Modification of Vegetable Oils. VII. Alkali Catalyzed Interesterification of Peanut Oil With Ethanol[1]

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THE alkali-catalyzed displacement of the glycerol in a fat by methanol or ethanol is an important reaction in fat and oil technology. Besides producing monoesters for use as such, the reaction simplifies the manufacture of some soaps, especially anhydrous soaps (2, 3); and it is valuable in conjunction with processes for fractionating fatty acids. Potentially the reaction is important in producing mono- and diglycerides of unsaturated acids, and it presents interesting possibilities in the field of "tailor-made" fats.

In a typical large-scale operation alcoholysis (the type of interesterification under discussion) is carried out in an open kettle by mixing substantially neutral fat with approximately 1.6 equivalents of anhydrous methanol or ethanol in which has been dissolved a fraction of 1% (on an oil basis) of sodium or potassium hydroxide. Mixing is discontinued when the solutions become homogeneous. After standing an hour or two at 80° C. the free glycerol which has separated and settled to the bottom of the tank is withdrawn, and the monoesters are purified by washing with water.

The alcoholysis reaction as described above has been discussed in several publications; however, a number of interesting questions have been left unanswered, and some of the conclusions reported are at variance with those reached by the present authors. Toyama and co-workers (10) found that the reaction rate of alcoholysis increases with temperature, but no quantitative data were offered to indicate the extent of this acceleration or its effect on the composition of the reaction product. Wright, *et al.* (14), investigated the ethanolysis of cottonseed and coconut oil with the idea of establishing the effect of the variables, ethanol, water, and alkali, on the yield of glycerol. Their primary interest was to show exactly how various amounts of water lowered the glycerol yield and how excess sodium hydroxide and/or alcohol compensated in some measure for the presence of water. They did not report reaction times and temperatures; and, like Toyama and co-workers, stated the reactions were complete in an hour or two. Bradshaw (2) described the process of alcoholysis in connection with the preparation of soaps and recovery of glycerol but presented very little experimental data.

Several investigators (4, 6, 9), employing conditions other than those described above, have found that when alcohol, fat, and alkali are allowed to interact, the acetyl value of the fatty portion obtainable from such a mixture increases to a maximum value and then decreases with time; and there is agreement as to the different types of compounds to be found in a reacting mixture. It has been claimed by Toyama and Tsuchiya (11) that the acetyl value of the reaction product is independent of the extent of alcoholysis. However, as far as the present authors are aware, no data have heretofore been presented to show the actual composition of a reacting mixture or the change in composition of the interesterification mixture as alcoholysis proceeded.

In the present report data are presented to show the actual rate of alcoholysis and how it is affected by the concentration of catalyst and alcohol as well as the rate of catalyst disappearance through saponification. In addition, the formation of mono- and diglycerides during the course of alcoholysis is discussed, and an attempt is made to elucidate the mechanism of the reaction in terms of the composition of the reaction product.

Experimental

Preparation of Reactants. In the work reported here a single lot of peanut oil was employed. This oil was prepared from a representative sample of crude oil by refining heavily with caustic soda solution in the customary manner, filtering out all soap particles, washing several times with hot distilled water, and bleaching with 6% of neutral activated clay. To insure thorough removal of the last traces of water the bleached oil was stripped with hydrogen while under a partial vacuum and at a temperature of approximately 100° C. The finished oil had a free fatty acid content of 0.02% and a hydroxyl value of 2.8. After saponifying the oil, the glycerol yield, determined by the method mentioned below, was 10.52%. The mean molecular weight of the fatty acids obtained from the oil after saponification was 281.7. Since the free fatty acids had no hydroxyl value, it was assumed the oil contained 96.9% of triglycerides having a mean molecular weight of 883.1 and 3.1% of diglycerides having a mean molecular weight of 619.5.

Absolute ethanol was used in all the interesterification experiments. The commercial product was refluxed with sodium and ethyl phthalate according to the method of Manske (7) to remove the last traces of moisture. Sometimes a preliminary dehydration with sodium was necessary. The dehydrated alcohol contained less than 0.05% water by the acetylene-cuprous chloride method of Weaver (12), which is generally applied as a qualitative test but can be made approximately quantitative by adding a known amount of water to a series of samples.

