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✿ Transesterification Kinetics of Soybean Oil¹

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Transesterification of soybean oil (SBO) and other triglycerides with alcohols, in the presence of a catalyst, yields fatty esters and glycerol. Di- and monoglycerides are intermediates. Reactions are consecutive and reversible. Rate constants have been determined for each reaction with a computerized kinetic program. The effects of the type of alcohol, 1-butanol or methanol (MeOH); molar ratio of alcohol to SBO; type and amount of catalyst; and reaction temperature on rate constants and kinetic order were examined. Forward reactions appear to be pseudo-first order or second order depending upon conditions used. Reverse reactions appear to be second order. At a molar ratio of MeOH/SBO of 6:1, a shunt reaction was observed. Energy of activation was determined for all forward and reverse reactions under a variety of experimental conditions from plots of $\log k$ vs $1/T$. Values ranged from 8–20 kcal/mol.

Transesterification of vegetable oils with simple alcohols has long been a preferred method for preparing fatty esters. These esters have good potential as an alternative or emergency fuel to replace #2 diesel oil in farm tractors. Because of this potential, we have focused our attention on variables that affect the yield of these esters (1,2) as well as analysis of intermediates and products as determined by an Iatroskan analyzer (3). In the present paper we report on a study of the kinetics of the transesterification of soybean oil (SBO). A capillary gas chromatographic (CGC) method used to support this study has been described (4). One of our objectives was to determine how variations in type of alcohol, molar ratio of alcohol to SBO, catalyst type and reaction temperature affected kinetic order, reaction rates and energies of activation. Another objective was to gain a more fundamental understanding of the chemistry involved in the transesterification of vegetable oils.

Various mechanisms have been proposed for both acid- and alkaline-catalyzed transesterification (5-7). A number of kinetic studies have been reported for the transesterification of simple (non-fatty) esters with alcohols (6,8-10) and dimethylterephthalate with ethylene glycol (11,12). Only a few kinetic studies have dealt with the transesterification of vegetable oil or fatty esters. These include the conversion of castor oil to

methyl ricinoleate (7), the glycerolysis of methyl oleate (13) and the transesterification of the esters of 9(10)-carboxystearic acid (14) and methyl 9(10)-carboxymethylstearate (15). The present study was undertaken with a commercially important vegetable oil, SBO, utilizing a computerized kinetic program (16) to shed additional light on the kinetics of transesterification reactions.

EXPERIMENTAL

Materials. Refined SBO was obtained from Central Soya, Chattanooga, Tennessee. The molecular weight was assumed to be 872.4. Methanol (MeOH) and 1-butanol (BuOH) were MCB Omnisolv (spectrograde) and were stored over molecular sieves 4A. A solution of sodium butoxide (NaOBu) was prepared by the reaction of 240 mg of sodium with 10 ml of BuOH at 59-99 C with stirring. Sulfuric acid was purchased from B&A, Allied Chemical, Morristown, New Jersey. Sodium methoxide (NaOCH₃) was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin.

Reaction conditions employed in kinetic studies. The scope of our kinetic studies is outlined in Table 1. Experiments were designed to determine kinetic order and rate constants using two simple alcohols, two molar ratios of alcohol to SBO, acidic vs alkaline catalysis, two weight percentages of NaOBu and two temperature ranges each containing five temperatures. All reactions studied were conducted at atmospheric pressure.

Transesterification reaction and sampling. The first two of five systems shown in Table 1 utilized a 250-ml round-bottomed four-necked flask, equipped with a mechanical stirrer, thermometer, condenser and/or drying tube and stopper (for sample removal). The remaining systems in Table 1 employed a 400-ml custom-made reaction flask with five necks. The additional neck was equipped with a thermocouple connected to a digital pyrometer. This pyrometer provided rapid temperature readings that were essential to follow the very fast reactions. The larger size flask enabled us to scale up the reaction and possibly permitted more vigorous agitation.

The reaction flask was immersed in a Polyscience Series 9000 refrigerated constant temperature bath and circulator. The operating range of this bath was -15 to +150 C, with a control accuracy of ± 0.02 C. The temperature control of the reaction mixture was generally ca. 0.1 C.

