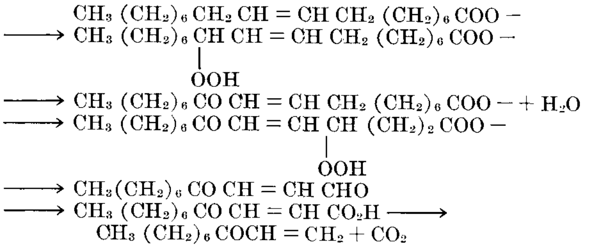

$$
\begin{aligned}
& CH_3\,(CH_2)_6\,CH_2\,CH = CH\,CH_2\,(CH_2)_6\,COO -\\
\longrightarrow\ & CH_3\,(CH_2)_6\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,CH = CH\,CH_2\,(CH_2)_6\,COO -\\
\longrightarrow\ & CH_3\,(CH_2)_6\,CO\,CH = CH\,CH_2\,(CH_2)_6\,COO - + H_2O\\
\longrightarrow\ & CH_3\,(CH_2)_6\,CO\,CH = CH\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,(CH_2)_2\,COO -\\
\longrightarrow\ & CH_3(CH_2)_6\,CO\,CH = CH\,CHO\\
\longrightarrow\ & CH_3\,(CH_2)_6\,CO\,CH = CH\,CO_2H \longrightarrow\\
& \quad CH_3\,(CH_2)_6\,COCH = CH_2 + CO_2
\end{aligned}
$$

This last compound is suspected to represent Peak C (Fig. 2) but this has not yet been checked against an authentic sample. Its elution time is very close to, but not identical with, that of the isomeric heptylidene acetone,

$$CH_3\ (CH_2)_5 - CH = CH\ COCH_3.$$

The other major "unknown" peak, F, could be the lower homologue, vinyl hexyl ketone,

$$CH_3\ (CH_2)_5\ CO\ CH = CH_2,$$

produced via a double bond shift in the oxidizing oleic radical.

Finally, the production of the quantitatively less important, but positively identified, methyl ketones could be accounted for by the oxidation of the vinyl ketones by some such mechanism as the following:

$$
\begin{aligned}
& COCH = CH_2 \xrightarrow{O_2} - COCH^* - CH_2\,OO^*\\
& \longrightarrow - COCH^* - CHO + OH^* \xrightarrow{RH} - CO\,CH_2\,CHO + R^*\\
& \xrightarrow{O} - COCH_2\,CO_2H \longrightarrow - COCH_3 + CO_2
\end{aligned}
$$

In this way vinyl hexyl and vinyl heptyl ketones would give rise to methyl hexyl and methyl heptyl ketones, respectively, both of which are positively identified in the neutral reaction products. When the initial formation of a carbonyl group occurs on the side of the oleic double bond nearer to the glycerol residue this mechanism implies the formation of thermostable keto glycerides, which are also found in practice.

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Selectivity and Isomerization During Partial Hydrogenation of Cottonseed Oil and Methyl Oleate: Effect of Operating Variables

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Results are now available for hydrogenation of cottonseed oil and methyl oleate in which sufficient agitation was provided to eliminate mass transfer resistances from the catalyst surface. The ratio of the *trans*-to-*cis* isomers of oleic acid groups approaches 2.0 even at high pressures and high degrees of agitation. The rates of hydrogenation for both *cis* and *trans* isomers and for positional isomers are all essentially identical. A reaction scheme has been devised that is consistent with extensive experimental data, and the method of evaluating the relative reaction rate constants for each step is outlined. Using these rates constants, selectivity can be quantitatively evaluated.

HYDROGENATION of vegetable oils and animal fats (which are predominantly triglycerides) involves several consecutive and simultaneous reactions. Changes of the operating variables often affect the rates of the individual reactions and hence the overall course of the reaction. Selectivity of hydrogenation as defined here refers to the preferential hydrogenation of the polyunsaturated acid groups, such as linolenic or linoleic acid groups, relative to monounsaturated acid groups, such as oleic acid groups. Two types of isomerization also always occur during hydrogenation. *Cis-trans* geometrical isomerization of the carbon-carbon double bonds has a significant effect on the softening point and consistency of the fats. Positional isomerization also occurs as the double bonds migrate along the fatty acid chain (2,3,7,8), but presumably this isomerization does not have too much effect on the physical properties unless perhaps when the double bonds migrate close to the ends of the fatty acid chains.

