virtually constant, to about ±1° C. There were no visible variations of pressure in the system except at intervals when vacuum was momentarily broken (by the admission of hydrogen) to permit withdrawal of a sample. The complete apparatus is depicted in Figure 1.

All experiments were carried out with mixed fatty acids derived from peanut oil which had an iodine value of 94.4; the acids had an average molecular weight of 285.0. The glycerine used was of C.P. grade, and contained 94.7% glycerol, by analysis. Equivalent proportions of fatty acids and glycerol were used in all the experiments.

Kinetics of the Uncatalyzed Reaction

A SERIES of uncatalyzed esterifications was carried out at 20 mm. pressure and varying temperatures. The progress of the reaction in each case, in terms of the free fatty acid content of the reacting material at specified times is shown in Table 1.

TABLE 1

Esterification at different temperatures (°C.) of equivalent proportions of glycerol and mixed fatty acids from peanut oil.
(At 20mm. pressure.)

Reaction time, hrs.	Free fatty acid content of reaction mixture, percent						
	166°	178°	190°	204°	216°	225°	241°
0	90.3	90.3	90.3	90.3	90.3	90.3	90.3
1	83.0*	83.5	75.5	67.8	79.2	82.2	54.3
1-1/3	73.7	68.5*	58.4*	48.8	60.2	57.4	33.2
1-2/3	66.1	57.2	46.1	36.9*	40.1*	37.4	23.2*
2	60.0	49.9	39.0	30.1	29.5	27.6*	17.5
2-1/3	55.0	44.2	34.0	26.0	24.0	22.1	14.5
3	47.2	36.3	27.6	20.7	18.2	16.2	11.0
4	39.4	29.0	21.9	16.4	14.0	12.2	8.47
5	34.0	24.5	18.5	13.7	11.6	9.91	7.05
6	30.0	21.4	16.2	12.0	10.1	8.31	6.03
7	26.9	19.1	14.5	10.7	8.98	7.15	5.34
8	24.5	17.3	......	......	......	......	......

*First sample after batch had reached operating temperature.

In the experiments of this series plots of the reciprocal of the free fatty acid concentration against elapsed reaction time yield straight lines (Figure 2); this indicates that the reaction is of the second order.

In each case, however, the course of the reaction clearly may be resolved into two successive stages consisting of a period of relatively rapid disappearance of free fatty acids followed by a period during which esterification of the acids proceeds less rapidly. The velocity constant, *k*, corresponding to each stage may be determined graphically, from plots similar to those of Figure 2 and the well known equation for bimolecular reactions involving equivalent initial concentrations of the reactants,

$$t = \frac{1}{k}\left(\frac{1}{a-x}\right) - \frac{1}{ka} \qquad (1)$$

where t = reaction time, a = initial concentration of one of the reacting substances, and x = amount of that substance reacting in time, t.

The velocity constants corresponding to the initial and final stages of the reaction at each temperature and the point at which the reaction velocity changes in each case are listed in Table 2. Since the data obtained are intended for practical use, for calculation of the velocity constants concentrations have not been expressed conventionally in moles per liter but in the more convenient terms of moles of fatty acids per 100 g. of the reaction mixture. Time is expressed in hours; the velocity constant *k*, therefore, has the dimensions, 100 g. moles^{-1} hours^{-1}. The effect on the concentration of progressive loss of water from the reacting materials has been disregarded. On a weight basis the loss corresponding to complete esterification would amount to 5.7% of the original reaction mixture. Over the range of esterification covered in the experiments the possible corrections introduced by consideration of this factor are probably less than the experimental error of the method.