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TABLE 1
Reaction Conditions Employed in Kinetic Studies

Alcohol used	Molar ratio of alcohol/SBO	Weight of reactants		Catalyst	Temperature (C) ^a
		Alcohol (g)	SBO (g)		
1-Butanol	30:1	51	20	1% H ₂ SO ₄	77, 87, 97, 107, 117
1-Butanol	30:1	51	20	1% NaOBu	20, 30, 40, 50, 60
1-Butanol	30:1	102	40	0.5% NaOBu	20, 30, 40, 50, 60
1-Butanol	6:1	51	100	1% NaOBu	20, 30, 40, 50, 60
Methanol	6:1	22	100	0.5% NaOCH ₃	20, 30, 40, 50, 60

^aTemperature control: ± 0.1 C.

The reaction flask and its associated equipment and other glass apparatus used for handling starting materials were first heated to expel moisture. Calculated amounts of SBO and alcohol were added to the reaction flask that was brought to a predetermined temperature using the constant temperature bath. A calculated amount of catalyst was quickly added to the reactants, and timing of the reaction was begun.

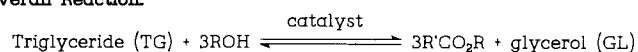
Samples (0.5 ml each) were removed from the reaction mixture at various intervals, depending upon reaction conditions. For example, alkali-catalyzed reactions at 60 C were sampled initially at 15-sec intervals and then over longer intervals during the course of one hr. For the acid-catalyzed reaction at 117 C, early samples were taken at 6-min intervals, and later samples were taken at 30-min intervals during the course of three hr. Samples were immediately quenched in 0.5 ml water, thus stopping the reaction. Because the oil layer did not always cleanly separate from the water, salting out and centrifuging were used to enhance separation. The resulting oil was used for both thin layer chromatography (TLC) and CGC analysis.

TLC was used initially to determine the qualitative composition of each sample of the reaction mixture and to determine which samples were to be quantitatively analyzed. This TLC procedure has been described previously (2). The reaction was stopped when TLC indicated high conversion to the ester. Fourteen samples were taken, of which nine were quantitatively analyzed by the CGC. The CGC method provided a quantitative analysis of the triglyceride (TG), diglyceride (DG), monoglyceride (MG) and ester composition needed for the kinetic study.

Preparation of CGC samples and their analysis. Samples from the oil layers obtained above were accurately weighed and silylated, internal standard was added, and the concentration was adjusted and then analyzed by CGC as previously described (4). A computerized program was used to analyze CGC data. The output from this program gave wt %, μ mol or mmol, standard deviation and relative standard deviation for each component.

Computerized kinetic program. A computerized kinetic program, described previously (16), was used to determine whether a proposed kinetic order appeared possible. The program requires that a specific kinetic scheme be proposed for each reaction being studied. The reactions studied are shown in Figure 1. Additional

Overall Reaction:



Stepwise Reactions:

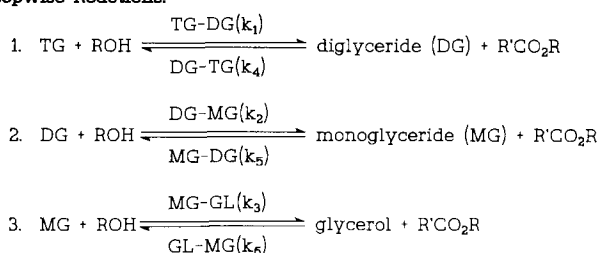


FIG. 1. Chemistry of the transesterification of vegetable oils.

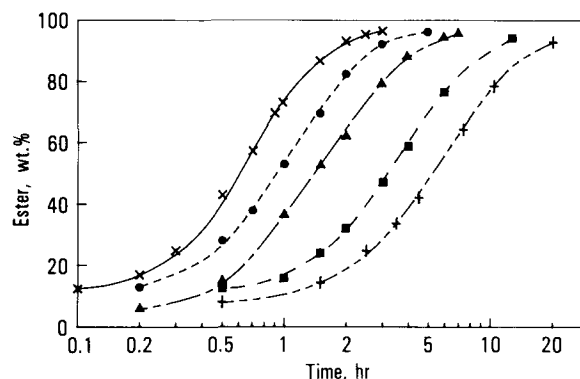


FIG. 2. Effect of time and temperature on ester formation. BuOH/SBO (30:1), 1% H₂SO₄, 77–117 C. X, 117 C; •, 107 C; ▲, 97 C; ■, 87 C; +, 77 C.