Operating variables which affect the selectivity of the hydrogenation also affect both the *cis-trans* and positional isomerization (6). Those operating variables which increase the concentration of hydrogen at the catalyst surface decrease selectivity and both types of isomerization (9). Mass transfer of the reactants and products to and from the surface is obviously of importance, and changes in the degree of agitation will affect the resistances to mass transfer. The true effect of the operating variables, such as temperature, pressure, and catalyst concentration, on the reactions occurring on the catalyst surface can only be evaluated when mass transfer resistances are eliminated. Only three investigations (1,9,13) are known in which these resistances were eliminated, and the results of these studies should be especially important for evaluating the effect of operating variables on the rates of the various reactions that occur during hydrogenation.

Several reaction schemes have been proposed previously, and reaction rate constants were evaluated for the various reactions (6,9,11,12). All of the re-

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action schemes proposed are incomplete for cottonseed oil hydrogenation. A complete scheme should certainly include a reversible reaction for *cis-trans* isomerization. The present paper is an attempt to provide a reasonably complete reaction scheme and to evaluate the reaction rate constants for each step of it. In order to make the necessary calculations, the results of previous investigations were used, and hydrogenations were made with methyl oleate at high rates of agitation to obtain more information.

Equipment and Operating Procedure

Methyl oleate was hydrogenated in the dead-end hydrogenator used by Wisniak (13) who hydrogenated cottonseed oil at pressures up to 1500 p.s.i.g. The system used is also similar to those employed previously by Albright and coworkers (1,9). The desired amounts of methyl oleate and Rufert nickel catalyst flakes were added to the reactor and were heated under vacuum to the desired operating temperature. The start of each run was considered to be the time when hydrogen was introduced (by bubbling upward through the ester) into the reactor, and a constant pressure was maintained in the reactor throughout the run. High degrees of agitation were provided using a high-speed turbine agitator in the baffled reactor.

Five to seven ester samples were collected at intervals during each run, which was usually allowed to continue until a relatively low iodine value was obtained. The hydrogenated ester samples were analyzed for iodine value by the conventional Wijs method (4), for *trans* methyl esters by the infra-red technique (5) and with some samples for various methyl esters by gas-liquid chromatography through the courtesy of Swift and Co.

Emery 2301 methyl oleate was obtained from Emery Industries, Inc. Chromatographic analyses indicated 76.6% methyl oleate, 7.2% other monounsaturated methyl esters (primarily methyl palmitoleate), 7.3% methyl linoleate, and the remainder as various saturated esters. Infra-red analysis indicated 4.5% *trans* isomers.

Results of Methyl Oleate Hydrogenation

Ten runs were made at temperatures from 130 to 140°C; catalyst concentrations from 0.05 to 0.20% nickel by weight; a pressure of 300 p.s.i.g.; and agitator speeds of 1250 and 1700 rpm. The reaction was followed by plotting the logarithm of the iodine value (I.V.) of the ester versus the time (t) in min. The resulting plots were straight lines within experimental accuracy after the induction period (defined here as the time at which the straight line extrapolates back to the initial iodine value). Figure 1 shows the results for methyl oleate at 140°C and 0.05% nickel catalyst; the induction time was about 14 min. On the same graph are shown the results of a cottonseed oil run of Wisniak (13) which is at comparable conditions except the temperature is 110°C. The induction period of this run is 32 min. but the rate of reaction after the induction period is essentially identical to that of the methyl oleate run. Obviously at comparable temperatures, the cottonseed oil used here would have hydrogenated much more rapidly than the methyl oleate.

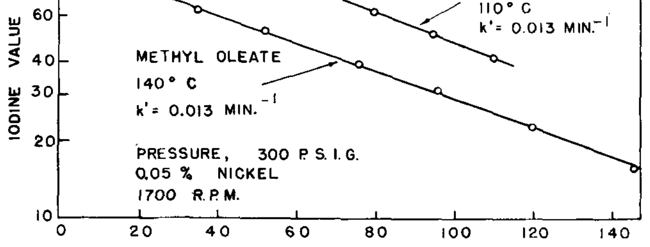


FIG 1. Rates of hydrogenation for cottonseed oil and methyl oleate.