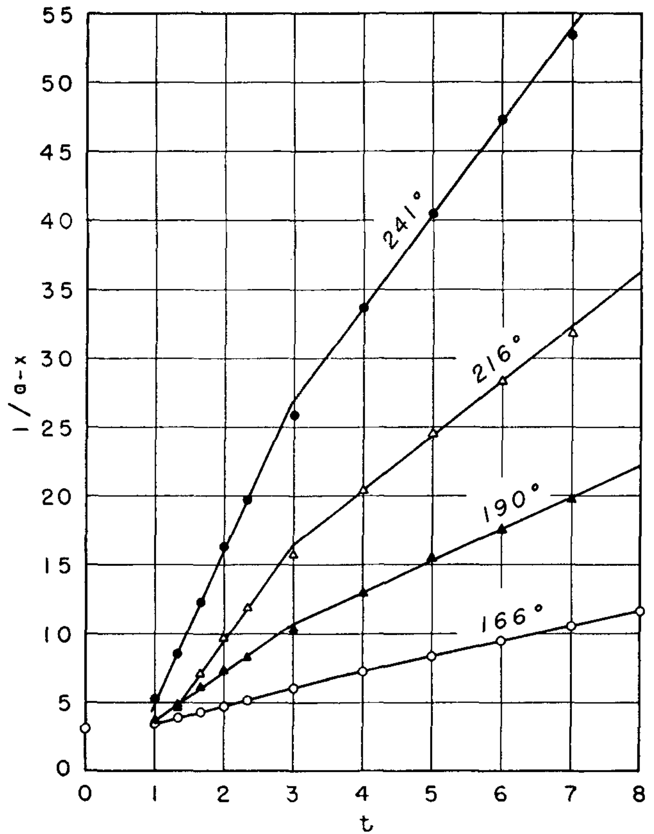


FIG. 2. Curves showing bimolecular nature of the uncatalyzed reaction at various temperatures (°C.). Reciprocal of free fatty acid concentration (moles per 100 g.) *vs.* reaction time (hours).

TABLE 2

Esterification of equivalent proportions of glycerol and peanut oil fatty acids at 20 mm. pressure: Velocity constants (100 g. moles^{-1} hours^{-1}) of the initial and final stages of the reaction, and concentration of free fatty acids in the mixture corresponding to the end of the first stage.

Temp. °C.	Velocity constant, *k*		FFA concentration percent, at end of initial stage	
	Initial stage	Final stage	On basis entire reaction mixture	On basis original FFA conc.
166	1.32	1.11	42.7	47
178	2.21	1.70	33.8	37
190	3.53	2.28	27.1	30
204	4.92	3.19	20.3	22
216	6.97	3.93	17.6	19
225	7.93	5.61	18.2	20
241	10.49	6.69	10.5	12

It is evident from the experimental data, as represented in Figure 2, that the reaction velocity constant changes somewhat gradually rather than abruptly as the reaction progresses from the first into the second stage. However, for convenience in assigning a numerical value to the free fatty acid concentration at which the change occurs, the point of change has been taken at the intersection of the two straight lines resulting from plotting t against $\frac{1}{a-x}$ for each experiment (cf. Figure 2).

As the temperature of esterification is increased, there is a progressive decrease in the free fatty acid concentration at which change in the velocity constant occurs. This concentration, expressed in terms of the original concentration of free fatty acids, varies from about 47% at 166° C. to 12% at 241° C. Presumably, the step-wise character of the reaction is related to the circumstance that glycerol is a trihydric alcohol and thus may successively form mono-, di-, and triglycerides. At present, however, no complete explanation can be offered, either of the two-stage nature of the reaction, or of the above mentioned effect of temperature.

The relationship between the velocity constant, *k*, and the absolute temperature, *T*, is given by the Arrhenius equation,

$$k = se^{\frac{-\Delta H_a}{RT}} \qquad (2)$$

where *s* is a constant, the so-called frequency factor; *R* is the molar gas constant, equal to 1.987 calories degree^{-1} mole^{-1}; and ΔH_a is the heat of activation, in terms of calories mole^{-1}. Equation *(2)* may also be written in the form,

$$\log k = \left(\frac{-\Delta H_a}{2.303\,R}\right)\left(\frac{1}{T}\right) + \text{constant} \qquad (3)$$

hence by plotting logarithms of the experimentally determined velocity constants against the reciprocal of the absolute temperature a straight line should be produced with a slope equal to $\frac{-\Delta H_a}{2.303\,R}$. Such a plot is shown in Figure 3. Points corresponding to both the initial and final stages of each esterification experiment do in fact fall quite closely upon straight lines. The heats of activation, determined from the slopes of the lines as calculated by the method of least squares were 12,300 calories mole^{-1} for the initial stage of the reaction and 10,800 calories mole^{-1} for the final stage. These values are of the same order of magnitude as those which have been reported for the esterification of fatty acids with monohydric primary alcohols (5, 8, 14) (10,000 to 15,000 calories mole^{-1}) and the value of 10,652 calories mole^{-1} found by Blagonravova and Lazarev (2) for the heat of activation in the esterification of C_{18} fatty acids with pentaerythritol.