input consists of the concentration of each component with time. Concentration units were either mmol or μ mol/ml depending on requirements of the program. The program utilizes these data to produce plots of concentration vs time, which are shown later. A separate plot is produced for each temperature. Based upon the kinetic scheme being tested, the program attempts to draw a line through the points. A close fit of the lines to the points suggests that the kinetic scheme employed is adequate, and from this a kinetic order can be proposed. On the other hand, a poor fit of the lines to the points

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suggests that an incorrect scheme was proposed and/or the data are faulty.

The program also reports two types of errors associated with the fit of the lines to the points at each temperature. The first is the "summed squared error," which is the sum of all vertical distances squared between points and lines. The greater the coincidence between points and lines, the smaller the error. The second error reported is the "average error," which is the square root of the summed squared error divided by the number of data points (concentrations). By comparing the total of either the summed squared or average errors of the various schemes being tested at all temperatures, one can determine which scheme gives the best fit. Finally, the computer program reports rate constants for each reaction at each temperature.

RESULTS AND DISCUSSION

Chemistry of the transesterification of vegetable oils. The stoichiometry of the overall transesterification reaction requires 1 mol of TG for 3 mol of alcohol to give 3 mol of ester and 1 mol of glycerol (GL) (Fig. 1). This reversible reaction, which is either acid- or alkaline-catalyzed, involves stepwise conversions of TG to DG to MG to GL producing 3 mol of ester in the process. One objective of this study was to determine the rate constants for all forward and reverse reactions. Rather than use k_1 to designate the rate constant for the conversion of the TG to DG, we have chosen to use the designation TG-DG. Similarly, designations for the other rate constants are shown in Figure 1. It should be noted that the transesterification reaction consists of consecutive as well as reversible reactions that must be accounted for in any kinetic study.

Effect of time and temperature on ester formation. To determine the effect of temperature on ester formation for the reaction of BuOH with SBO at a molar ratio of 30:1 catalyzed by 1% H_2SO_4 , five temperatures ranging from 77-117 C were examined. The results of this study showed that ester formation is essentially complete in 3 hr at 117 C, compared to 20 hr at 77 C (Fig. 2). It will be noted that the curves have spacing which indicates a distinct rate change for every 10 C temperature rise. The curves also indicate the reaction begins at a slow rate, proceeds at a faster rate and then slows again as the reaction nears completion. The shapes of the curves at two adjacent temperatures enabled us to predict the approximate shapes of the curves for the remaining three temperatures. This information was valuable for determining both when samples should be taken and when to stop the reaction. Similarly shaped curves for the esters were observed for alkaline-catalyzed reactions.

Kinetics of acid-catalyzed transesterification reactions. We undertook a kinetic study of the reaction of BuOH with SBO using a 30:1 molar ratio with 1% H_2SO_4 at five temperatures. A 30:1 molar ratio was chosen because at molar ratios of 6:1 and 20:1, conversion to ester was unsatisfactory (1). The results obtained at 117 C are shown in Figure 3. Because we used a large excess of alcohol over that required by the stoichiometry, we expected the forward reactions to follow pseudo-first-order kinetics. The reverse reac-

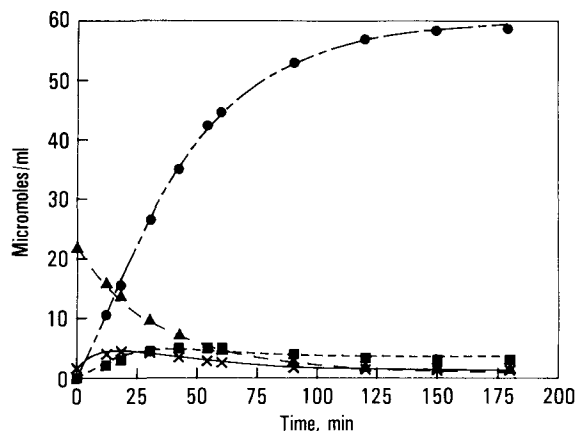


FIG. 3. Change of component concentration with time for a molar ratio of BuOH/SBO (30:1), 1% H_2SO_4 , 117 C. •, Soybean butyl esters; ▲, soybean oil; X, diglyceride; ■, monoglyceride.

