury seal and a stirrer, previously described (5), and a thermometer well. Water formed during the reaction passed through an exhaust opening below the mercury well into a condenser and suitable receiver. Mild suction was applied to the receiver to help draw off the water vapor. The thermometer support was removable to allow addition of catalyst after the glycerol-acid charge reached operating temperature. The entire flask was inserted in an insulated thermoregulated chamber heated by an electric coil.

The charge in each instance consisted of 150 grams of glycerol and fatty acid in the molecular ratio of one to three. After the flask contents reached 175°C. (29 minutes plus or minus 1 minute) the finely ground catalyst was added to the extent of 0.01 molar gram per 100 grams fatty acid. The reaction was followed by withdrawing samples through the thermometer well and determining acid, ester, and iodine values. The reaction was discontinued after 15 hours.

Results

Decrease of acid number with time for the reactions involving stearic acid is shown in Table I. It is evident that some catalysis was afforded by all the fluorides, but that only zinc fluoride, and perhaps cobalt fluoride, was outstanding. They were therefore chosen for further investigation. Table I also shows the effect of increasing the concentration of these two catalysts to 0.1 mole. Increasing the cobalt concentration appeared to have little effect, but a striking acceleration of reaction velocity was afforded by the larger amount of zinc fluoride.

Subsequent reactions involving oleic and linolenic acids are summarized in Table II. Cobalt fluoride, zinc fluoride, and antimony trifluoride served as catalysts. The last, commonly employed as a fluorinating agent in Swarts type reactions, was included as an afterthought and as expected caused the greatest darkening of product. Results for the 0.1 mole concentration of this substance indicated severe decomposition.

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[1] Awarded doctorate as result of investigation constituting the basis of this paper.

TABLE II

Esterification of Oleic and Linolenic Acids With Glycerol at 175°C.
Decrease of Acid Number With Time

Hours	Oleic Acid				Linolenic Acid						
	Control	$CoF_2 \cdot 2H_2O$ 0.01 mole	ZnF_2 0.01 mole	ZnF_2 0.1 mole	Control	$CoF_3 \cdot 2H_2O$ 0.01 mole	ZnF_2 0.01 mole	ZnF_2 0.1 mole	SbF_3 0.005 mole	SbF_3 0.01 mole	SbF_3 0.1 mole
0.0	179.1	179.1	179.1	179.1	181.5	181.5	181.5	181.5	181.5	181.5	181.5
.5	138.0	133.0	130.5	87.0	136.0	133.5	130.0	106.5	129.0	107.0	164.0
1.0	113.5	106.0	97.0	64.5	118.0	112.5	96.5	80.5	103.5	72.5	149.0
1.5	98.5	91.5	76.0	54.0	102.0	96.5	75.5	65.0	84.0	53.0	133.0
2.5	80.0	70.5	53.0	39.0	85.0	74.0	57.5	47.0	58.5	42.5	93.0
4.0	65.0	54.5	40.5	28.0	69.0	57.5	44.0	36.0	....	35.5	65.0
6.5	50.0	40.0	27.5	20.5	54.5	42.5	35.0	26.0	33.5	25.5	47.5
9.0	43.0	32.5	20.0	15.5	45.5	34.5	26.5	20.0	30.0	18.5	42.5
15.0	34.0	20.5	13.0	12.5	32.5	25.5	13.0	15.5	20.0	14.5	....
	Iodine Values				Iodine Values						
0.0	79.0*	79.0	79.0	79.0	207.0†	207.0	207.0	207.0	207.0	207.0	207.0
1.5	80.5	82.5	82.5	84.5	213.0	207.0	216.0	216.5	....	225.0	....
6.5	73.0	84.5	84.0	84.5	218.0	....	218.5	219.0	....	....	....
15.0	67.0	81.5	80.5	83.5	215.0	195.0	212.0	212.0	....	209.0	....

* Theoretical value for a mixture of oleic acid (I_2 value 87.5) 90% and glycerol 10%.

† Theoretical value for a mixture of linolenic acid (I_2 value 229.0) 90% and glycerol 10%.

Physical Properties of Products

In all cases the catalyst settled as a distinct layer from which liquid esters could be decanted. Stearates were conveniently chipped away after solidification.

Four general color groups resulted among the stearates. Bismuth, lead, potassium ferric, potassium acid, and potassium fluorides gave black to black-brown products. Zinc, aluminum, nickel, and chromium fluorides yielded a dark brown material resembling bitter chocolate. The control reaction and that catalyzed by potassium titanium fluoride furnished a medium brown similar to sweet chocolate. The other fluorides afforded a light gray color. Acid and ester values indicated that severe decomposition was not produced in any reaction. No attempts were made to decolorize the products.