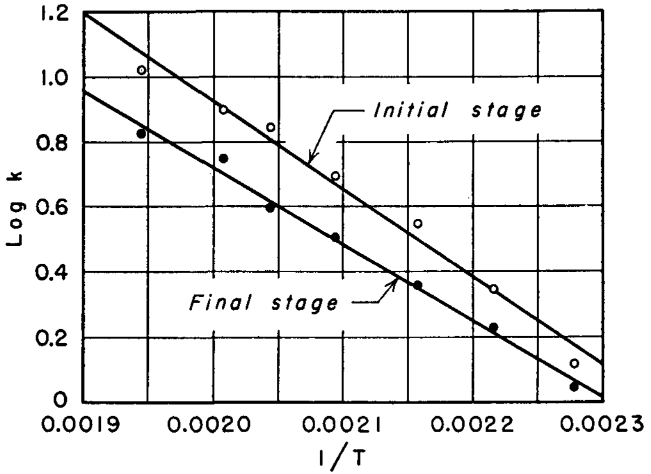


FIG. 3. Correspondence of experimental data (uncatalyzed reaction) with Arrhenius equation. Logarithm of velocity constant, *k*, *vs.* reciprocal of absolute temperature.

From Equation *(2)* and the preceding values for the heat of activation, equations can be derived which will predict the velocity constants at any temperature. These equations are as follows:

For k_i, the velocity constant of the initial reaction,

$$k_i = 2.00 \times 10^6\, e^{\frac{-12{,}300}{1.987T}} \qquad (4)$$

For k_f, the velocity constant of the final reaction,

$$k_f = 2.77 \times 10^5\, e^{\frac{-10{,}800}{1.987T}} \qquad (5)$$

Catalytic Effect of Various Metallic Oxides and Salts

A VARIETY of metallic oxides and salts were tested for catalytic activity by conducting a series of esterifications at 200° C. and 20 mm. pressure and employing as a catalyst in each case the desired compound in the amount of 0.0008 mole per 100 g. of fatty acids. Results of these tests are shown in Table 3, the catalytic effect of each substance being stated in terms of the free fatty acid content of the reaction mixture at the end of specified reaction times.

TABLE 3

Catalytic effect of various compounds in the esterification of glycerol and peanut oil fatty acids. All reactions carried out at 200° C. and 20 mm. pressure with 0.0008 mole of the compound per 100 g. fatty acids.

Catalyst	g. compound used per 100 g. FA's	g. metal per 100 g. FA's	FFA content of mixture, percent at end of specified reaction time		
			2 hrs.	4 hrs.	6 hrs.
Control	none	none	41.8	21.6	16.1
$AlCl_3 \cdot 6H_2O$	0.193	0.022	39.2	22.2	17.1
Al_2O_3[a]	0.082	0.043	39.6	20.9	15.1
SnO_2[a]	0.121	0.095	42.1	21.1	15.2
$SbCl_3$	0.183	0.097	33.1	20.2	15.2
$HgCl_2$	0.217	0.160	38.3	20.0	15.0
FeO[a]	0.058	0.045	38.0	19.2	13.9
$NiCl_2 \cdot 6H_2O$	0.190	0.047	36.8	18.6	13.8
NaOH	0.032	0.018	39.1	19.5	13.8
$MgCl_2 \cdot 6H_2O$	0.163	0.019	40.5	19.2	13.7
MgO	0.032	0.019	37.6	18.3	13.6
$MnCl_2 \cdot 4H_2O$	0.158	0.044	38.4	18.4	13.2
$PbCl_2$[a]	0.222	0.166	37.7	17.5	12.0
ZnO	0.065	0.052	30.9	15.0	11.8
$FeCl_3 \cdot 6H_2O$	0.216	0.045	32.5	14.9	11.4
$CdCl_2 \cdot 2\frac{1}{2}H_2O$	0.183	0.090	32.5	14.8	11.0
PbO	0.178	0.166	35.7	16.3	10.9
MnO_2	0.070	0.044	34.8	15.8	10.8
$ZnCl_2$	0.109	0.052	26.5	7.8	3.5
$SnCl_2 \cdot 2H_2O$	0.180	0.095	8.2	3.5	2.8
$SnCl_4 \cdot 5H_2O$	0.280	0.095	11.3	3.2	2.4
HCl	0.058[b]	……..	37.4	18.9	13.8