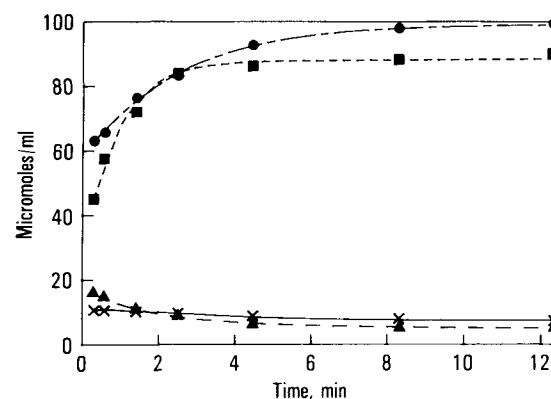


FIG. 4. Change of component concentration with time for a molar ratio of BuOH/SBO (6:2), 1% NaOBu, 30 C. •, Soybean butyl esters; ■, monoglyceride $\times 10$; ▲, soybean oil; X, diglyceride.

tions would be expected to be second order. The fit of the lines to the points was excellent for all four components. Similarly, good fits were obtained for the other four temperatures studied. These findings support our kinetic assignment for the forward and reverse reactions. The curves for all four components shown in Figure 3 are characteristic of consecutive reactions and confirm that the transesterification reaction consists of a series of consecutive reactions. It should be noted that both the forward and reverse reactions are consecutive. The rate constants obtained for these reactions are discussed later.

Kinetics of alkaline-catalyzed transesterification reactions. Alkaline-catalyzed transesterifications proceed at considerably faster rates than acid-catalyzed transesterifications (2,17). Partly for this reason and partly because alkaline catalysts are less corrosive to industrial equipment than acid catalysts, most commercial transesterifications are conducted with alkaline catalysts. Sodium alkoxides are among the most efficient catalysts used for this purpose (5,6,18) and were therefore used in our study.

The molar ratio of alcohol to SBO has an important bearing on the kinetic order of the reaction. We have

shown that acid catalysis of the forward reaction employing a 30:1 molar ratio of BuOH to SBO followed pseudo-first order kinetics. This was expected because of the large molar excess of alcohol. Similarly, we expected alkaline-catalyzed transesterifications using a 30:1 molar ratio of alcohol to SBO to follow pseudo-first order kinetics. We conducted two studies, both using molar ratios of BuOH to SBO of 30:1, at five temperatures between 20 and 60 C in which the catalysts were 1% and 0.5% NaOBu by weight. The data obtained from these experiments were used in computerized plots of concentration vs time as previously discussed. These plots strongly supported our assumption that the NaOBu-catalyzed forward reactions at 30:1 followed pseudo-first order kinetics.

We next studied the effect of lowering the molar ratio from 30:1 to 6:1 with 1% NaOBu as catalyst. It has previously been shown that with alkaline catalysis, a 6:1 molar ratio of alcohol to vegetable oil results in high conversions (93–98%) of vegetable oil to ester, whereas below the 6:1 ratio conversion decreases (1). A 6:1 molar ratio would therefore probably be the preferred ratio in commercial operations. At this ratio a second-order reaction appeared more likely than a pseudo-first-order reaction because the excess alcohol was only twice that of theory compared to 10 times that of theory for a 30:1 ratio. Both schemes, however, were tested using the computerized kinetic program. Again it was assumed that the consecutive, reverse reactions were second order. This program indicated a better fit of lines to points for the second-order reaction than for the pseudo-first-order reaction. The summed squared errors for the second-order reactions at 20–60 C were 46.5, 3.4, 17.4, 27.7 and 22.7, for a total of 117.7. The summed squared errors for the pseudo-first-order reactions at 20–60 C were 235.2, 7.1, 33.2, 44.2 and 25.6, for a total of 345.3. The average errors for the second-order reactions were 1.3, 0.4, 0.8, 1.0 and 0.9, for a total of 4.4. The average errors for the pseudo-first-order reactions were 2.9, 0.5, 1.1, 1.3 and 1.0, for a total of 6.8. Thus both the total of the summed squared errors and the average errors were lower for the second-order reaction compared to the pseudo-first-order reaction. These differences appear to be significant and were the basis for choosing the second-order reaction. A plot of data for component concentration vs time for a 6:1 molar ratio of BuOH to SBO with 1% NaOBu at 30 C, assuming a second-order reaction, is shown in Figure 4. The fit of the lines to the points in this case was excellent. Good fits were also observed at the other four temperatures. These results suggest that at a 6:1 molar ratio with 1% NaOBu, the reaction of BuOH with SBO follows consecutive, second-order kinetics.