The overall rate (r) of hydrogenation can be represented in the region where the data of Figure 1 are a straight line by the following equation:

$$r = -\frac{d\,(I.V.)}{dt} = k^1\,(I.V.) \qquad 1)$$

where k^1 is the overall first order reaction rate constant. Table I indicates the k^1 value and the induction time for each run. Most, if not all, of the original methyl linoleate was hydrogenated during the induction period. Runs 1, 4 and 8 plus some preliminary runs indicated that both the rates of hydrogenation and the amounts of *trans* methyl oleates formed were similar regardless of changes in agitation speed. As a result, mass transfer resistances must have been essentially eliminated at agitator speeds of 1700 r.p.m.

Figure 2 indicates the relationship between first order reaction rate constant (k^1) and the catalyst concentration at 140°C. The degree of *trans* isomerization was somewhat higher at 0.05% nickel than at 0.10% nickel or greater concentrations where isomerization was essentially identical. The shape of the curve of Figure 2 differs from those found for the cottonseed oil runs (9,13) where k^1 was found, in general, to be directly proportional to the amount of catalyst. The degree of selectivity and isomerization was also found for the cottonseed oil runs to be independent of catalyst concentration, especially at higher concentrations. Apparently the methyl oleate used contained some catalyst poisons which effectively decreased the amount of catalyst available during the entire run. The cottonseed oil used, however, had been refined and bleached for hydrogenation purposes so that it was probably essentially free of such poisons. This explanation also seems consistent with the slower rates of hydrogenation found in this investigation as compared to those for cottonseed oil (1,9,13).

It is thought, however, that there are temporary catalyst poisons in both the cottonseed oil and methyl oleate which accounts for the relatively long induction periods. Presumably, these poisons are preferentially absorbed on the catalyst, but they are slowly

TABLE I

Reaction Rate Constants and Induction Periods for Hydrogenation of Methyl Oleate at 300 p.s.i.g.

Run	Temperature °C.	Catalyst % Ni	Agitator Speed r.p.m.	k^1, Min^{-1}	Induction period min.
1	140	0.10	1700	0.029	12
2	140	0.05	1700	0.013	14
3	140	0.20	1700	0.085	5
4	140	0.10	1700	0.029	12
5	140	0.20	1700	0.085	8
7	140	0.15	1700	0.058	10
8	140	0.10	1250	0.030	16
9	130	0.10	1700	0.014	26
10	130	0.20	1700	0.037	24
11	135	0.10	1700	0.022	18

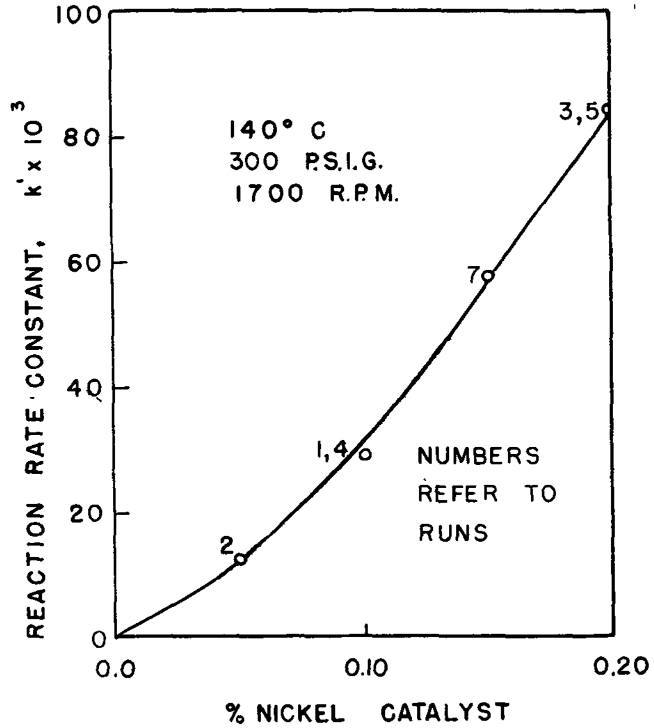


FIG. 2. Effect of catalyst concentration on rate of hydrogenation of methyl oleate.

hydrogenated (and hence eliminated); the catalyst is then available for hydrogenation. Simultaneously most of the color improvement of the fatty materials occurs during the induction period. In this investigation and in Wisniak's for cottonseed oil (13), the length of the induction period was dependent on the operating variables. Higher catalyst concentrations and especially higher temperatures decreased the induction time. The longer induction time for the cottonseed oil run shown in Figure 1 is probably caused by the lower operating temperature. More investigations are planned on this subject.