The sodium hydroxide employed was of reagent grade and contained 98.7% sodium hydroxide by analysis, the remainder being almost entirely sodium carbonate.

Equipment. The interesterifications were carried out in a 2-neck, 500-ml. capacity, round-bottom Pyrex flask which was immersed almost completely in a water bath. The bath was agitated and electronically controlled to maintain a temperature within ± 0.1° C. of that desired. Agitation of the oil solution was accomplished by a stainless steel paddle type

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stirrer inserted through a stuffing box in one of the necks. Tests showed the bath and oil temperatures always agreed within about 0.1° C., except in those instances which are discussed below.

Method of Interesterification. For each experiment alcoholic sodium hydroxide solution of the desired strength was freshly prepared; and approximately the amount required for 100 g. of oil was transferred, with precautions at each step to exclude atmospheric moisture, to a small separatory funnel-like container. The weight of the transferred solution was accurately determined and corrected for drainage; then the corresponding amount of peanut oil was weighed into the reaction flask. Air which remained in the reaction flask was flushed out with dry nitrogen, and the flask was sealed and immersed in the constant temperature bath. The vessel containing the alcoholic sodium hydroxide was also warmed. When both reactants reached the temperature at which the experiment was to be conducted, the agitator in the reaction flask was started and the alcoholic sodium hydroxide was added quickly. The flask was again sealed and the reaction conducted under dry nitrogen at atmospheric pressure. The reaction was stopped at the proper time with 100 ml. of aqueous acetic acid solution, the concentration of which was adjusted so that 100 ml. contained sufficient acetic acid to react with the free alkali and soap present and provide an excess of 1.0-1.5 g. of acid.

Analysis of the Reaction Product. The oil-water mixture obtained at the moment the reaction was stopped was washed with distilled water or a dilute solution of sodium chloride, and the wash water was analyzed for free glycerol using a slight modification of the periodic acid oxidation method developed by Pohle, Mehlenbacher, and Cook (8) for determining monoglyceride content. The fatty portion, after drying and filtering, was analyzed for monoglyceride content by the method of Pohle, *et al.*, or by a modification of this method (5). The hydroxyl value of the fatty portion was determined by the acetic anhydride-pyridine method of West, Hoagland, and Curtis (13). The content of free fatty acid was determined in the usual manner (1). The data provided by these determinations when used in conjunction with those obtained on the original oil made it possible to calculate the composition of the reacting mixture at the time the alcoholysis was stopped.

Influence of Catalyst and Ethanol Concentration on Glycerol Yield. Establishment of the fact that the reactants involved in alcoholysis are or are not present as a single phase during a given reaction is of primary importance in evaluating the influence of the concentration of alcohol and catalyst on glycerol yield; therefore, as a preliminary step to the actual alcoholysis investigations, the solubility of ethanol in peanut oil was determined at different temperatures. The data obtained are reproduced in Figure 1. Since 15.65 g. of ethanol is required theoretically to react with 100 g. of the peanut oil used, it is evident that reactions conducted at 50° C. with 2 equivalents or less of alcohol per equivalent of fat are carried out in solutions in which the reactants are present in a single homogeneous phase.

Actually, Figure 1 represents a minimum solubility curve. As soon as alcoholysis commences, ethyl esters and soap are produced. Ethanol is quite soluble in the ethyl esters, and the soap acts as a blending agent for alcohol and fat-like products. In fact, in all experiments presented here the alcoholic sodium hydroxide and fat formed a perfectly clear and homogeneous solution within 2-15 seconds after addition of the alcoholic sodium hydroxide.