In order of decreasing hardness as determined with a penetrometer the series of stearates was almost identical with listing of Table I, i.e., with the completeness of reaction:

The glycerides of oleic and linolenic acids were transparent red-brown, oily liquids. Only antimony trifluoride formed an opaque product, which in addition was considerably more viscous than either starting acid.

Discussion

Evaluation of the various fluorides as catalysts may be secured in several ways depending on the manner in which data are handled. The simplest method involves merely an inspection of Table I to determine the relative rapidity with which the acid number was reduced. A second evaluation is based on the time needed to reduce the acidity to that corresponding to the monoglyceride (acid number 120.9) and the diglyceride (acid number 61.7). These times, in minutes, form a part of Table IV. The residual acid content after 15 hours is also shown.

A third method involves the determination of velocity constants. Fig. 1 is based on data for the control reaction and for two concentrations of zinc fluoride and indicates that all three are essentially second order. Similar plottings were found for the other catalyzed reactions. The velocity constant for a bimolecular reaction between equivalent concentrations of reactants may be calculated from the equation:

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \qquad (1)$$

where k is the velocity constant

t is the time
a is initial molar concentration of one reactant
x is moles reacting in time t

Substituting a—c for x, where c are residual moles at time t,

$$k = \frac{1}{t} \cdot \frac{a-c}{ac} \qquad (2)$$

For an initial mixture containing 90% stearic acid:

a is $\frac{90}{284}$ moles stearic acid per 100 grams mixture,

c is $\frac{\%\ \text{residual acid}}{284}$ moles per 100 grams mixture,

whence

$$k = \frac{1}{t} \cdot \frac{(90 - \%\ \text{residual acid})\ 3.155}{\%\ \text{residual acid}} \qquad (3)$$

With time expressed in hours and a and c in moles per 100 grams of mixture, the velocity constant has the dimensions: 100 grams moles^{-1} hours^{-1}.

The reaction may be considered as progressing in two ways. In the first it may be assumed that certain glycerol radicals are linked rather rapidly to one, two, and then three acid radicals whereas other glycerol molecules are still inactive. Thus the mixture shortly contains all possible combinations and proceeds rather smoothly toward its final composition. Velocity constants based on this assumption for the data used in constructing Fig. 1 are given in Table III. The other alternative of reaction envisages three successive bimolecular combinations. In the first all, or nearly all, the glycerol is converted to the monoglyceride before appreciable further esterification occurs. Following this, most of initial product unites with another acid radical to form the diglyceride. Finally the triglyceride is formed. With this mechanism three reactions are postulated, and three velocity constants may be calculated. The time for calculation was set at one hour after the period of reaction had been entered, i.e., one hour after the reaction had passed acid numbers of 178.0, 120.9, and 61.7, respectively. Equation (2) was employed, the initial concentration of acid being varied to correlate with acid number. Constants are shown in Table IV for each reaction.

TABLE III

Esterification of Stearic Acid With Glycerol
Velocity Constants

Hr.	Control	ZnF_2 0.01 mole	ZnF_2 0.1 mole
0.5	1.43	2.94	5.41
1.0	1.40	2.71	4.97
1.5	1.25	2.76	4.55
2.5	1.11	2.66	4.87
4.0	.90	2.37	4.47
6.5	.73	2.01	3.68
9.0	.64	1.76	3.80
15.0	.47	1.78	3.58

Esterification of oleic and linolenic acids in the presence of cobalt, zinc, and antimony fluorides presented the same general evidence as for stearic acid and thus does not warrant detailed discussion. Of particular interest, however, was the apparent stability of the double bond system as indicated by sustained iodine values shown in Table II. Heat bodying of the glycerides as formed, except with antimony trifluoride, was at a minimum since this would both increase the viscosity and decrease the iodine value.

Similarly, a series of esterifications were made at 150°C. and indicated the same general results as at 175°C. though reactions were slower. Data are not considered sufficiently singular to include here.