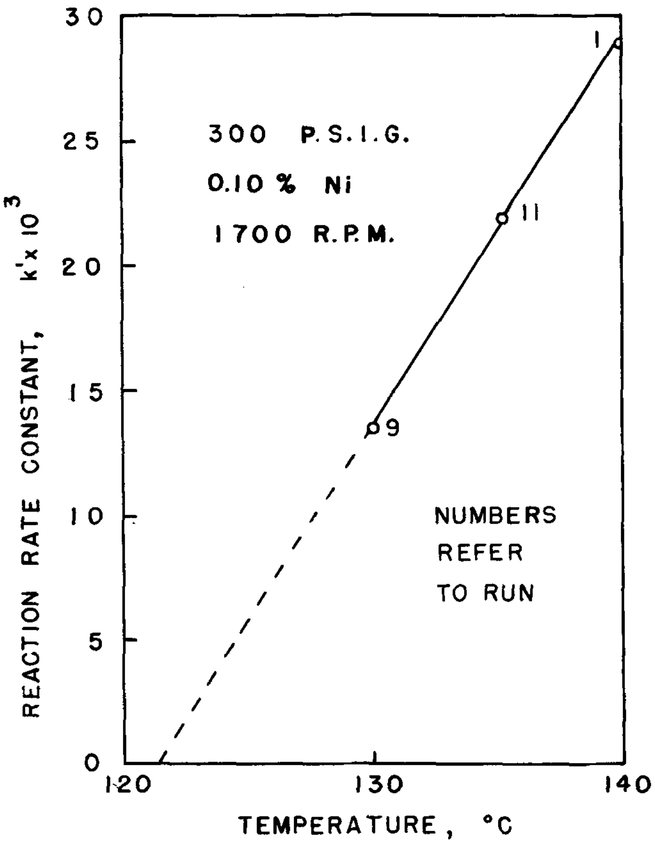


FIG. 3. Effect of temperature on rate of hydrogenation of methyl oleate.

Figure 3 indicates that the k^1 values for the methyl oleate runs are linearly proportional to the temperature. The isomer formation during these runs increases, at most, only slightly with increased temperature. Similar findings were also noted for cottonseed oil runs at high rates of agitation (9,13). The extrapolation of the straight line relationship of Figure 3 to a zero value of k^1 occurs at a higher temperature than it does for the cottonseed oil runs.

Calculation of Relative Reaction Rate Constants

Methyl oleate was hydrogenated primarily to determine how the *trans/cis* ratio of the methyl oleate groups varied during the hydrogenation. Since the number of reactions that occur are limited, it was hoped that a better understanding could be obtained of the isomerization reaction and the relative rates of reaction for the *cis* and *trans* esters. Within experimental accuracy, the *trans/cis* ratio approached 2.0, which is the approximate value at equilibrium. Note for example that such a ratio is obtained at lower I.V.s in Figure 4, even though the operating conditions for the run were not conducive for isomerization (because of high agitation and a relatively high pressure of 300 p.s.i.g.).

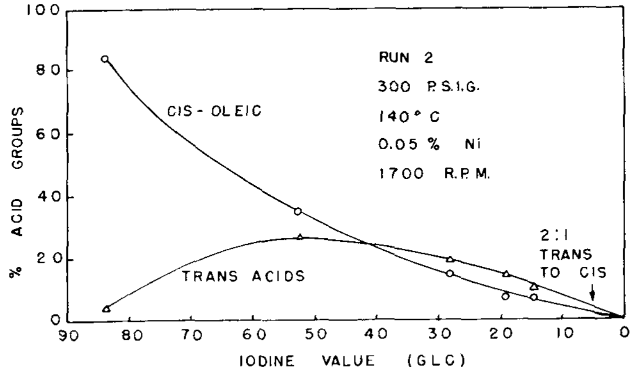


FIG. 4. Hydrogenation of methyl oleate.