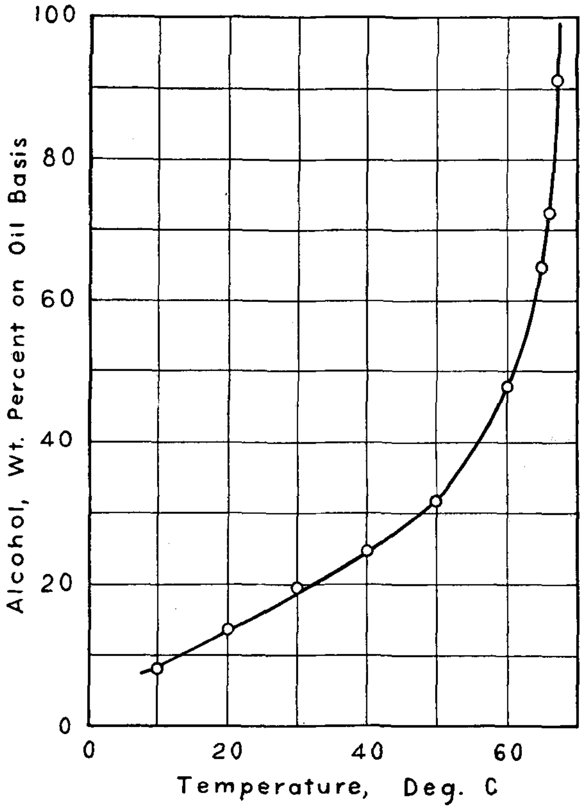

FIG. 1. Amount of ethanol miscible with peanut oil at different temperatures.

To determine the influence of catalyst and ethanol concentration on the free glycerol obtained by alcoholysis, several series of runs were made at 50° C. In each series a specific concentration of ethanol and sodium hydroxide was adhered to. The individual experiments in a series were stopped after various reaction times and analyzed for free glycerol content. The results are shown in Figure 2. A striking feature of the group of curves in Figure 2 is the sudden change in the rate of glycerol formation after a reaction time of about 15 minutes. Since the same change occurs with different concentrations of catalyst and alcohol, other than simple mass law considerations must be involved. Another fact evident from the curves is that under certain conditions considerable alcoholysis occurs after one or two hours. From other data not reproduced here it appears that alcoholysis may continue practically indefinitely but, of course, at a constantly diminishing rate.

No glycerol yields were determined for reaction times of less than five minutes because of the rapid changes in temperature during the first few minutes. On addition of the alcoholic sodium hydroxide solution to the peanut oil the temperature dropped from 1° to 5° C. in one minute or less because of the negative heat of solution of the alcohol. At this point the exothermic heat of the alcoholysis reaction became appreciable and raised the temperature of the reacting mixture to equal or exceed by one or two degrees that of the constant temperature bath. After about four or five minutes the temperature of the reacting mixture decreased to that of the water bath.

In most instances the physical condition of the reacting systems changed with time. The series employing two equivalents of alcohol to one of oil and 0.4% sodium hydroxide on a fat basis is typical and is described as follows:

When the alcoholic sodium hydroxide was added during a period of 12 seconds, the reacting mixture became perfectly clear within one or two seconds after the addition was completed. About 1½ minutes after the addition of alcohol was begun, the mixture suddenly became turbid as a result of separation of the glycerol from solution. The turbidity rapidly increased to a maximum value and then decreased slowly, and after 40 minutes the reaction mixture was only slightly turbid. Undoubtedly when the glycerol phase appeared, some alcohol dissolved in it and hence left the reaction zone; however, this quantity must have been small for the appearance and disappearance of a glycerol phase had no discernible effect on the rate of glycerol formation. In the series involving a 1:1 ratio of alcohol to fat and 0.2% sodium hydroxide, glycerol never separated out of solution.

Effect of Temperature. The temperature range in which interesterification of peanut oil with ethanol can be conducted at atmospheric pressure covers roughly 80° on the centigrade scale, the lower limit of which is set by the solidification point of the oil and reaction products, whereas the upper limit is determined by the boiling point of the alcoholic solution. The preferred temperature has generally been in the upper part of this range because of the logical claim that an increase in temperature increases the rate of alcoholysis.

To establish the extent of this temperature effect three experiments were made at temperatures of 30°, 50°, and 70° C., respectively. An alcohol concentration of two equivalents of alcohol to one of oil and a catalyst concentration of 0.2% sodium hydroxide on an oil basis was chosen for these tests because these conditions normally produce a glycerol yield of approximately 55% in 20 minutes. Temperature effects should be most marked for a reaction of this rate. The glycerol yield-temperature data obtained are presented in Figure 3.

