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The Effect of Metallic Fluorides on Oleic Acid at Elevated Temperatures

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THE EFFECT OF METALLIC FLUORIDES

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OLEIC ACID AT ELEVATED TEMPERATURES

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By Lorraine W. Dupuis

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A Thesis Submitted to Marquette University in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science

MILWAUKEE, WISCONSIN

January, 1948

The problem of finding the effect of metallic fluorine compounds on oleic acid at elevated temperatures was presented in connection with the thesis of J. J. Wocasek of Marquette University (3). Doctor Wocasek had used fluorine compounds as catalysts in an attempt to find a substitute for tung oil. He used the fluorides as catalysts in the esterification of glycerol with unsaturated acids.

PREFACE

Tung oil or China wood oil is used by the paint and varnish industries as a drying oil to produce paints and lacquers. It was formerly supplied by China in sufficient quantities to satisfy the needs of the manufactuers. Most of the trees producing this oil have been destroyed in the wars which have been ravaging China in recent years. Attempts have been made to grow this tree in the southern parts of the United States, but they have all proved commercially unsuccessful (3). The climate here is not sufficiently stable for their growth. Because of this, many attempts have been made and are still being made to produce substitute oils with the sufficient number of conjugated double bonds necessary for good drying oils.

In his thesis Doctor Wocasek assumed that the fluorine compounds acted merely as catalysts and took no other part in the reaction. The author became interested in discovering if these compounds did more than

- (8). Wocasek, J. J., Fluoride Catalysis of the Reaction Glycerol Plus Fatty Acids, Milwaukee, Wisconsin, (1947).
- (3) Gardner, H. A., Butler, P. H., and Scofield, F., Tung Oil Culture, Scientific Section National Paint, Varnish, and Lacquer Association, Inc., Washington, D. C., (1941), 10

catalyze the reaction. The possibilities of salt formations, breakdown of the double bond, or formation of addition products at these elevated temperatures presented themselves. Oleic acid, the simplest unsaturated fatty acid, was chosen to heat with these compounds since the reaction products of oleic acid are easier to determine and predict than those of more highly unsaturated acids.

The author wishes to thank Doctor Koch, her major professor, Doctor Wocasek under whom she worked, and the chemistry department of Marquette University for the help they gave her in connection with this thesis.

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A. Object

These experiments aim to determine the effect produced at the double bond of oleic acid or elsewhere in the molecule when the acid is intimately mixed with various metallic fluorides for several hours at elevated temperatures. The problem is of importance since the use of fluorine compounds as catalysts is contemplated in the esterification of unsaturated acids with glycerol as a means of producing synthetic oils. Since the exclusion of air in an industrial process of this sort would prove expensive, the effect of this heating in a stream of air as well as in a fairly airtight chamber will be determined.

1

Oleic acid seemed to be a logical choice as a typical unsaturated fatty acid. It has acidic properties and the general structural characteristics of both saturated and unsaturated organic acids. Since it has only one double bond, the effects of the various metallic fluorides should be evident without too much difficulty. The action is localized, the reaction products can be predicted, and the presence of one double bond does not affect the stability of the compound to a marked degree. Oleic acid is readily obtainable for experimentation, and it is of great interest to many classes of investigators. The reactions of this acid are comparitively easy to follow, but it also serves to indicate the possible reactions of a more highly unsaturated compound.

B. Oleic Acid

Oleic acid is an 18 carbon unsaturated acid containing one double bond, the double bond being between the ninth and tenth carbon atoms and the formula being $C_{17}H_{33}COOH$. The glycerol ester, olein, of this acid is found in many fat and vegetable oils. The acid is colorless, solidifies to white needles in the cold, and can not be volatilized without some decomposition (1). It is tasteless, odorless, and produces no reaction on litmus. However, it becomes yellow by oxidation in air and acquires a randid odor. The acid exists in two isomeric forms. Oleic acid, the cis form, has a melting point of 13 C; elaidic acid, the trans form, has a melting point of 44 C.

$$\begin{array}{c} HC-(CH_2)_7-CH_3 & CH_3-(CH_2)_7-CH \\ HC-(CH_2)_7-C_{OH}^{<0} & HC-(CH_2)_7C_{OH}^{<0} \end{array} (2)$$

Oleic acid is insoluble in water but soluble in alcohol. When distilled at ordinary pressure, it breaks down partially. However, it passes over unchanged in an atmosphere of superheated steam.