We also expected the reactions of MeOH with SBO at a 6:1 molar ratio with 0.5% NaOCH₃ at 20–60 C to be second order. MeOH, however, behaved differently from BuOH in this regard. Although a second-order scheme was evaluated by our computer program for the reaction of MeOH/SBO at 6:1, the average error obtained was somewhat larger than that observed with BuOH/SBO at 6:1. This increase in error is because of the rapid appearance of ester without a corresponding rapid increase and decrease of DG and MG. Because consecutive reactions could not explain the rapid

appearance of ester without the appearance of intermediate DG and MG, a shunt-reaction scheme was tested. This shunt-reaction scheme comprised both the second-order reactions and a shunt reaction in which 3 mol of MeOH directly attacked 1 mol of TG. By using the shunt-reaction scheme, we obtained much better fits of the data. Thus, the kinetics which best describe the reaction of MeOH/SBO at 6:1 molar ratio consist of a combination of second-order consecutive and fourth-order shunt reactions.

The shunt-reaction scheme was further supported by comparing certain results obtained from kinetic studies of both the shunt and second-order schemes. Two criteria were used in this comparison. The first was a comparison of summed squared and average errors. The summed squared errors for the second-order scheme at 20–60 C were 1.5, 3.4, 2.9, 6.7 and 4.1, all values $\times 10^{-5}$, for a total of 18.6×10^{-5} . The summed squared errors for the shunt-reaction scheme at 20–60 C were 1.5, 0.4, 1.9, 1.8 and 1.5, all values $\times 10^{-5}$, for a total of 7.1×10^{-5} . The average errors for the second-order scheme were 0.8, 1.1, 1.0, 1.6 and 1.3, all values $\times 10^{-3}$, for a total of 5.8×10^{-3} . The average errors for the shunt-reaction scheme were 0.8, 0.4, 0.8, 0.8 and 0.8, all values $\times 10^{-3}$, for a total of 3.6×10^{-3} . Thus both the total of the summed squared errors and the average errors were lower for the shunt-reaction scheme compared to the second-order scheme. A plot of data for component concentration vs time for MeOH/SBO at a 6:1 molar ratio with 0.5% NaOCH₃ at 40 C, assuming the shunt-reaction scheme, is shown in Figure 5. The close fit of lines to points, at this temperature and the other four temperatures studied, strongly supports the validity of this scheme. The second criterion was correlation coefficients obtained by linear regression from plots of $\log k$ vs $1/T$. These plots were used to determine energy of activation, E_a , and are discussed later. The correlation coefficients obtained with the shunt-reaction scheme were generally higher than those from the second-order scheme. Thus, the shunt reaction must be used in conjunction with the second-order reaction to fully explain the kinetics for the reaction of MeOH with SBO at a 6:1 molar ratio. Shunt reactions have been observed in kinetic studies of the hydrogenation of conjugated diene (19) and SBO and linseed oils (20).