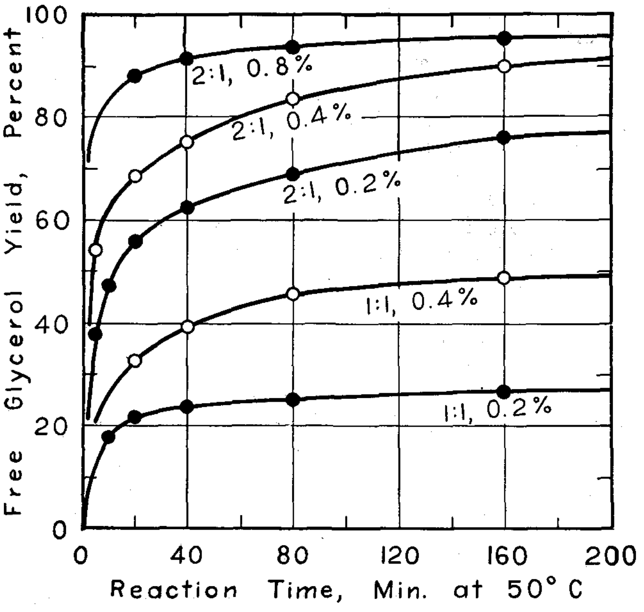

FIG. 2. Glycerol yields under various conditions of alcoholysis. The ratios given indicate the number of equivalents of ethanol reacted with one equivalent of peanut oil. The percentages given indicate the amount of sodium hydroxide (on an oil basis) employed as catalyst.

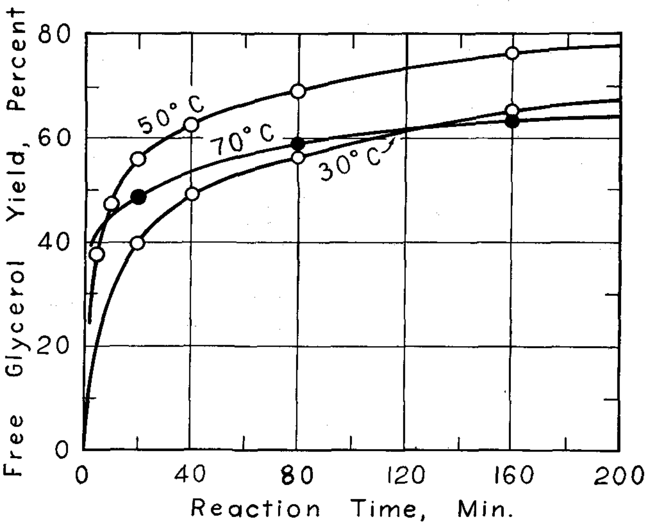

FIG. 3. Variation of glycerol yield with temperature. All reactions were conducted with two equivalents of ethanol per equivalent of oil and 0.2% sodium hydroxide on an oil basis.

Of the curves relative to the three yields the one obtained at 70°C. shows the smallest slope or reaction rate after the first 10 minutes, and the points plotted on this curve lie below those on the curve of the reaction at 50° C.; nevertheless, from the slope of the curve it is reasonable to assume that for the first few minutes of reaction time the rate of alcoholysis is greatest at 70° C. The maximum glycerol yield, however, appears to be obtained at 50° C. Further tests with longer reaction times substantiated this probability. The glycerol yield at 70° never increased much beyond that shown. Incidentally, no glycerol separates out of solution at 70° C. The glycerol yield at 30° C. never exceeded that obtained at 50° C. A reaction time of 16 hours gave a glycerol yield of 86.0% at 30° C. and a yield of 91.0% at 50° C. In other words, there is an optimum temperature for the interesterification of peanut oil with ethanol, and this temperature lies close to 50° C.

Disappearance of Catalyst. When the end products from a number of alcoholysis reactions were analyzed and when the quantities of free fatty acids found in the products were used to calculate the amounts of sodium hydroxide destroyed during the course of each reaction, it became apparent immediately why the curves for the yield of glycerol shown in Figure 2 break so sharply at reaction times of about 15 minutes. The analyses showed that in every instance 50% or more of the sodium hydroxide was destroyed in the first 15-20 minutes. Under these conditions the rapid decrease in the rate of alcoholysis is the cumulative effect of at least two factors, namely, the decrease in the concentration of the reactants and the destruction of the catalyst for the reaction. It explains why the alcoholysis reaction virtually ceases at different levels of glycerol yield. The rapid destruction of catalyst also explains the existence of an optimum temperature with respect to glycerol yield, *i.e.*, the alcoholysis reaction and the reaction involved in the destruction of catalyst respond differently to temperature changes.

