

Kinetics of Copper-Chromite Hydrogenation in Soybean and Linseed Oils: Effect of Pressure¹

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ABSTRACT

Although a prime impetus for study of copper catalysts has been the selective reduction of linolenic acid in soybean oil, recent economic developments raise the possibility that hydrogenated linseed oil might be a suitable edible oil. Consequently the effect of two hydrogen pressure levels in soybean and linseed oils on the kinetic pathway and on the final distribution of residual double bonds was investigated. The course of the reaction was studied by removing a sample at intervals corresponding to a small iodine value drop, and constituents were determined analytically. The higher pressure increased the rate of reduction, decreased the concentration of conjugated dienes and somewhat reduced the migration of double bonds.

INTRODUCTION

In the framework of various studies undertaken at the Northern Laboratory concerning hydrogenation of lino-

lenate in soybean oil with a copper-containing catalyst, it yet remained to follow the course of hydrogenation under the conditions previously established (1). We also studied how kinetic pathways and rates of several consecutive and simultaneous reactions occurring during hydrogenation of soybean oil and linseed oil could be affected by an increase of pressure. Previous research with nickel catalysts showed that selectivity and isomerization (geometrical and positional) decrease with an increase in pressure, which condition would lead to a high concentration of hydrogen on the catalyst surface (2,3).

This report is also an attempt to provide information on the influence of this factor during hydrogenation with a commercial copper-chromite catalyst.

EXPERIMENTAL PROCEDURES

Materials

Refined and bleached soybean (iodine value = 134) and linseed (iodine value = 189) oils came from commercial sources. These were re-refined and bleached in the laboratory before hydrogenation in a Parr apparatus as previously described (1).

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TABLE I

Hydrogenation of Soybean and Linseed Oils^a

Experiment	Oil		Pressure, psi
	Source	Volume, ml	
A	Soybean	600	30
B	Soybean	550	75
C	Linseed	600	8
D	Linseed	600	75
E	Linseed	400	8
F	Linseed	600	75

^a170 C; 1800 rpm and 1% w/v Copper-chromite catalyst.

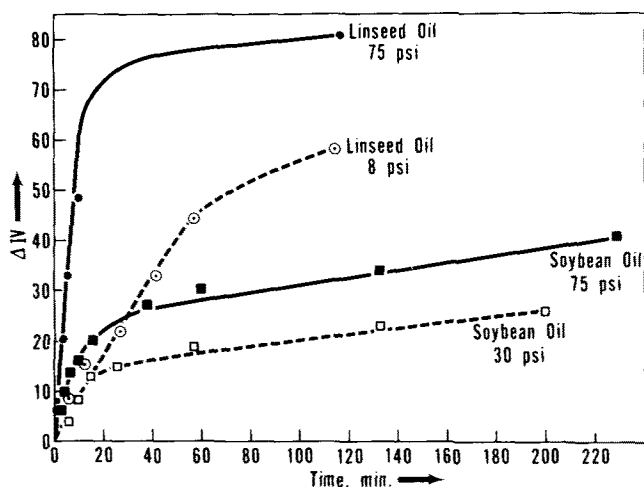


FIG. 1. Activity of catalyst in terms of hydrogen absorption (Δ iodine value) vs. time.