[a] Did not dissolve completely in reaction mixture.
[b] 0.0016 mole per 100 g. fatty acids.

Although some degree of activity was exhibited by a number of compounds, the ones which were outstandingly effective as catalysts were zinc and tin chlorides. Further work with catalysts was accordingly confined to the use of these materials.

Reesterification Using Tin and Zinc Chlorides as Catalysts

A SERIES of esterifications was carried out at 20 mm. pressure and at various temperatures in which 0.0008 mole of substantially anhydrous zinc chloride ($ZnCl_2$) per 100 g. of fatty acids was used as a catalyst. A similar series was carried out with the use of an equivalent concentration of stannous chloride ($SnCl_2 \cdot 2H_2O$) as a catalyst. Results of these experiments are shown in Table 4.

TABLE 4

Esterification of glycerol and peanut oil fatty acids at 20 mm. pressure and various temperatures, employing zinc and stannous chlorides as catalysts.

Reaction time, hrs.	Percent FFA in reacting material at end of reaction times indicated; temp. of reaction in °C.							
	Zinc chloride				Stannous chloride			
	250°	225°	200°	175°	225°	200°	175°	150°
0	90.3	90.3	90.3	90.3	90.3	90.3	90.3	90.3
1	88.3	83.4	84.6	82.3*	67.2	68.6	78.0*	83.7*
1-1/3	......	53.6	54.8*	64.4	23.4*	30.9*	49.8	71.8
1-2/3	......*	23.7*	36.5	52.9	6.3	16.0	34.8	63.7
2	8.4	13.8	26.5	44.1	3.9	9.3	25.5	55.7
2-1/3	......	9.2	20.1	37.4	......	5.8	19.3	49.4
3	2.8	5.5	13.0	26.1	......	3.1	12.0	39.3
4	......	......	7.8	21.4	......	1.8	6.8	31.8
5	......	......	5.1	16.4	......	......	4.5	25.8
6	......	......	3.5	12.9	......	......	3.5	21.4
7	......	......	......	10.2	......	......	2.9	18.1
8	......	......	1.3	8.2	......	......	......	......
13	......	......	......	2.9	......	......	......	......

*First sample after batch had reached operating temperature.

It is evident that in the presence of tin or zinc chlorides esterification follows an entirely different course from that of the uncatalyzed reaction or of the reaction catalyzed by other compounds, including other metal chlorides. The course of reaction with any catalyst other than tin chloride or zinc chloride is similar to that of the uncatalyzed reaction; a plot of t against $\frac{1}{a\text{-}x}$ yields a curve consisting of two successive straight lines. In the case of the reactions catalyzed with either zinc chloride or tin chloride a similar plot produces a line which is continuously concave upward from the time axis (Figure 4).