It was found that after alcoholysis has proceeded for about 20 minutes the rate of catalyst destruction proceeds at a greatly reduced rate. For example, when one equivalent of oil is interesterified with two equivalents of ethanol at 50° C. in the presence of 0.8% sodium hydroxide, 60.2% of the sodium hydroxide is removed from the reaction in 20 minutes and 75.2% is removed in 160 minutes. Often this reduced rate remains practically constant over appreciable periods of time.

Figure 4 shows two examples of the actual amounts of sodium hydroxide consumed during the course of alcoholysis under conditions which are identical except for the original concentration of catalyst. Curves showing the extent of alcoholysis are also plotted for comparison of the percentage of the completion of alcoholysis with the percentage of catalyst consumed.

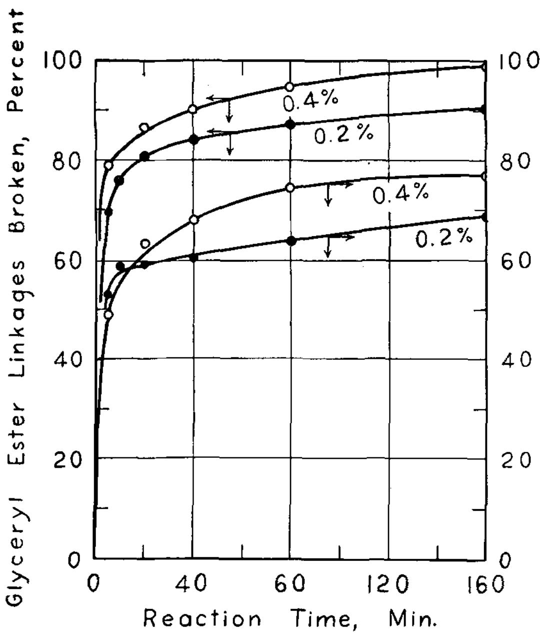

FIG. 4. Catalyst consumed *vs.* reaction time and extent of alcoholysis *vs.* reaction time for two series of reactions. Both series were conducted at 50° C. with two equivalents of ethanol per equivalent of peanut oil. The catalyst concentration for each series is as shown and is calculated on an oil basis.

Table I gives the amounts of catalyst destroyed after a reaction time of 20 minutes under various conditions. These data show that the lower the temperature, the less is the amount of catalyst destroyed. It also shows that as the alcohol concentration is increased, the amount of catalyst destroyed is decreased.

TABLE 1

Amounts of Sodium Hydroxide Catalyst Destroyed After Ethanolysis of Peanut Oil Has Proceeded for 20 Minutes

Orig. Catalyst Conc.,[a] %	Alcohol to Fat Ratio[b]	Temp., °C.	Catalyst, Consumed, %	Glycerol Yield,[c] %	Glyceryl Linkages Broken,[d] %
0.1	1:1	50	90.4	16.1	49.6
0.2	1:1	50	85.2	24.2	57.7
0.4	1:1	50	89.9	32.9	62.7
0.2	2:1	50	59.0	56.0	80.9
0.4	2:1	50	63.2	68.8	86.8
0.8	2:1	50	60.2	88.1	96.7
0.2	2:1	70	98.4	48.9	76.3
0.2	2:1	30	52.4	39.8	69.0

[a] Calculated on an oil basis.
[b] Expressed in equivalents of alcohol per equivalent of fat.
[c] Expressed as per cent of the maximum amount obtainable.
[d] Equal to per cent completion of the alcoholysis reaction.