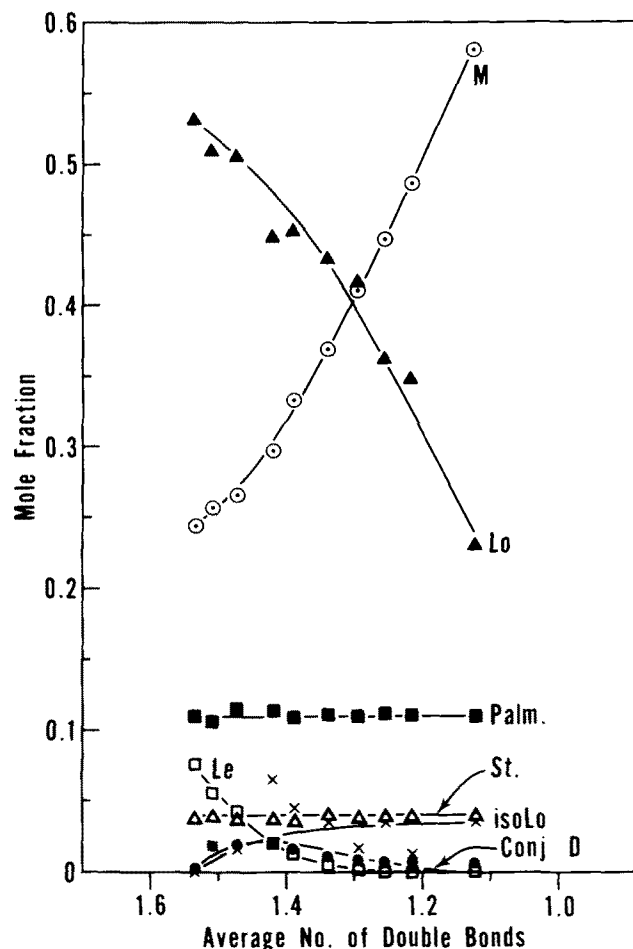


FIG. 2. Change in fatty acid composition during hydrogenation of soybean oil at 30 psi. Le, linolenate; Lo, linoleate; M, monoene; Palm, palmitate; St, stearate; IsoLo, isolinoleate; and Conj D, conjugated diene.

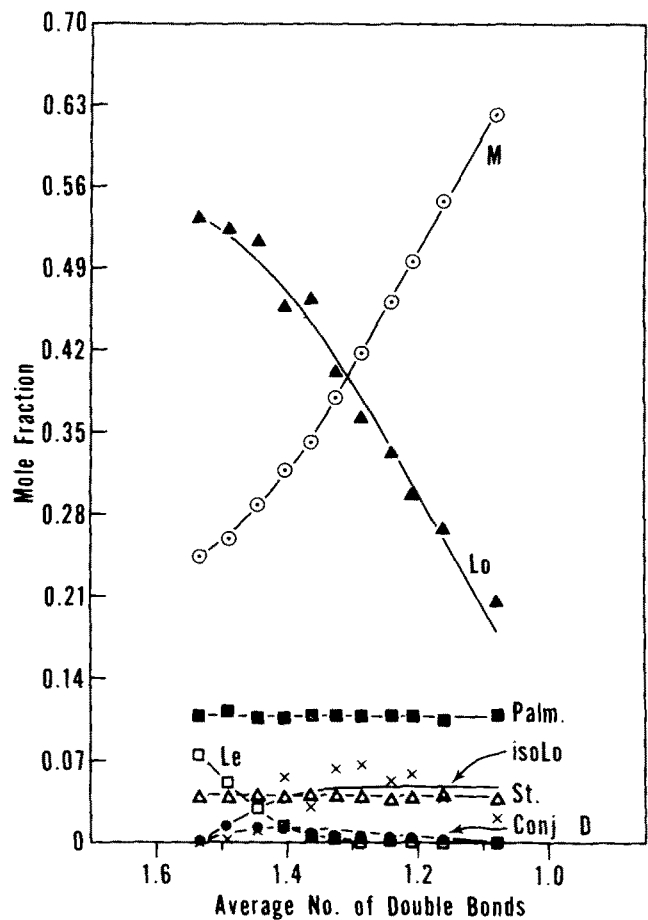


FIG. 3. Change in fatty acid composition during hydrogenation of soybean oil at 75 psi. Abbreviations same as Fig. 2.