An inspection has also been made of those hydrogenation results for cottonseed oil in which sufficient agitation was provided to eliminate mass transfer resistances (1,9,13). Again the *trans/cis* ratio for the oleic acid groups approached 2.0 when the data were obtained to relatively low I.V.s. Wisniak's results (13) at 1000 p.s.i. and 110°C. are shown in Figure 5 as an example. It is realized that the curves in Figure 5 must be interpolated about 23 I.V. units, so that Figure 5 does not give conclusive information regarding the ultimate *trans/cis* ratio. Figure 6 indicates conditions which are more favorable for isomerization (namely lower pressure); the *cis/trans* ratio here not only approaches 2.0, but remains at 2.0 over about 35 I.V. units in one run (1). Some investigators (2,10) who used less vigorous agitation and who apparently had significant mass transfer resistances have also found that the *trans/cis* ratio approached 2.0. Others report the ratio approaches values other than 2.0; perhaps this apparent discrepancy is caused by differences in the degrees of

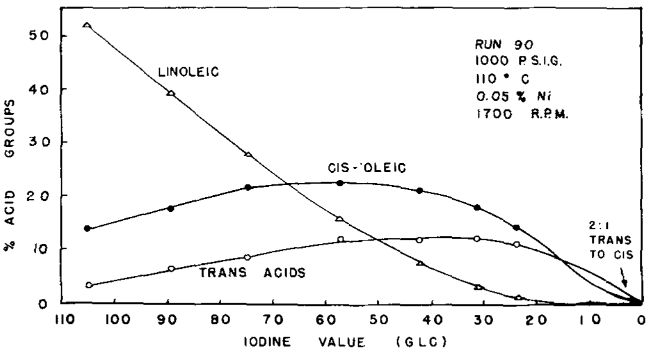


FIG. 5. Hydrogenation of cottonseed oil at 1000 p.s.i.g.

agitation of the various runs. Also the calculated *trans/cis* ratio is sensitive to small analytical errors, particularly the I.V. which is normally used to calculate the total monene content. The I.V.s calculated from the gas-liquid chromatographic results were found in general to be slightly less than those determined by the Wijs method. More research will be required before the relative accuracies of the two I.V. methods are determined.

The results of this investigation, plus those for cottonsed oil in which mass transfer resistances were eliminated, have been used to evaluate the relative reaction rate constants occurring during hydrogenation. Since the overall rate of hydrogenation is directly proportional to the I.V. (i.e., the reaction is first order and irreversible), probably each hydrogenation step can also be considered first order and irreversible. Other investigators (6,9,11,12) have made a similar assumption. Furthermore, it should be emphasized that the k^1 value for a run remained essentially constant even though the *trans/cis* ratio of oleic acid groups varied from essentially zero up to 2.0, where it became constant. In addition, positional isomerization that is known to occur (2,3,7,8) did not change the k^1 values. The following conclusions were made:

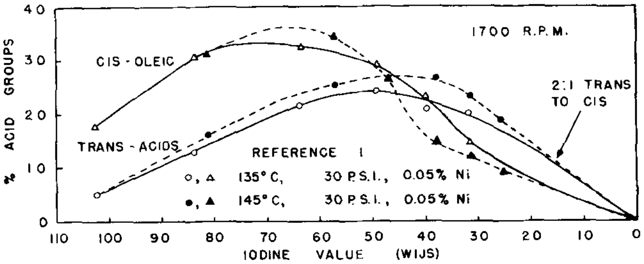


FIG. 6. Hydrogenation of cottonseed oil at 30 p.s.i.g. with high rates of agitation.

1) *Cis* and *trans* isomers of oleic acid groups hydrogenate at the same rate.
2) Positional isomers also hydrogenate at the same rate.
3) The first order reaction rate constant for isomerization of *cis* oleic groups is twice as large as that for the reverse reaction. (This conclusion is expected from equilibrium considerations).

Since all isomers of oleic acid groups hydrogenate at essentially the same rates, the following simplified reaction scheme was tested for the results of Wisniak (13) and Eldib and Albright (9). The rate equations were developed using the assumption of irreversible, first order equations:

$$\begin{array}{ccccc} \text{Linoleic acid} & \xrightarrow{k_{LO}} & \text{Oleic acid} & \xrightarrow{k_{OS}} & \text{Saturated acid} \\ \text{groups (L)} & & \text{groups (O)} & & \text{groups (S)} \end{array}$$

The scheme was found applicable for runs up to about 60 p.s.i.g. but increasingly inapplicable at higher pressures (up to 1500 p.s.i.g.). The reaction was then expanded as follows:

$$\begin{tikzcd} & \text{Oleic acid groups (O)} \arrow[dr, "k_{OS}"] & \\ \text{Linoleic acid groups (L)} \arrow[ur, "k_{LO}"] \arrow[rr, "k_{LS}"] & & \text{Saturated acid groups (S)} \end{tikzcd}$$