Some of the reactions of oleic acid are as follows: (4)

- 1. At ordinary temperatures oleic acid treated with nitrous acid will yield the isomeric form, elaidic acid.
- Oleic acid treated with sodium bisulphate under pressure at a temperature between 175 C to 180 C also yields elaidic acid.
- Oleic acid treated with sulphurous acid under pressure at 200 C will yield elaidic acid. This reaction is reversible.
- (1) Bernthsen, A., Organic Chemistry, London and Glasgow, Blackie and Son Limited, (1927), 171.
- (2) Fieser, Louis F., and Fieser, Mary, Organic Chemistry, Boston, Heath and Company, (1944), 287.
- (4) Lewkowitsch, J., Chemical Analysis of ⁰ils, Fats, Waxes and of the Commercial Products Derived Therefrom, London, Macmillian and Co., Limited, (1909), 141-45.

- Oleic acid treated with potassium permanganate produces a monobasic and a dibasic acid.
- 5. If air is blown through the acid at 120 C for certain periods of time oxidation will take place in the following percentages.

2 hours 4 hours Time 6 hours 10 hours 0.62% 2.6% % oxidized 3.5% 6.0% 0.9238 Sp. Gravity 0.0980 0.9098 0.9121 of product

- When oleic acid is digested with sulfur at 130-150 C, the sulfur is absorbed with no evolution of sulphuretted. hydrogen.
- The oxidation of oleic acid with nitric acid yields dibasic acids plus volatile acids.
- 8. Oleic acid plus excess alcoholic potassium permanganate in cold solution yields dihydroxystearic acid as the main product.
 - The acid absorbs one molecule of bromine forming dibromostearic acid.
 - 10. The acid absorbs iodochloride forming a saturated acid.
 - 11. When heated with caustic potash, palmitic acid, oxalic acid, and acetic acid are formed.
 - 12. When dissolved in cold concentrated sulfuric acid, stearic acid hydrogensulphate is formed.
 - Stearic acid can be formed by the reduction of oleic acid. The oleic acid is heated with iodine at 270-280 C.

A mixture of fatty substances which are separated by distillation is formed. This process gives a 70% yield, but it is costly. A 50% yield is obtained with electrical charges in the presence of an atmosphere of hydrogen. 14. When heated with zinc powder to about 350 C, carbon di-

oxide, hydrogen, and hydrocarbons are formed.

C. Fluorine, Its Compounds, and Its Uses

The chemistry of fluorine and its compounds is only of recent development. Because of this there is not a great deal of information that can be found about it or its compounds. As yet, the reactions of fluorine and its compounds are rather unpredictable; but much progress is being made in the study, and certain fluorine compounds have been put to a wide variety of uses especially in the recent war years.

Fluorides have a tendency to form double salts; therefore, many inorganic compounds of fluorine are possible. They also form many crystalization compounds with hydrogen fluoride. Such a compound is sodium or potassium bifluoride. Fluorine is involved in complex ion formation. Such a complex ion of iron and fluorine is the basis of the use of potassium difluoride in the removal of rust from clothes. When other elements combine with fluorine, they exhibit their highest valence state. Fluorine in organic compounds causes the aromatic nucleus to be quite stable. The compound is more resistant to hydrolysis than the corresponding chlorine compound. Organic fluorides vary in their chemical properties from the very inert to those of extreme reactivity (7).

(7) Simons, J. H., Indust. and Eng. Chem., 39, 240, (1939).

Fluorine compounds have a variety of uses. Some of its present uses are in freon aerosols, anhydrous hydrogen fluoride in aviation gas production, boron trifluoride in the petroleum industry (5), and in the hydrogen fluoride torch which develops a temperature of 6000 F (6). Many future uses have been predicted.

5

"Scientists forsee a whole new field of chemistry in the development of fluorine compounds, Some of the outstanding ones are:

A nonflammable toxic liquid with a high enough boiling point and specific gravity that it can replace mercury in the present mercury boiler making the most efficient vapor engine practical and safe.

A gas already developed but requiring elemental fluorine to manufacture, which is a nearly perfect insulator for high voltages uses in x-ray and nuclear physics.

A lubricating oil so stable that it will not oxidize or break down under any present engine or mechanical operations dreamed of by designers because no lubricant made could withstand their pressure and friction.

An insecticide already made by the Germans but too costly to be practical with present methods.