TABLE IV

Esterification of Stearic Acid With Glycerol

Catalyst	Monoglyceride		Diglyceride		Triglyceride	
	Vel. Const.	Min. to form	Vel. Const.	Min. to form	Vel. Const.	Acidity 15 Hr. %
ZnF_2	2.71	36	2.75	132	2.28	9.5
ZnF_2*	4.92†	18	5.50‡	72	4.89	4.5
$CoF_2 \cdot 2H_2O$	1.63	54	1.95	216	1.28	13.0
$CoF_2 \cdot 2H_2O$*	1.47	60	1.81	220	1.52	12.5
KF	1.88	48	1.68	222	1.25	15.0
BiF_3	1.92	42	1.81	264	.75	18.0
PbF_2	1.97	48	1.52	294	.93	18.5
$CuF_2 \cdot 2H_2O$	1.88	48	1.14	318	.93	17.0
KHF_2	1.67	54	1.38	300	.88	20.0
$KFeF_4$	1.47	60	1.38	342	.59	20.0
CaF_2	1.47	66	1.34	372	.55	22.5
$AlF_3 \cdot H_2O$	1.58	60	1.28	384	.55	24.5
NiF_2	1.58	60	1.28	414	.55	25.5
MnF_2	1.79	48	1.21	450	.43	24.5
$KTiF_4 \cdot H_2O$	1.51	60	1.08	546	.10	28.0
CrF_3	1.79	48	1.02	822	.09	30.5
Control	1.40	66	.94	576	.24	28.0

* 0.1 mole catalyst.
† Calculated after 18 minutes.
‡ Calculated after one-half hour.

Summary

1. In uncatalyzed reactions the esterification of stearic, oleic, and linolenic acid proceeded at the same general rate though the speed was somewhat enhanced as the degree of unsaturation of the fatty acid increased. None of the reactions went to completion, after 15 hours being 72%, 83%, and 84%, respectively, completed. Only a small fraction of the distearate was converted to the triglyceride; a greater amount of the dioleate was esterified to the trioleate and about half the dilinolenate was changed to the trilinolenate.

2. Of 15 metallic fluorides studied, all afforded some catalysis, but only antimony trifluoride and zinc and cobalt fluorides were outstanding. Antimony trifluoride was the most active although in large amount it caused severe decomposition and charring of the products. Zinc fluoride had the best general properties, approaching antimony trifluoride yet causing practically no decomposition even in high concentration. Its activity was enhanced with an increase in amount, the best concentration apparently being 0.1 mole per 100 grams fatty acid. Antimony trifluoride was also better in larger amount within limits, but cobalt fluoride did not exhibit this property.

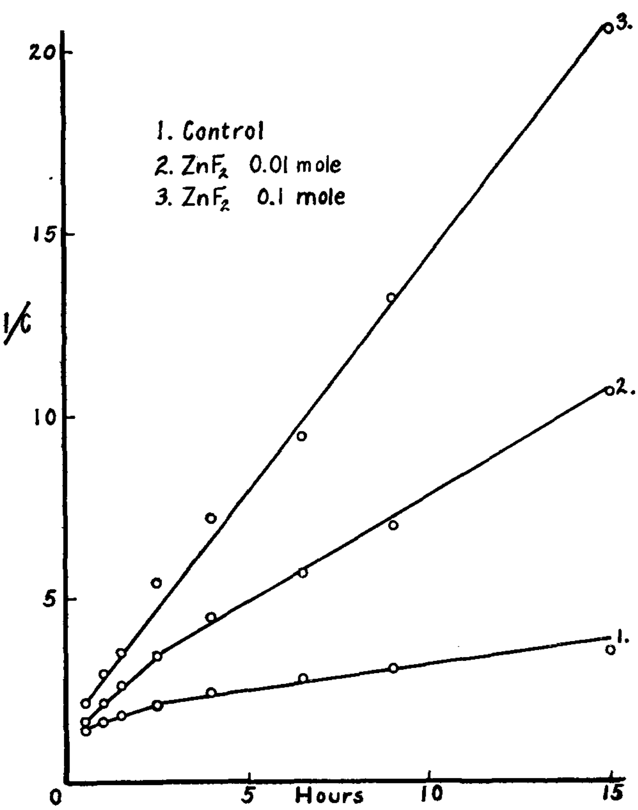

FIG. 1

3. With zinc fluoride as catalyst the reactions of stearic, oleic and linolenic acids after 15 hours were 95%, 94%, and 92%, respectively, completed. At least three-fourths of the diglycerides were converted to triglycerides. From a study of reaction velocities, zinc fluoride caused the monoglyceride to form at a rate approximately four times that of the uncatalyzed reaction and the diglyceride at a six-fold rate. The triglyceride was formed at an almost undiminished rate whereas in the uncatalyzed reaction the formation of triglyceride was diminished rapidly.

4. Unsaturation and viscosity were not affected seriously in the presence of the fluorides except antimony trifluoride. Certain other fluorides caused severe darkening but without accompanying serious decomposition.

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