The first order irreversible equations developed are shown below:

$$2)\quad -\frac{dL}{dt} = k_{LO}\ L + k_{LS}\ L$$

$$3)\quad -\frac{dO}{dt} = -\,k_{LO}\ L + k_{OS}\ O$$

$$4)\quad L = L_O\ e^{-(k_{LO}+k_{LS})t}$$

$$5)\quad O = \frac{k_{LO}\ L_O}{k_{OS}-1}(e^{-(k_{LS}+k_{LO})t} - e^{-k_{OS}t}) + O_o e^{-k_{os}t}$$

where L and O are the compositions of linoletic and oleic acid groups present at the time, (t) ; L_O and O_o are the compositions of these groups for unhydrogenated oil. The compositions used in each case are those of the main body of the fatty oil.

The actual time during the hydrogenation run was not used in these equations because of the induction

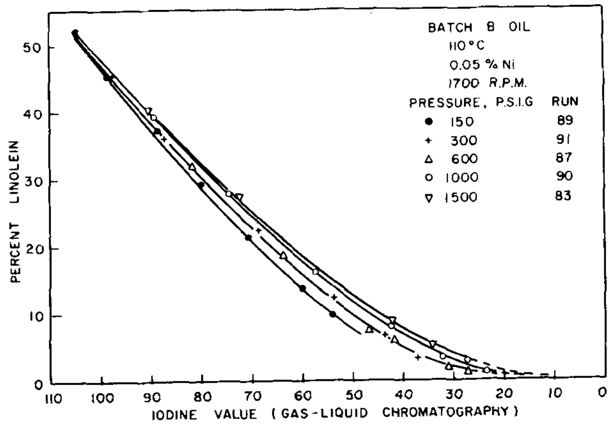


FIG. 7. Effect of pressure on selectivity.

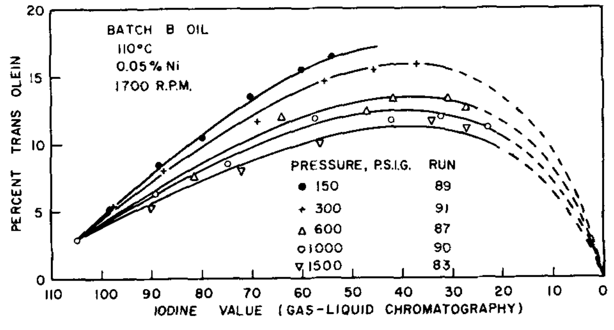


FIG. 8. Effect of pressure on isomerization.

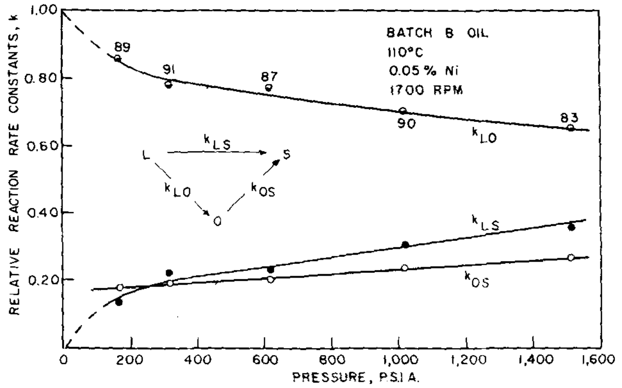


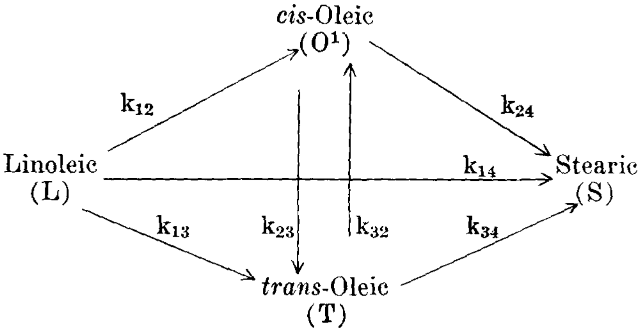
FIG. 9. Effect of pressure on relative reaction rate constants.

period. Rather for each hydrogenated oil sample obtained during the run, the pseudo time (t) was calculated assuming that $k_{LO} + k_{LS} = 1.0$; values of L and L_0 are known from the oil analyses. The pseudo time was found in general to be linearly proportional to the actual time after the induction period. A trial-and-error procedure was then used to determine values of the various k values. In all cases, k values were found so that the equations fit the experimental data within, generally, experimental accuracy even at pressures up to 1500 p.s.i.g.