Other uses for Fluorine compounds now definitely within the realm of possibility include heat transfer and dielectric media, other insecticides, fungicides, fumigants, germicides, stable solvents, anesthetics, fire extinguishers and fireproffing materials, resins and plastics, and weed killers." (9)

(5) McH	ee, E.	T .,	Chem.	and	Eng.	N.,	24,	2461-2,	(1946)	
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(6) Rosen, R., Chem. and Eng. N., 24, 2462, (1946).

(9) Chem. and Eng. N., 24, (1946).

3. Gine Flipschdata

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A. General Method

The oleic acid was kept at 170 C with the finely divided catalyst. One tenth mole of catalyst per 100 grams of acid was used. Observations were made at the end of three hours, and a sample was removed. The heating was continued for three hours more. Tests for acid number, saponification value, and iodine value were run on these samples which were removed after three hours and six hours.

B. Catalysts

1. Potassium bifluoride: molecular weight - 59.104 grams

formula - KHF₂ two grams were used. molecular weight - 178.76 grams formula - SbF₃ 5.4 grams were used. molecular weight - 103.38 grams formula - ZnF₂ 3.1 grams were used molecular weight - 125.9 grams formula KBF₄

3. Zinc fluoride:

2. Antimony trifluoride:

15 SOCO 12 4045

was then added, and sus spirition was b

4. Potassium fluoro-

Loid was adapad, and the

borate:

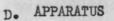
3.8 grams were used

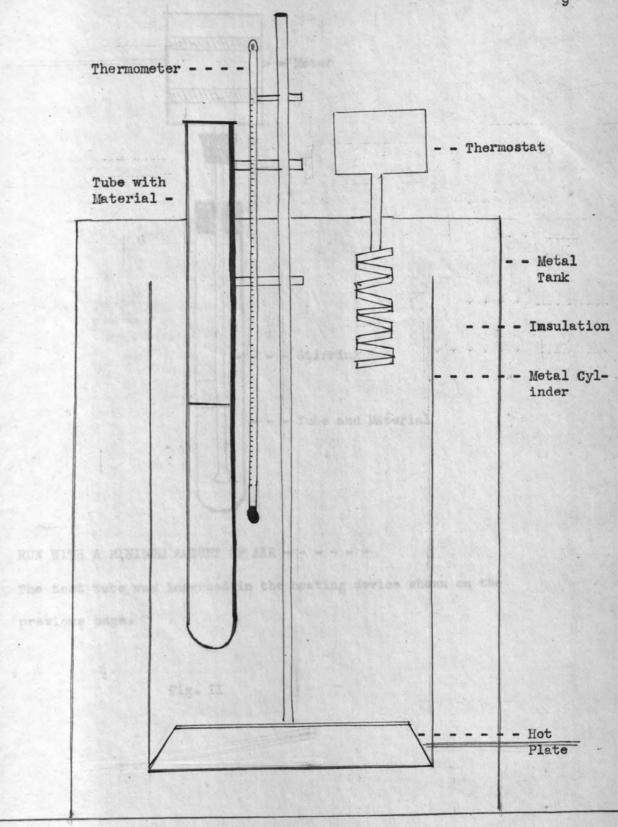
C. Preparation of Solutions

Hanus solution - the Hanus solution is used in the determination of iodine values. Three liters of the solution were prepared. About 39 grams of iodine were dissolved in 2400 ml. of glacial acetic acid. 25 ml. of this solution were titrated with standard thiosulfate solution. Bromine was dissolved in 600 ml. of glacial acetic acid. This bromine solution was added to the iodine solution until it doubled its halogen content.

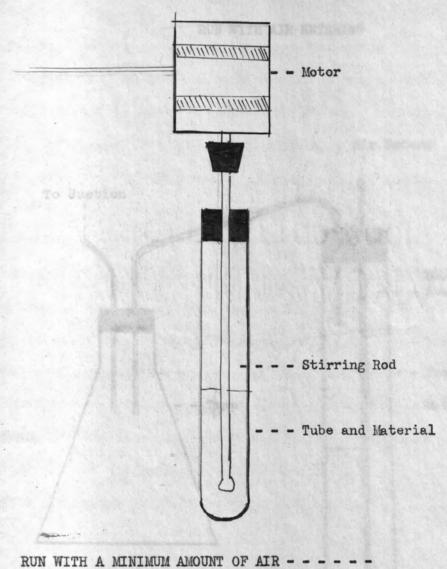
Thiosulfate solution: - this solution is also used for determining iodine values. To prepare an approximately 0.1 normal solution, 75 grams of sodium thiosulfate were weighed out and dissolved in 3000 ml. of water which had been previously boiled and cooled. The solution was standardized with copper wire. The wire was dissolved in concentrated nitric acid and water. When solution was complete, bromine water was added; and the solution was boiled until the bromine was expelled. Strong ammonia was added until a deep blue color formed. The solution was boiled until the deep blue was replaced by a light blue green color. Strong acetic acid was added, and the solution was cooled. Potassium iodide was then added, and the solution was titrated with the thiosulfate.