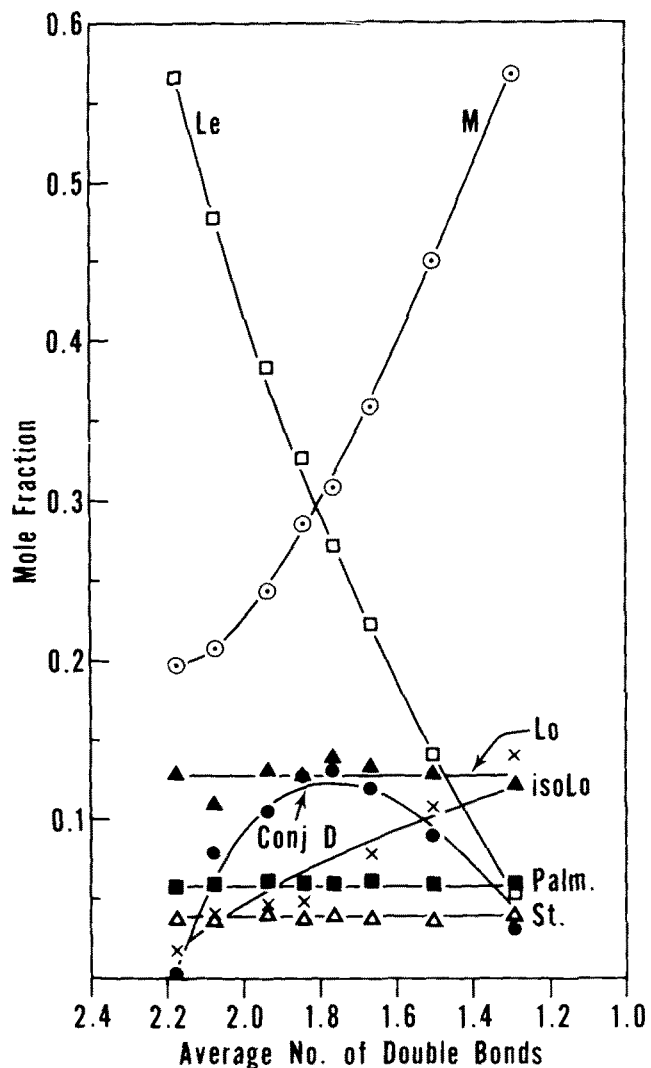


FIG. 5. Hydrogenation of linseed oil at 8 psi (Experiment C).

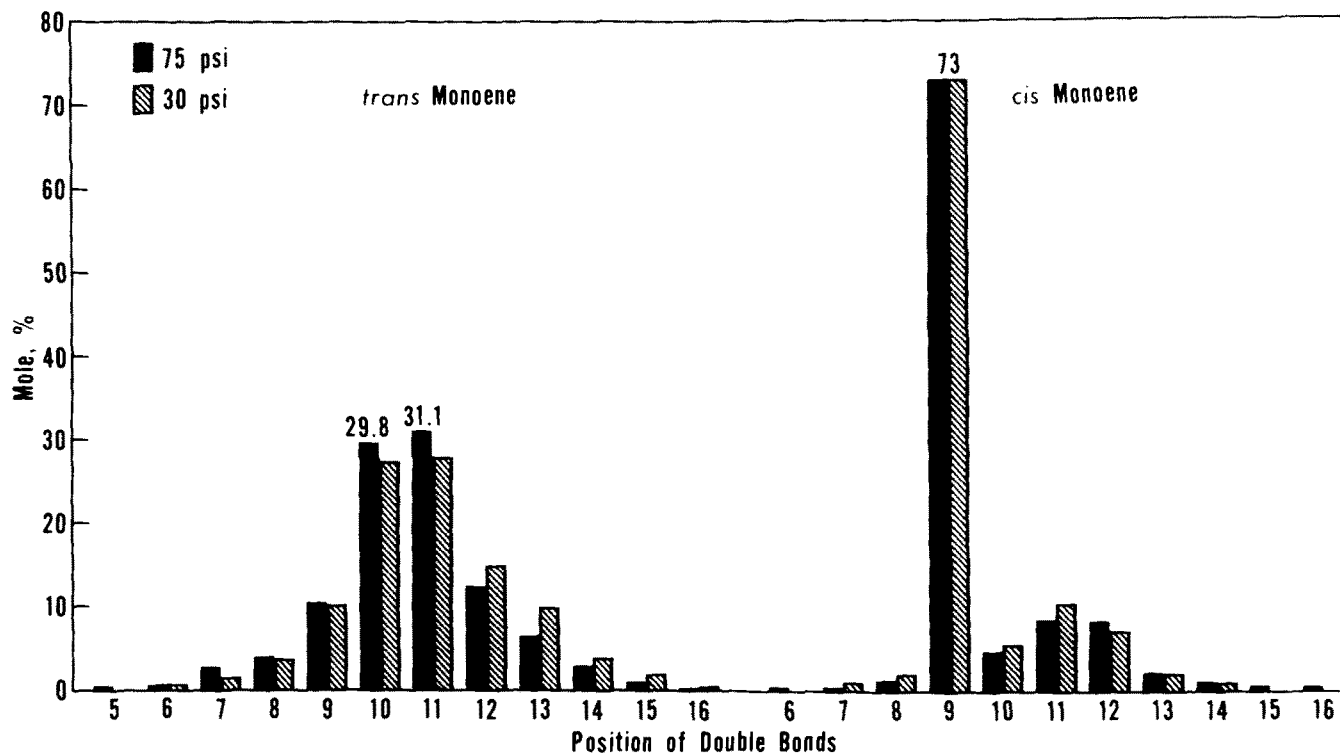


FIG. 4. Double bond distribution in *cis* and *trans* monoenes from hydrogenated soybean oils.