For the cottonseed oil runs (13), the effects of pressure on selectivity and on geometrical isomerization are shown in Figures 7 and 8, respectively, at pressures from 150 to 1500 p.s.i.g. (13). Figure 9 indicates the effect of pressure on the relative reaction rate constants (k).

The reaction of linoleic acid groups directly to stearic acid groups is of increasing importance as the pressure increases. It should be emphasized, however, that the linoleic acid groups probably hydrogenate in all cases by steps first to an oleic acid group and then to a saturated form. In the reaction scheme when the linoleic acid groups appear to hydrogenate by steps, the oleic acid groups formed are transferred from the catalyst surfaces back to the main body of the oil. Later, the oleic group will be transferred back to the catalyst and hydrogenated. In the scheme when the reaction from linoleic to stearic groups appears to be a single step, the oleic acid group formed originally is hydrogenated before it is transferred back to the main body of the liquid. Obviously, lower pressures would decrease the probability of that type of hydrogenation so that the apparent one step hydrogenation of linoleic acid groups would be essentially non-existent at low pressures.

Now the reaction scheme is expanded as follows, combining all *cis* and *trans* positional isomers in groups:



Based on the simplified scheme of the reaction:

6) $k_{24} = k_{34} = k_{OS}$

7) $k_{14} = k_{LS}$

8) $k_{12} + k_{13} = k_{LO}$

The differential equations for the reactions shown above are:

9) $$-\frac{dL}{dt} = (k_{12} + k_{13} + k_{14})\, L$$

10) $$-\frac{dO^1}{dt} = (k_{23} + k_{24})\, O^1 - k_{12}L - k_{32}T$$

11) $$-\frac{dT}{dt} = (k_{32} + k_{34})\, T - k_{13}L - k_{13}O^1$$

The above equations could be integrated, but the resulting equations would be extremely complicated. In order to calculate the unknown constants, an "Ease" analog computer was programmed with Equations 9-11. Using pseudo time values calculated from Equation 4, and using a trial-and-error procedure, constants were obtained that predict the experimental data well.

Table II indicates the effect of pressure and temperature on the k values. Since neither catalyst concentration nor agitation has any effect on selectivity or isomerization when mass transfer resistances are eliminated (9,13), these variables did not have to be evaluated here.

Table II indicates that pressure has an appreciable effect on both selectivity and isomerization. Temperature, however, has little effect as was previously

TABLE II

Effect of Pressure and Temperature on Relative Reaction Rate Constants

Run no.	Pressure p.s.i.	Temperature °C.	k_{12}	k_{13}	k_{14}	k_{23}	k_{32}	$k_{24} = k_{34}$	N
89	150	110	0.54	0.32	0.14	0.10	0.05	0.18	4.8
26	150	115	0.59	0.33	0.08	0.10	0.05	0.15	6.1
45	300	110	0.52	0.27	0.21	0.10	0.05	0.17	4.6
91	300	110	0.47	0.31	0.22	0.10	0.05	0.19	4.1
43	300	120	0.45	0.32	0.23	0.10	0.05	0.17	4.5
49	300	130	0.47	0.33	0.20	0.10	0.05	0.16	5.0
60	600	110	0.43	0.32	0.25	0.10	0.05	0.20	3.8
87	600	110	0.45	0.32	0.23	0.10	0.05	0.20	3.9
61	600	120	0.35	0.31	0.34	0.10	0.05	0.20	3.3
69	1,000	105	0.44	0.23	0.33	0.10	0.05	0.20	3.4
68	1,000	110	0.39	0.26	0.35	0.10	0.05	0.21	3.1
90	1,000	110	0.43	0.27	0.30	0.10	0.05	0.24	2.9
	1,000	121	0.30	0.28	0.42	0.12	0.06	0.25	2.3
75									
86	1,500	100	0.47	0.23	0.30	0.10	0.05	0.25	2.8
81	1,500	105	0.43	0.22	0.35	0.10	0.05	0.25	2.6
83	1,500	110	0.42	0.23	0.35	0.10	0.05	0.26	2.5