Hydrochloric acid - 0.1 mormal - concentrated hydrochloric acid was diluted to approximately 0.1 normal with distilled water. The solution was standardized against sodium carbonate using methyl orange as indicator. Alcoholic potassium hydroxide - 0.1 normal - about 18 grams of potassium hydroxide were dissolved in the smallest possible amount of water. This was added to 3000 ml. of alcohol. The carbonate formed was allowed to settle. This solution was then standardized against potassium biphthalate using phenolphthalein as the indiietor.



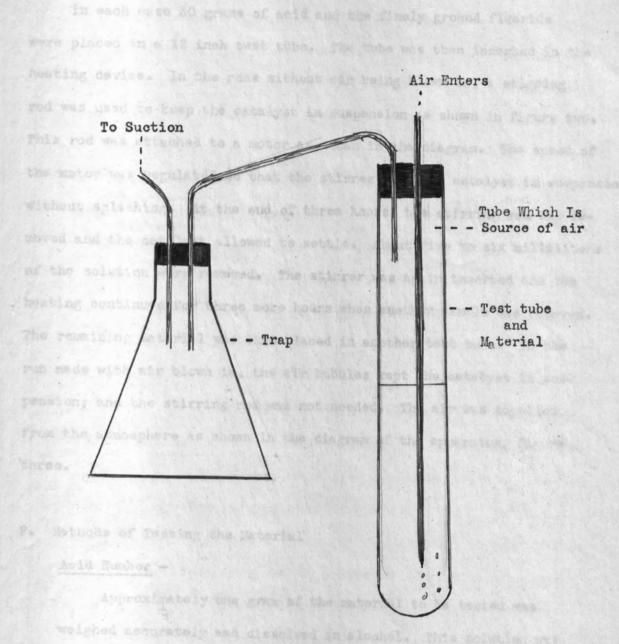






The test tube was inserted in the heating device shown on the previous page.

Fig. II



The test tube was inserted in the heating

device.

solution hereines bestelle Fig. III

yas laved and used to find the seponification white.

E. Method of Heating the Fluorides with Oleic Acid

In each case 30 grans of acid and the finely ground fluoride were placed in a 12 inch test tube. The tube was then inserted in the heating device. In the runs without air being blown in, a stirring rod was used to keep the catalyst in suspension as shown in figure two. This rod was attached to a motor as shown in the diagram. The speed of the motor was regulated so that the stirrer kept the catalyst in suspension without splashing. At the end of three hours, the stirring rod was removed and the catalyst allowed to settle. About five to six milliliters of the solution were removed. The stirrer was again inserted and the heating continued for three more hours when another sample was removed. The remaining material was then placed in another test tube. In the run made with air blown in, the air bubbles kept the catalyst in suspension; and the stirring rod was not needed. The air was supplied from the atmosphere as shown in the diagram of the apparatus, figure three.

F. Methods of Testing the Material

Acid Number -

Approximately one gram of the material to be tested was weighed accurately and dissolved in alcohol. This solution was titrated with approximately 0.1 normal alcoholic potassium hydroxide. Phenolphthalein was used as the indicator. The titration was complete when a red color which appears when the solution becomes basic lasted about 15 seconds. This material was saved and used to find the saponification value.

Saponification Number -

From a burette, 25 ml. of standard potassium hydroxide were run into the solution saved from the acid number determination. This was then heated under a reflux condensor for about 45 minutes. A blank was also run containing the same amount of alkali and enough alcohol to make the amount of liquid in each flask about even. When the heating was finished, the blank and the sample were titrated with standard hydrochloric acid. The difference in the two titrations gave the amount of potassium hydroxide used in the saponification of the sample. The titration was complete when the red color produced by the phenolphthalein faded.