We next reexamined the reaction of BuOH/SBO at 6:1

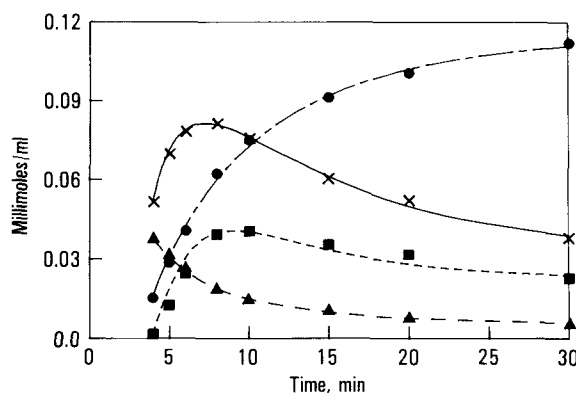


FIG. 5. Change of component concentration with time for a molar ratio of MeOH/SBO (6:2), 0.5% NaOCH₃, 40 C. •, Soybean methyl esters; X, diglyceride $\times 10$; ■, monoglyceride $\times 10$; ▲, soybean oil.

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to determine if the shunt-reaction scheme was applicable. Our computer program calculated a zero reaction rate, clearly indicating that the shunt reaction did not exist for the BuOH reaction. Why was the transesterification of SBO with MeOH different from that with BuOH at the 6:1 molar ratio? Two possible explanations can be proposed. The smaller size of the MeOH molecule relative to that of BuOH could facilitate the simultaneous attack of MeOH on all three chains of the TG. Also, the greater polarity of the methoxy anion compared to the butoxy anion might promote its attack on the ester carbonyl according to established mechanisms.

Rate constants. Rate constants were calculated by our computer program for all reactions included in our kinetic study. The rate constants determined for the reaction of BuOH with SBO at a 30:1 molar ratio using various catalysts are shown in Table 2. Because the forward and reverse reactions are not of the same kinetic order at a 30:1 molar ratio, a direct comparison of these rate constants cannot be made. The alkaline-catalyzed reactions had much larger rate constants than the acid-catalyzed reactions for both forward and reverse reactions, as expected. The higher rate constants for the

0.5% NaOBu- vs 1% NaOBu-catalyzed reactions was unexpected. This difference probably resulted because the 0.5%- and 1%-catalyzed reactions were run on different scales (see Table 1) and with different reactors (see Experimental). The larger size of the 400-ml flask may have permitted more vigorous agitation, which could have influenced reaction rates. Had the reactions been run under identical conditions, rates for the 1%-catalyzed reactions should have been higher than those for the 0.5%-catalyzed reactions. A number of kinetic studies have shown that reaction rates increase with increasing catalyst concentration (7,8,14).

Energy of activation. The relationship between reaction rate constant, k , and temperature is given by the integrated form of the Arrhenius equation: $\log_{10} k = (-E_a/2.303R)/T + C$ where E_a is the energy of activation, R the gas constant in calories $\text{mol}^{-1} \text{degree}^{-1}$, T the absolute temperature and C a constant. From a plot of $\log k$ vs $1/T$, the slope can be determined. This slope is equal to $(-E_a/2.303R)$. Thus, $E_a = -4.58$ (slope).

We determined energy of activation in this manner for most of the reactions. An example is shown in Figure 6 for the acid-catalyzed butanolysis of TG to DG at 77–117 C. Linear regression analysis of these data gave a slope of -3258.1 with a correlation coefficient of

TABLE 2

Effect of Various Catalyst Systems on Rate Constants

Rate designation	BuOH/SBO, 30:1, rate constants $\times 10^3$		
	1% H_2SO_4 , 77 C	1% NaOBu, 60 C	0.5% NaOBu, 60 C
TG-DG	3	3,822	26,626
DG-MG	8	1,215	3,584
MG-GL	7	792	2,373
DG-TG	0.02	121	439
MG-DG	0.05	7	8
GL-MG	0.03	11	7

For the forward reactions units are min^{-1} . For the reverse reactions units are $\text{ml mmol}^{-1} \text{min}^{-1}$ for the acid-catalyzed reaction, and $\mu\text{mol}^{-1} \text{min}^{-1}$ for the alkali-catalyzed reaction. TG, triglyceride; DG, diglyceride; MG, monoglyceride; GL, glycerol.