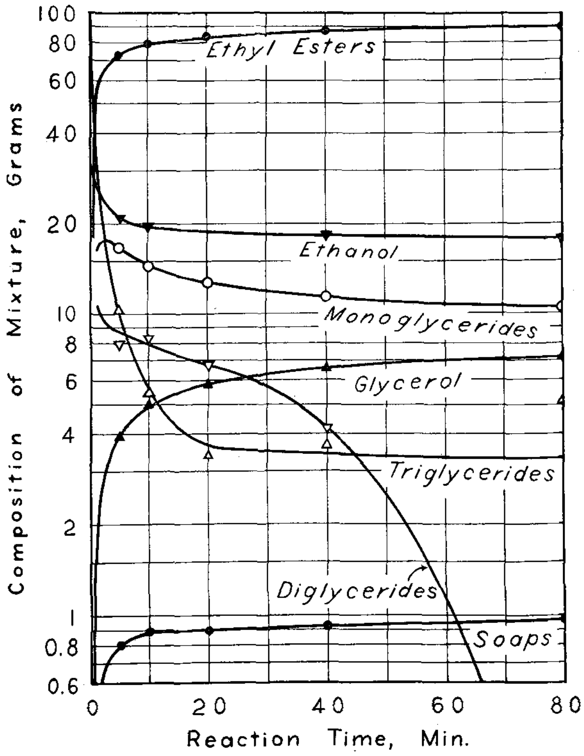

FIG. 5. Composition of product *vs.* time when 100 g. of peanut oil, 31.30 g. of ethanol, and 0.2 g. of sodium hydroxide are allowed to react at 50° C. The ratio of alcohol to oil provides two equivalents of alcohol per equivalent of oil.

However, the most significant fact brought out by these data is that under a given set of conditions the fraction of catalyst destroyed is practically independent of the amount of catalyst originally present.

Composition of the Reaction Products. In all of the alcoholysis experiments conducted in the course of the present investigation the end products were analyzed to establish the composition of the reacting mixture at the time alcoholysis was stopped. Data from one series of experiments are reproduced in Figure 5. The sodium hydroxide content could not be shown conveniently in Figure 5 and therefore is not given; however, it can easily be calculated from the soap content.

Table II contains data for a second series of experiments which are similar to the first series except for the fact that in the second series the catalyst concentration is twice that in the first. As a result, the reaction rate is faster in the second series. Table 2 also shows the percentage of completion of the alcoholysis reaction at different times.

The fact that alcoholysis can proceed rapidly and smoothly to practical completion, even when all products are present as a single homogeneous phase, suggests that ordinarily the reverse reactions have no significant effect on the composition of the reaction product. If this is true, then the fact that glycerol does or does not separate from solution during the course of reaction should have no bearing on the relative proportions of the reaction products. Under such a situation it was considered desirable to compare the actual composition of the various products with a theoretical composition calculated on the assumption that the glyceryl ester linkages originally present are broken in a random fashion. When only triglycerides are present at the beginning of the

TABLE 2

Composition of Product Obtained by Ethanolysis of Peanut Oil at 50° C.

Reaction Time, Min.	Weight of Components, in Grams								Glyceryl Linkages Broken,[a] %	Free Glycerol Yield,[b] %
	Mono-	Di-	Tri-	Ethyl Ester	Glycerol	Ethanol	Soaps	NaOH		
0[c]	0.00	3.1	97.10	0.0	0.00	31.3	0.00	0.400	0.0	0.0
5	13.40	3.8	7.36	81.4	5.71	19.2	1.48	0.205	78.9	54.3
20	9.65	2.8	3.46	89.3	7.24	18.0	1.92	0.147	86.8	68.8
40	7.96	1.1	3.36	92.5	7.94	17.6	2.06	0.129	90.0	75.5
80	5.26	2.9	0.00	97.3	8.82	16.8	2.27	0.102	94.8	83.8
160	3.94	0.8	0.00	101.5	9.47	16.2	2.34	0.092	98.9	90.0

[a] Equal to per cent completion of alcoholysis.
[b] Calculated as a percentage of the maximum amount obtainable.
[c] The amount of reactants present at the start are given in this line. The ethanol to oil ratio corresponds to two equivalents of ethanol per equivalent of oil.

alcoholysis, this theoretical composition is represented statistically by the random distribution of different proportions of two elements in combinations of three. Actually, the peanut oil used in these experiments contained about 3% of diglycerides. Since this amount of diglycerides has only a negligible effect (less than 1%) on the theoretical calculations in the regions under comparison, the more general case of 100% triglycerides was used as the basis for the theoretical calculations.