Iodine Value -

About 0.2 grams of the sample were accurately weighed in an iodine flask and dissolved in ten milliliters of chloroform. 25 ml. of Hanus solution were added from a burette. A blank containing chloroform and Hanus solution was also run. The flasks were placed in a cool dark place for 45 minutes. The were shaken from time to time during the 45 minute period. After this time elapsed, 50 ml. of distilled water and ben milliliters of 15% petassium iodide solution were added. This solution was then titrated with sodium thiosulfate using starch as the indicator. The titration was complete when the dark color produced by the action of iodine on starch faded. The difference in the amount of thiosulfate used by the blank and by the sample gave the amount of Hanus solution used by the sample.

III EXPERIMENTAL DATA and RESULTS

Catalyst	Hours	Acid No.		Sap. No.		Iodine Value	
Agid.		Actual	Total Change %	Actual	Total Change %	Actual	Total Change %
Control	0	186.2	0	2.9	0	88.8	0
Acid	3	192.6	3.51	4.9	61.8i	82.8	6.7d
alone	6	191.2	2.91	8.3	176.91	83.7	5.8d
KHF2	3	187.9	0.951	15.1	406i	86.2	2.9d
	6	177.6	4.6d	10.8	260.91	84.1	5.3d
SbF3	3	189.1	1.51	7.3	145.51	76.3	14.1d
	6	177.1	4.9d	3.99	33.51	74.8	15.7d
ZnF2	3	182.2	211d	7.9	164.81	85.9	3.2d
	6	194.2	4.31	1.2	57.9d	82.2	7.4d
KBF4	3	193.5	3.91	5.1	70.6i	83.2	6.2d
	6	194.7	4.51	7.2	139.8i	82.7	6.8d

Runs With the Minimum Amount of Air:

i - means increase in value

d - means decrease in value

Catalyst	Hours	Acid No.		Sap. No.		Iodine Value	
<u>iflatras</u>	<u>a31</u>	Actual	Total Change %	Actual	Total Change %	Actual	Total Change %
Control	0	186.2	0	2.9	0	88.8	0
Acid	3	183.0	1.6d	28.8	863.21	74.7	15.9d
alone	6	158.0	15.1d	48.6	1522.li	64.2	27.7d
KHF2	3	173.1	7.03d	15.1	403.3i	77.5	12.7d
	66	114.5	38.5d	20.9	597.3i	61.4	30.8d
SbF3	3	180.3	3.1d	13.3	343 .1 i	86.8	2.2d
	6	177.1	4.9d	12.3	311.3i	90.2	1.51
ZnF2	3	148.3	20.4d	61.1	1947.2i	66.6	25.0d
an an de	6	118.7	36.2d	59.6	1893.li	59.2	33.3d
KBF4	3	163.5	12.2d	28.2	838.li	73.9	16.7d
	6	144.9	22.1d	43.9	1366.5i	63.2	28.9d

Runs With Air Blown in:

sens very dark

The solor hs-

i - means increase in value

d - means decrease in value

the tube as in the case

of the soli clones

The odlor was a mailer

Observations of the materials after heating:

Minimum air	Air blown in	
The acid turned from a	The acid went	Acid alone
pale yellow color to a	from a pale	3 hours
rusty brown.	yellow to a	
ves a little slands-	dark brown.	
The acid turned a	The acid be-	6 hours
darker brown.	came almost	
pieper -	black.	
The acid turned a	The acid be-	With potassium
little darker but not	came almost	bifluoride
as dark as the acid	black.	3 hours
alone at the end of		
three hours.		
The acid became darker	The acid be-	6 hours
but not as dark as the	came very dark	Surgice Sta
acid alone after six	and more vis-	
hours. No oily residue	cous.	
was noted on cleaning		
the tube as in the case		
of the acid alone.		
The catalyst tended to	The color be-	With antimony
remain in suspension.	came very dark,	
The color was a muddy	and white needle	3 hours
blackish brown.	like crystals	
	were formed, cry	78-

tals on stirring rod.

The color remained about the same, but the catalyst settled out more. The acid became an orange brown. It

was a little cloudy. The color became very dark - almost black.

The color of the The color changed acid was about to a dark brown. the same as that of the acid alone after three hours. The color was like The acid rethat of the acid alone mained the same after six hours. as at the end of

The acid remained 6 hours about the same as at the end of three hours. The acid became Zinc fluoride black and syrup 3 hours like. The acid became 6 hours dark and very viscous and gummy. The color changed Potassium to a dark brown. fluoro borate 3 hours The acid re-6 hours mained the same

three hours.