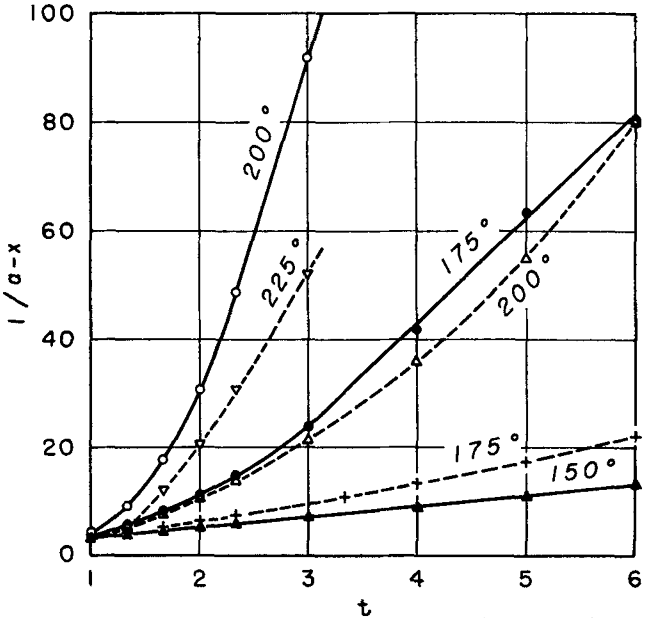
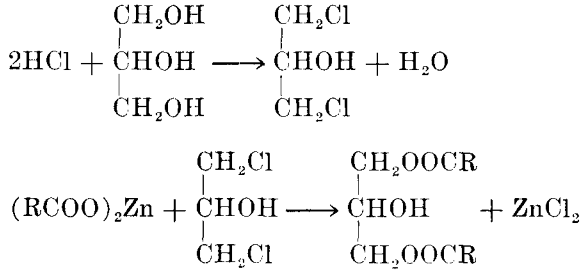


FIG. 4. Deviation of the stannous chloride (solid lines) and zinc chloride (dotted lines) catalyzed reactions from the second order. (Deviation from linearity of reciprocal of free fatty acid concentration, $1/a\text{-}x$, plotted against reaction time, t).

When the partially esterified reaction mixture of glycerol, fatty acids, and zinc chloride or tin chloride was extracted with hot water and the extract concentrated by boiling off the water, hydrogen chloride was evolved. This appeared to indicate that there was present an organic chlorine compound which was either water-soluble or easily hydrolyzed. When a mixture containing a high concentration of zinc chloride (0.008 mole per 100 g. fatty acids) was reacted with 20% excess of fatty acids and the reaction product distilled at 200°-220° C. and 2 mm. pressure with the aid of a current of hydrogen, the oily distillate gave no test for chlorides upon boiling with water, and only a doubtful test after sodium fusion. A similar product prepared with a 20% excess of glycerol yielded at 120°-140° C. and 2 mm. pressure a clear, white, water-soluble fraction, viscous and heavier than water, which gave a strong test for chlorides after fusion with sodium, and hence evidently contained chlorohydrins. It is believed that when tin chloride or zinc chloride is used as a catalyst, esterification takes place through the reaction of metallic soaps and chlorohydrins, according to the following typical equations:

$$ZnCl_2 + 2RCOOH \longrightarrow (RCOO)_2Zn + 2HCl$$



$$2HCl + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} + H_2O$$

$$(RCOO)_2Zn + \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} \longrightarrow \begin{array}{l} CH_2OOCR \\ | \\ CHOH \\ | \\ CH_2OOCR \end{array} + ZnCl_2$$

Effect of Pressure and of Catalyst Concentration

ESTERIFICATIONS were carried out at 200° C. with stannous chloride as a catalyst (0.0008 mole per 100 g. fatty acids), at 5 mm., 20 mm., and 80 mm. pressure to determine the effect of pressure on the reaction rate. Results of the experiments are shown in Table 5. Within the range of pressure covered, the reaction rate appeared to be little influenced by variations in pressure.

TABLE 5

Esterification of glycerol and peanut oil fatty acids at 200° C. with stannous chloride as a catalyst: Effect of pressure on the reaction rate.

Reaction time, hrs.	FFA content of reacting material at end of specified reaction times, at pressure indicated		
	5 mm.	20 mm.	80 mm.
0	90.3	90.3	90.3
1-1/3	39.5*	30.9*	30.0*
1-2/3	19.8	16.0	16.1
2	10.6	9.3	10.6
2-1/3	6.6	5.8	7.8
3	3.3	3.1	......

*First samples after batch reached operating temperature.

A series of esterifications was also carried out at 200° C., and 20 mm. pressure, with zinc chloride in varying amounts, to determine the effect on the reaction rate of variations in the catalyst concentration. Results of the experiments are shown in Table 6. There was a progressive decrease in the rate of reaction as the catalyst concentration was decreased, and at the lowest catalyst concentration (0.0004 mole per 100 g. fatty acids) the reaction approached closely the two-stage bimolecular character of the uncatalyzed reactions.