Comparison of such a theoretical composition with the composition actually found is presented graphically in Figure 6. The plotted points represent experiments conducted for different lengths of time using various temperatures, catalysts, and ethanol concentrations. The agreement between the actual and theoretical values is reasonably close. When all factors are considered, it is logical to assume that the glyceryl ester linkages are mostly broken in a random fashion.

The divergence observed might be attributed to any of a number of possible factors. For instance, the alcoholysis reaction is extremely fast at the start; and, during the few seconds required for the reactants to become homogeneous, alcoholysis may have proceeded to a considerable extent in isolated portions of the mixture. Also, it is well known that in the presence of soaps, monoglycerides and diglycerides decompose to yield glycerol and triglycerides. In this connection it is possibly significant that the products containing relatively large proportions of soaps and monoglycerides diverge furthest from the theoretical values. It is also possible that the sodium hydroxide destroyed is lost principally through preferential saponification of mono- and diglycerides since the destruction of catalyst is greatest when the mono- and diglyceride concentration is greatest.

Summary

1. The alcoholysis of peanut oil with ethanol, using sodium hydroxide as catalyst, has been investigated under conditions suitable for large-scale operations.

2. Data are presented to show the effect of time and concentration of alcohol and catalyst on glycerol yield. It was found that most reactions do not cease in one or two hours.

3. The existence of an optimum temperature for alcoholysis has been established, and it is shown that this optimum temperature lies close to 50° C.

4. The actual rate of catalyst disappearance through saponification has been determined for different conditions. It is shown that the rate varies greatly with the reaction time and is highest when alcoholysis commences and appreciable quantities of mono- and diglycerides are present. In the first 20 minutes more than 50% of the catalyst originally present is destroyed.

5. The composition of some reacting mixtures have been followed as alcoholysis proceeded. Curves and a table are presented to show the actual amounts of monoglycerides, diglycerides, triglycerides, ethyl esters, glycerol, ethanol, soap, and sodium hydroxide present in the reaction mixture at various times.

6. Data are presented showing that the glyceryl ester linkages of a vegetable oil are broken in a reasonably random fashion during alcoholysis. This random distribution of broken and unbroken glyceryl ester linkages corresponds statistically to the

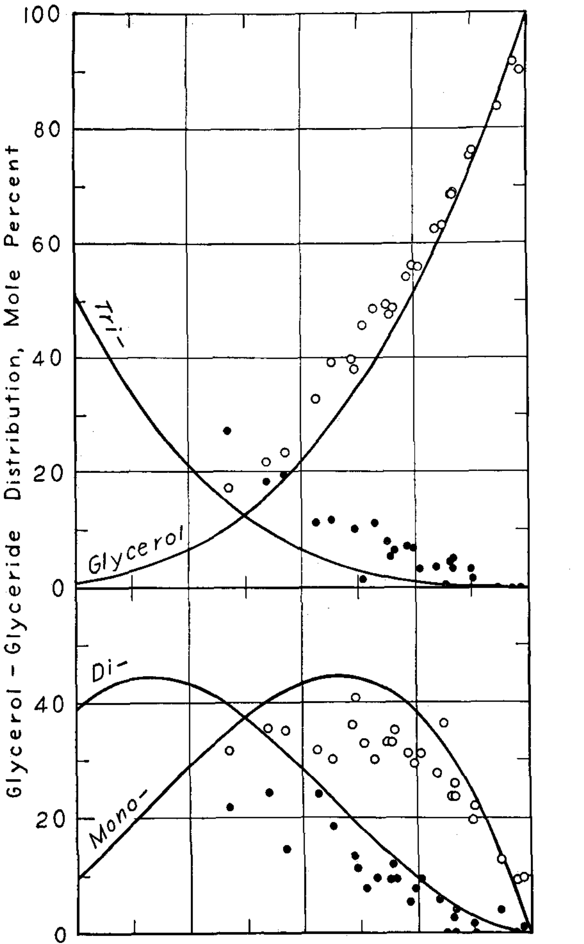

Fig. 6. Composition of glycerol-glyceride fraction in alcoholysis product *vs.* per cent completion of alcoholysis reaction. The curves represent theoretical values calculated on the assumption that glyceryl ester linkages are broken in a random fashion. The circles and dots represent values found experimentally.

random distribution of different proportions of two elements in combinations of three. The composition of the glycerol-glyceride fraction in the reaction product is determined by the fraction of glyceryl linkages broken. Reaction time, concentration of reactants and catalyst, and the temperature have no effect outside of determining the number of linkages broken.