Batch A oil: Runs 26 to 50.
Batch B oil: Runs 60 to 92.
Runs 60 to 76 were made with the portion of batch B that hydro-genated slower.

indicated when high degrees of agitation are used (9). At 150 and 300 p.s.i. selectivity appears to increase slightly with temperature; but at higher pressures, selectivity may decrease with temperature. The present results are not sufficiently accurate though to establish the temperature trend definitely. Rather surprisingly the ratio of k_{12}/k_{13} is fairly constant in all cases at about 1.5–1.7. Also k_{23} and k_{32} are generally 0.10 and 0.05, respectively. Selectivity can be expressed quantitatively as follows:

$$12) \quad N = \frac{k_{LO}}{k_{OS}} = \frac{k_{12} + k_{13}}{k_{24}}$$

Table II indicates variations of N values from 2.3 to 6.1; however, these values may be inaccurate by as much as 10–20% because of small errors in the values determined for the relative reaction rate constants.

The hypothesis (2,9) that isomerization is caused by a hydrogenation-dehydrogenation scheme involving atomic hydrogen is consistent with the present results. Further, the explanation (9) that selective hydrogenation is caused by preferential physical adsorption of polyunsaturated groups as compared to monounsaturated groups still seems probable. In each case an increased concentration of hydrogen at the catalyst surface, as would occur at higher hydrogen pressures, would decrease selectivity and isomerization. In this respect the equilibrium solubility of hydrogen in cottonseed oil was found to be essentially directly proportional to the hydrogen pressure, and to increase slightly with temperature (13). Based only on this information concerning temperature, selectivity and isomerization would be expected to decrease somewhat at higher temperatures when high degrees of agitation are provided. The relative rates of the various reactions probably change slightly, however, so that actually selectivity is relatively unchanged and isomerization increases to a small extent with increased temperatures. When relatively poor agitation is employed, both selectivity and isomerization increase with temperature, since the overall rates of reaction are increasing and since the high resistances to hydrogen transfer cause the hydrogen concentration on the catalyst to decrease.

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Properties of the Fatty Acid Esters of Amylose[1]

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To help establish the suitability of esters of amylose and fatty acids as dip-coating materials, esters of the even-numbered, saturated fatty acids, acetic through stearic, and of oleic and cottonseed oil fatty acids were prepared, and their properties were determined.

The various esters generally were prepared by the interaction of acid chlorides with the amylose suspended in a suitable mixture of solvents. Analyses for content of free fatty acid groups indicated that high proportions of the hydroxyl groups were esterified. Intrinsic viscosity decreased as the chain length of the acyl group increased, a reflection of the changing nature of the products rather than a decrease in the degree of polymerization of the amylose.

As the chain length of the saturated fatty acid group increased the softening point at first decreased and then increased, the minimum being obtained with the myristate. The stearate softened at 56.2°C. The stearate had a hardness index of 139, which was about equal to the index of 140 for completely hydrogenated cottonseed oil. Densities were greater than those of the corresponding triglycerides and decreased as the chain length of the fatty acid group increased. Permeability to water vapor also decreased as the chain length increased, the index being 620×10^{-12} for the acetate and 15×10^{-12} for the stearate. The acetate possessed the highest tensile strength, about 4.40 kg./sq. mm., while the palmitate had a tensile strength of about 0.49 kg./sq. mm. Elongation at the break point varied widely, being 632% for the caprate and 0.95% for the stearate.

ESTERS PREPARED from fatty acids and a film-forming polyhydric material like amylose should be useful as dip-type coatings on both foods and nonfoods and such use might provide a new, large-volume outlet for surplus fats and oils. While adequate information on the physiological properties of such esters is not available, presumably they can be shown to be edible, and they might be digestible, at least to some extent.

Among the film-forming polyhydric materials available, amylose is one of the preferred. It can be derived from corn, another surplus commodity, by a relatively simple procedure. Some new varieties of corn yield a starch containing over 70% amylose (12).

Amylose and cellulose have a straight-chain molecular structure of identical chemical composition. However, the d-glucopyranose units of the amylose molecule are joined by alpha-1:4 linkages, while those of the cellulose molecule are joined by beta-1:4 link-

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