Removal of Catalyst from the Esterified Product

SAMPLES of fat which had been esterified with zinc chloride and with tin chloride as catalysts were subjected to various treatments for removal of the catalyst, and thereafter tested by a quantitative

TABLE 6

Esterification of glycerol and peanut oil fatty acids at 200° C. and 20 mm. pressure with zinc chloride catalyst: Effect of concentration of catalyst on the reaction rate.

Reaction time, hrs.	FFA content of reacting material at end of specified reaction times, with conc. of catalyst (moles per 100 g. FA's) indicated		
	0.0004	0.0008	0.0016
0	90.3	90.3	90.3
1-1/3	59.8*	54.8*	47.5*
1-2/3	36.1	36.5	27.4
2	28.7	26.5	18.8
2-1/3	23.1	20.1	13.2
3	17.0	13.0	7.0
4	11.7	7.8	3.2
5	8.8	5.1	......
6	7.2	3.5	......
7	6.1	......	......
8	5.1	......	......

*First samples after batch reached operating temperature.

spectrochemical method for zinc and tin content. The treatments used included various combinations of ordinary alkali refining and bleaching with fuller's earth, washing with 20% sulfuric acid, and treatment with strong phosphoric acid according to the method of Eckey and Clark (4).

Analyses of the various treated samples are listed in detail in Table 7. The results indicate that ordinary caustic soda refining, alone or followed by bleaching with fuller's earth, can be depended upon to reduce the metal content of the esterified oils to negligible values. Treatment with strong phosphoric acid is an effective means of removing tin, but not of removing zinc from the products, whereas washing with dilute sulfuric acid effectively removes zinc but not tin.

TABLE 7

Metal content of fats esterified with zinc chloride and with tin chloride as catalysts, and subjected to various treatments for removal of the catalyst.

Processing treatment	Zinc content, percent; when $ZnCl_2$ was used as a catalyst	Tin content, percent; when $SnCl_2 \cdot 2H_2O$ was used as catalyst
None	0.036	0.116
Refined with NaOH, 0.40% excess	0.0001	$<$0.00032
Refined as above, and bleached with 4% B-C earth	$<$0.00001	$<$0.00032
Washed with 20% H_2SO_4	0.0001	0.0113
Washed as above, and refined with 0.40 excess NaOH	$<$0.00001	0.0006
Washed and refined as above, bleached with 4% earth	$<$0.00001	$<$0.00032
Treated with strong H_3PO_4	0.0094	$<$0.00032
Treated with H_3PO_4 as above, refined with NaOH	$<$0.00001	$<$0.00032

Effect of the Catalysts on Polymerization and Conjugation of the Oil and Color of the Esterified Product

A NUMBER of viscosity and iodine value determinations were made on different samples of oil, to determine whether the tin and zinc chloride catalysts caused polymerization of the oil during the esterification process. The complete data are contained in Table 8. It is evident from the relatively low viscosities of the esterified products and the small differences in iodine value among the various samples that neither of these catalysts had any appreciable tendency to cause the oils to polymerize.

TABLE 8

Viscosity and iodine value of oils prepared by esterification of peanut oil fatty acids with glycerol.

Sample	Viscosity at 210° F., centipoises	Iodine value
Peanut oil from which fatty acids were derived	7.79	91.6*
Mixture of equal parts alkali-refined and bleached oil from uncatalyzed esterifications, 7 hrs. and 20 mm., at 178°, 190°, and 216° C.	8.54	90.1
Alkali-refined and bleached oil from esterification at 200° C. and 20 mm. for 6 hrs., 0.0008 mole stannous chloride per 100 g. FA's used as catalyst	8.05	91.1
Alkali-refined and bleached oil from esterification at 225° C. and 20 mm., for 6 hrs., 0.0008 mole zinc chloride per 100 g. FA's used as catalyst	8.39	88.4

*Calculated from iodine value of separated fatty acids.