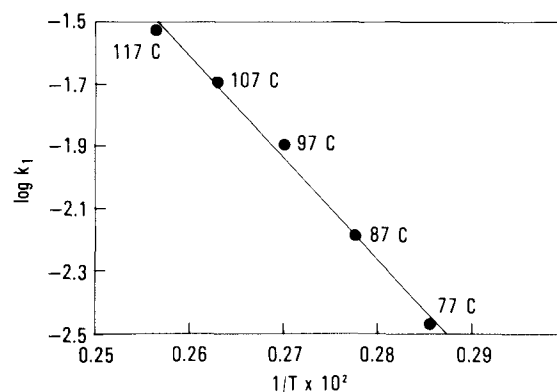


FIG. 6. Plot of $\log k$ vs $1/T$ for the butanolysis of triglyceride to diglyceride with 1% H_2SO_4 at 77–117 C.

TABLE 3

Energy of Activation (E_a) Under Studied Conditions

Rate designation	E_a (cal/mol): reaction conditions				
	BuOH/SBO, 30:1			BuOH/SBO, 6:1	MeOH/SBO, 6:1
	1% H_2SO_4 , 77–117 C	1% NaOBu 20–60 C	0.5% NaOBu 20–60 C	1% NaOBu 20–60 C	0.5% NaOCH_3 , 20–60 C
TG-DG	14,922	15,360	15,662	17,092	16,062
DG-MG	16,435	11,199	13,053	12,137	17,247
MG-GL	15,067	11,621	13,395	10,693	—
DG-TG	19,895	17,195	15,587	15,925	15,843
MG-DG	16,885	—	13,336	15,816	13,571
GL-MG	12,196	—	13,110	8,181	—
TG-GL	—	—	—	—	20,022

TG, triglyceride; DG, diglyceride; MG, monoglyceride; GL, glycerol.

-0.9964. By using this slope in the equation $E_a = -4.58$ (slope), an E_a of 14,922 cal/mol was calculated for this reaction. Correlation coefficients for the other five reactions of BuOH/SBO, 30:1 catalyzed by 1% H_2SO_4 , were -0.9918, -0.9965, -0.8918, -0.9795 and -0.9905.

Energies of activation determined for other reactions in our study ranged from 8,000-20,000 cal/mol (Table 3). Other investigators have reported E_a values within this range for other transesterification reactions (6,8,9-12). E_a for the shunt reaction TG-GL had a value of 20 kcal/mol. The spread of values seen in Table 3 for E_a is due partly to experimental error. In addition, the simplified model used in the equation $\log_{10}K = (-E_a/2.30R)/T + C$ may not be adequate to account for all the variables involved. This might also explain why E_a for some reverse reactions are greater than those of the corresponding forward reactions. Further research is needed to develop a model that might provide a narrower range of E_a values.

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✿ Study on the Oxidative Rate and Prooxidant Activity of Free Fatty Acids

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Oleic, linoleic and linolenic acids were autoxidized more rapidly than their corresponding methyl esters. Addition of stearic acid accelerated the rate of autoxidation of methyl linoleate and the decomposition of methyl linoleate hydroperoxides. Therefore, the higher oxidative rate of FFA's than their methyl esters could be due to the catalytic effect of the carboxyl groups on the formation of free radicals by the decomposition of hydroperoxides. Addition of stearic acid also accelerated the oxidative rate of soybean oil. This result suggests that particular attention should be paid to the FFA content that affects the oxidative stability of oils.

carboxyl groups in the decomposition of peroxides. He also said in this review (3) that this idea has been supported by the work of Privett et al., in which addition of linoleic acid to methyl linoleate peroxide accelerated its decomposition. However, it was not clear whether its decomposition was promoted by the catalytic action of the carboxyl group in linoleic acid or oxidized products of this acid, and the effect of FFA's on the autoxidation of esters has not been investigated.

In this paper, we report the detailed data for the difference in oxidative rates between FFA's and their methyl esters with periodic measurement of the unoxidized substrate content by GLC and POV, and elucidate the catalytic action of the carboxyl group in FFA's on the autoxidation of oils by the use of stearic acid as a catalyst which is not autoxidized under the conditions of the present experiment.

MATERIALS AND METHODS

Preparation of materials. Oleic, linoleic and linolenic acids

A few papers (1,2) have been published on the comparison of the oxidative rate of free fatty acids (FFA) and their esters. Holman et al. (2,3) reported that FFA's were oxidized more rapidly than their esters, and he suggested that this effect probably was due to participation of the

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