IV DISCUSSIONS

said option - option and in every instances the decoders track the

There is a general trend for the iodine value to decrease with time. In some cases the decrease is more noticable than in others. The general decrease is greater when air is blown through the mixture than when air is not blown through. The exception to this is the case when antimony trifluoride is present. Here the decrease in iodine value is greater in the absence of an air stream than in its presence. No explaination is offered for this phenomenon. In general however it may be assumed that the iodine value decrease is due to either:-

- A. The addition of oxygen at the double bond
- B. The splitting of the double bond with consequent production of new acidic endings.

If the later were true, a marked increase in acid number should accompany a marked decrease in iodine value. If the former were true, an increase in acid number, saponification number, or both might be expected depending upon the stability of the inner oxide in the presence of alcoholic potassium hydroxide.

In the absence of large amounts of air the greatest increase in acid number is 4.5%, but in several cases the acid number decreases as much as 4.9%. In no case did the percent increase in the acid number equal the percent decrease in iodine number. This eliminates the complete rupture and oxidation to the carboxyl group at the double bond because in this event two carboxyl groups would be produced by the oxidation of one double bond and the percent increase in acid number should be about twice the percent decrease in iodine value. The occassional decrease in acid number also eliminates this mechanism. In the series in which air was blown into the reaction mixture the acid number decreased in every instance; the decrease after six hours being over 35% for potassium bifluoride and zinc fluoride. This evidence convincingly removes the possiblity of rupture and oxidation to the carboxyl group.as the mechanism of the reaction. The general decrease in acid number with time would appear therefore to be due to the formation of a metallic soap by reaction of the oleic acid with the metallic fluoride with oxygen probably accelerating the reaction.

The general decrease in iodine value with time, and the accelerated decrease in the presence of a stream of air, is therefore probably due to the addition of oxygen at the double bone. The process is probably similar to that encountered in the drying of oils, and indeed oleic acid is often a constituent of drying oils. Here the oxygen may be added in a variety of ways. An atom of oxygen may attach itself to a single molecule of the acid at the double bond thus in effect removing the unsaturation and forming an inner oxide. A molecule of oxygen may attach itself at the double bond and produce an inner peroxide linkage. Two molecules of oleic acid may be joined together at the double bond by cross linkages with or without the addition of oxygen forming a saturated dimer having the same acid value as the original oleic acid. Probably all three of these mechanisms occur although one or more may be accelerated or inhibited by the presence of metallic fluorides. The resulting mixture may react with potassium hydroxide especially at elevated temperatures thus resulting in an exagerated saponification number. An examination of saponification numbers reveals an increase in every instance except one. The increase after six hours in a stream of air is generally greater than that after three hours.

V SUMMARY and CONCLUSIONS

- The greatest change was noticed in the saponification value. This
 was obtained with zinc fluoride as catalyst in the case where air
 was blown in. The saponification value was changed from 2.9 to
 61.6.
- 2. The acid number of the oleic acid was found to change from 186.2 to 114.5 when potassium bifluoride was used in the presence of a stream of air. Zinc fluoride was almost as effective, but other fluorides produced much smaller changes.
- 3. The iodine value changed from 88.8 to 59.2 when zinc fluoride was used in the presence of the stream of air at 170 C. Potassium bifluoride and potassium fluoroborate were almost as effective.
- 4. Since the iodine value decreases in most instances, especially when air was blown in, it seems evident that oxygen or oxygen containing groups were taken on at the double bond.
- 5. Since the saponification value increased it would seem probable that some splitting might occur at the double bond under the conditions of the experiment. The extra acids, in so far as they were formed, would increase the saponification number.

VI SUGGESTIONS FOR FURTHER STUDY

- Furthur study should be made of the formation of the metallic soaps in the presence of oxygen. It is suggested that a saturated acid, such as stearic acid, be used so that the action would be limited.
- 2. Separation and identification of the products of oleic acid exidation should be undertaken with a view towards establishing the structures produced.
- 3. The peculiar activity of antimony trifluoride should receive furthur study since it apparently inhibits the activity of oxygen and does not unite to any great extent with the acid to form soaps.
- 4. The effect of the elevated temperatures on the metallic fluorides should be determined.
- If metallic soaps are formed by double decomposition, hydrogen fluoride is a byproduct. An attempt should by made to verify its presence.

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> The methods and results of the reaction of glycerol plus fatty acids using fluoride catalysts.

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