Samples of the oils were also examined spectroscopically to determine whether the catalysts were inclined to induce conjugation of double bonds in the unsaturated fatty acids. Results of the spectroscopic examinations are given in Table 9. The percentages of conjugation in each sample were calculated from ultraviolet absorption measurements carried out with a photoelectric spectrophotometer by the method of Bradley and Richardson (3). The coefficients used for diene and triene conjugation were those recently recommended by Kass (11). It is to be noted that a slight degree of diene conjugation existed in the fatty acids of the original peanut oil, probably from the action of the earth used in bleaching the oil (13). In no case was conjugation significantly increased during esterification.

TABLE 9

Conjugation in peanut oil, fatty acids derived from the oil, and oils prepared from the fatty acids by reesterification with and without catalysts.

Sample	Diene conjugation	Triene conjugation
	percent	*percent*
Original peanut oil	1.65	0.00
Peanut oil fatty acids	0.95	0.12
Mixture of equal parts alkali-refined and bleached oil from uncatalyzed esterifications at 178°, 190°, and 216° C.	1.06	0.36
Alkali-refined oil from esterification with stannous chloride catalyst* at 200° C.	1.53	0.20
Alkali-refined oil from esterification with zinc chloride catalyst at 225° C.*	1.37	0.22

*Reaction conducted at 20 mm. pressure for 6 hrs. with 0.0008 mole catalyst per 100 g. FA's.

There was in all cases some tendency for the reacting material to darken as esterification proceeded. As the color of the final product appeared to depend principally upon the temperature and the time of esterification, the products prepared with the aid of zinc or tin catalysts were much lighter in color than comparable products prepared without use of a catalyst. In general, the refined products obtained from crude (undistilled) fatty acids with the aid of a catalyst were but little darker than the crude acids. Thus, for example, an oil prepared by the esterification of crude acids for 6 hours at 200° C. with tin chloride as a catalyst had a Lovibond color of 35 yellow, 5.3 red after refining and bleaching, whereas the color of the crude acids was 35 yellow, 3.9 red. Another oil similarly prepared at 225° C. with zinc chloride as a catalyst also had a color of 35 yellow, 5.3 red. From distilled fatty acids very light esterified oils could be prepared; for example, one such product esterified for 5 hours at 200° C. and 20 mm. pressure with 0.0008 mole of tin chloride per 100 g. fatty acids had a Lovibond color of 10 yellow, 1.5 red without refining or bleaching.

Summary

1. An investigation has been made of the esterification of glycerol and peanut oil fatty acids under reduced pressure, with and without the assistance of various metal chlorides and oxides as catalysts.

2. The uncatalyzed reaction is bimolecular in character but proceeds in two successive stages, of which the latter has the lower velocity constant. Velocity constants have been determined for the initial and final stages of the reaction, at intervals between 166° and 241° C. The calculated heats of activation for the initial and final stages of the reaction are respectively 12,300 and 10,800 calories per mole. The free fatty acid concentration corresponding to the termination of the first stage decreases progressively as the temperature of the reaction is increased.

3. Of a wide variety of metal oxides and chlorides tested, zinc and tin chlorides were outstanding in catalytic activity. The reaction, when catalyzed with these materials, is complex and no longer simply bimolecular. It is believed that tin and zinc chlorides react initially with free fatty acids and free glycerol to form metal soaps and chlorohydrins, and that esterification proceeds through interaction of these two initial reaction products. Other metal chlorides, including the chlorides of aluminum, antimony, mercury, nickel, magnesium, manganese, lead, iron, and cadmium, do not appear to be capable of reacting in this manner, and are relatively poor catalysts. The oxides of tin and zinc are also deficient in catalytic activity, as is hydrochloric acid.

4. The reaction proceeds at a reasonable speed, i.e., the FFA content of the product is reduced to about 3% in 6 hours, if 0.0008 mole of tin chloride per 100 g. of fatty acids is used as a catalyst at 175° C. or if a similar amount of zinc chloride is used as a catalyst at 200° C. Equally rapid esterification is obtained without a catalyst only above 250° C. Esterification is assisted by maintaining a vacuum upon the reaction vessel to remove water vapor from the reacting material as rapidly as it is formed. A vacuum of about 20 mm. pressure of mercury is satisfactory.