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Semi-Micro Analysis of Soap. III. Semi-Micro Determination of Potassium.

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THE classical method for the determination of potassium involves precipitation of the potassium by chloroplatinic acid. This is the basis of the A.O.C.S. Official Method (1). In this laboratory we have secured consistently better reproducibility of results by precipitating sodium as the sodium uranyl zinc acetate (2, 3, 4) and determining potassium indirectly by difference. In addition, the "triple acetate" method, as it has been called, effects a decided saving in time. These facts have accordingly governed our choice of selecting the "triple acetate" method for use on a semi-micro scale. The presence of potassium in a soap can be readily ascertained by a flame test or by the use of p-dipicrylamine (5).

Semi-Micro Determination of Potassium in Soap

Reagents Required

Uranyl Zinc Acetate Solution. Prepare the following solutions:

a) Mix 10 grams of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, 6 grams of 30% acetic acid and 50 ml. of water and warm to dissolve.

b) Mix 30 grams of zinc acetate, $Zn\ (C_2H_3O_2)_2 \cdot 3H_2O$, 3 grams of 30% acetic acid and 50 ml. of water, and warm to dissolve.

Prepare the uranyl zinc acetate solution by mixing equal volumes of solutions a) and b), allowing to stand 24 hours, and then filtering off the precipitate of sodium uranyl zinc acetate usually formed from traces of sodium in the reagents. If no precipitate is formed, add a small amount of sodium chloride to saturate the solution with the triple acetate. Allow the solution to stand with occasional shaking at a controlled temperature of 18 to 20°C. for 12 hours, filter at 18 to 20°C. and use in the method at approximately the same temperature to avoid errors due to solubility changes.

95% Ethyl Alcohol (Saturated With Sodium Uranyl Zinc Acetate)

Shake 95% ethyl alcohol with a small portion of sodium uranyl zinc acetate at room temperature until saturated. The sodium uranyl zinc acetate may be prepared by precipitating sodium chloride with uranyl zinc acetate solution and washing the precipitate with small volumes of the precipitant.

Procedure

Ethyl Ether or Acetone

Transfer about 25 mg. of the sample, accurately weighed, to a 10-ml. beaker. If the sample is a liquid soap or one containing a high percentage of moisture, take sufficient sample to insure approximately 25 mg. of dry soap. Add 5 ml. of water and heat on the steam bath to complete solution. Transfer the solution quantitatively to a 25-ml. volumetric flask and bring to volume with water at room temperature. Transfer a 2-ml. aliquot, very carefully measured by a pipet, to a 10-ml. platinum dish. Evaporate to dryness on the steam bath. Ignite over a low Bunsen flame to complete charring. Add 2 ml. of water and warm on the steam bath to dissolve all soluble matter. Filter through a paper filter (No. 40 Whatman, 35 mm. in diameter) and wash the charred matter with hot water, catching the filtrate in a 25-ml. platinum dish. Return the filter paper and contents to the 10-ml. platinum dish and ash completely. Cool and dissolve the residue in hot water. Add the solution to the filtrate in the 25-ml. platinum dish. Evaporate to a volume of 1 ml. or less.

Add 10 ml. of uranyl zinc acetate solution previously kept at 18 to 20°C. for several hours, mix, and allow to stand for 30 to 60 minutes at 18 to 20°C. An improvised apparatus for maintaining the precipitation vessel at 18 to 20°C. is readily constructed as shown in Fig. 1. If available, a constant temperature bath may be employed instead.

Filter off the precipitate of sodium uranyl zinc acetate in a Gooch crucible, suck dry, and wash the precipitation dish, crucible, and precipitate with 5 to 6 small portions of the reagent, draining the crucible well each time.

Next, wash 5 times with 0.5-ml. portions of ethyl