5. If zinc or tin chloride catalysts are employed, the metals may be completely removed from the esterified oils by ordinary alkali refining. These catalysts do not cause the oil to polymerize during the course of esterification, do not cause conjugation in the oils, and are not detrimental to the color of the product.

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REFERENCES

1. Bhattacharya, R. and Hilditch, T. P., Proc. Roy. Soc. *129A*, 468-76 (1930).
2. Blagonravova, A. A. and Lazarev, A. M., Zhurnal prikladnoi khimii (Journal of Applied Chemistry, USSR) *13*, 879-83 (1940).
3. Bradley, T. F. and Richardson, D., Ind. Eng. Chem. *34*, 237-42 (1942).
4. Eckey, E. W. and Clark, C. C. (to Procter and Gamble Co.), U. S. Pat. 2,065,520 (1936).
5. Fairclough, R. A. and Hinshelwood, C. N., J. Chem. Soc. *1939*, 593-600.
6. Garner, T. L., J. Soc. Chem. Ind. *47*, 278-80T (1928).
7. Gruber, F., Fr. Pat. 677,711 (1929).
8. Hinshelwood, C. N. and Legard, A. R., J. Chem. Soc. *1935*, 587-96.
9. I. G. Farbenindustrie A.-G., Fr. Pat. 654,535 (1928); Ger. Pats. 514,403 and 556,558 (1930).
10. Johnson, J. Y., Brit. Pat. 302,411 (1928).
11. Kass, J. P., in "Protective and Decorative Coatings," edited by J. J. Mattiello, Wiley, New York, Vol. IV, pp. 362-405 (1944).
12. Long, J. S., Kittelberger, W. S., Scott, L. K., and Egge, W. S., Ind. Eng. Chem. *21*, 950-55 (1929).
13. Mitchell, J. H., Jr. and Kraybill, H. R., J. Am. Chem. Soc. *64*, 988-94 (1942).
14. Smith, H. A. and Reichardt, C. H., J. Am. Chem. Soc. *63*, 605-08 (1941).

Abstracts

Oils and Fats

Edited by
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DEVELOPMENT OF COMMERCIAL LECITHIN. M. Schofield. *Manufg. Chemist 16*, 135-7 (1945). New outlets for the cheaper commercial forms of lecithin are being found in a number of directions other than in the processing of foods or of fats. It is being used with plant sprays, in creosote emulsions, as softening and wetting agents and in many other ways. This paper reviews the scattered literature of the subject up to date, and indicates the major applications found and suggested.

THE VITAMIN A POTENCY OF CREAMERY BUTTER PRODUCED IN MINNESOTA. R. Jenness and L. S. Palmer. *J. Dairy Sci. 28*, 473-94 (1945). In 1,019 samples analyzed in 1943 the unweighted mean vitamin A and carotene contents were respectively 6.21 ± 0.03 and 3.68 ± 0.04 ug. per g. The means weighted by regional and seasonal butter production were respectively 6.14 and 3.71 ug. per g.; these values correspond to a total potency of 13,958 I. U. per pound if vitamin A itself is considered to have a potency of 4.00 I. U. per ug. With a few exceptions, and for all practical purposes the butters of the state were rather uniform in vitamin A potency in any given season of the year. Marked seasonal fluctuations in potency, similar to those reported elsewhere, and undoubtedly attributable to variations in feeding conditions were found to occur. From Jan. 1 to April 22, 1943, the samples averaged 9,000-10,000 I. U. per pound. With the beginning of pasturing, a rapid rise occurred until the summer level of 16,500- 18,500 I. U. per pound was attained in the period May 21 to June 17. This level persisted until early October whereupon the potency gradually declined nearly to the winter level during the remainder of the year. The picture for the first half of the year was corroborated by analyses of samples secured from Jan. 1 to June 15, 1944. No evidence was found for loss of vitamin A potency by butter during storage.

THE DETERMINATION OF THE PEROXIDE VALUE OF EDIBLE FATS AND OILS: THE INFLUENCE OF ATMOSPHERIC OXYGEN IN THE CHAPMAN AND MCFARLANE METHOD. C. H. Lea. *J. Soc. Chem. Industry 64*, 106-9 (1945).