Copper chromite was a commercially available catalyst containing ca. 53% CuO and 39% CrO₃.

Analytical Methods

Methyl esters were prepared from triglycerides by transesterification in methanol with 0.5% sodium methoxide catalyst. Their compositions were determined from gas chromatography (GC) curves obtained with a Varian Aerograph GC instrument equipped with dual 6 ft x 1/8 in. stainless steel columns packed with 15% EGSS-X on Gas Chrom P 100-120 mesh and with a flame ionization detector. The chromatograph was operated at 190 C with a nitrogen gas flow of 20 ml/min. The area under each peak was determined with a Disc integrator.

Contents of conjugated dienes, linoleate and linolenate were estimated by AOCS Official Method (4) with a Cary Model 14 recording spectrophotometer.

The percentage of isolated *trans* isomers was measured by IR absorption at 10.36 μ of methyl esters in carbon disulfide with methyl elaidate as the standard.

Fractionation

Methyl esters of the last sample of hydrogenation were separated into dienes, palmitate plus monoenes, and stearate on a rubber column (5) with a mixture of acetone-water 88:12 v/v as the eluent.

Monoene fractions were further separated into palmitate, *cis* and *trans* monoene fractions, by chromatography on a silver-saturated cation exchange resin (6).

The position of the double bonds in *cis* and *trans* monoenes was determined by reductive ozonolysis, in which triphenylphosphine was used, and by GC (7).

Calculation of Rate Constants

Relative rate constants were determined by a digital computer according to a program written earlier (8). Data were fit with respect to average number of double bonds as calculated from compositional data. This method of calculation eliminated time as an independent variable and permits only ratios of rate constants to be determined.

Hydrogenation

The conditions of hydrogenation are shown in Table I.

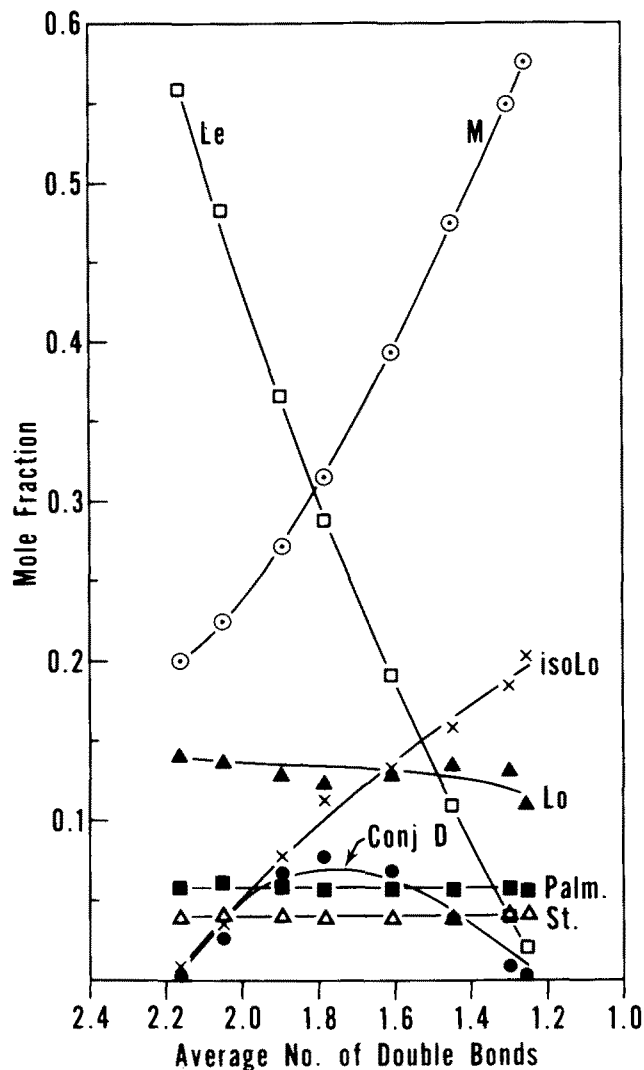


FIG. 6. Hydrogenation of linseed oil at 75 psi (Experiment D).

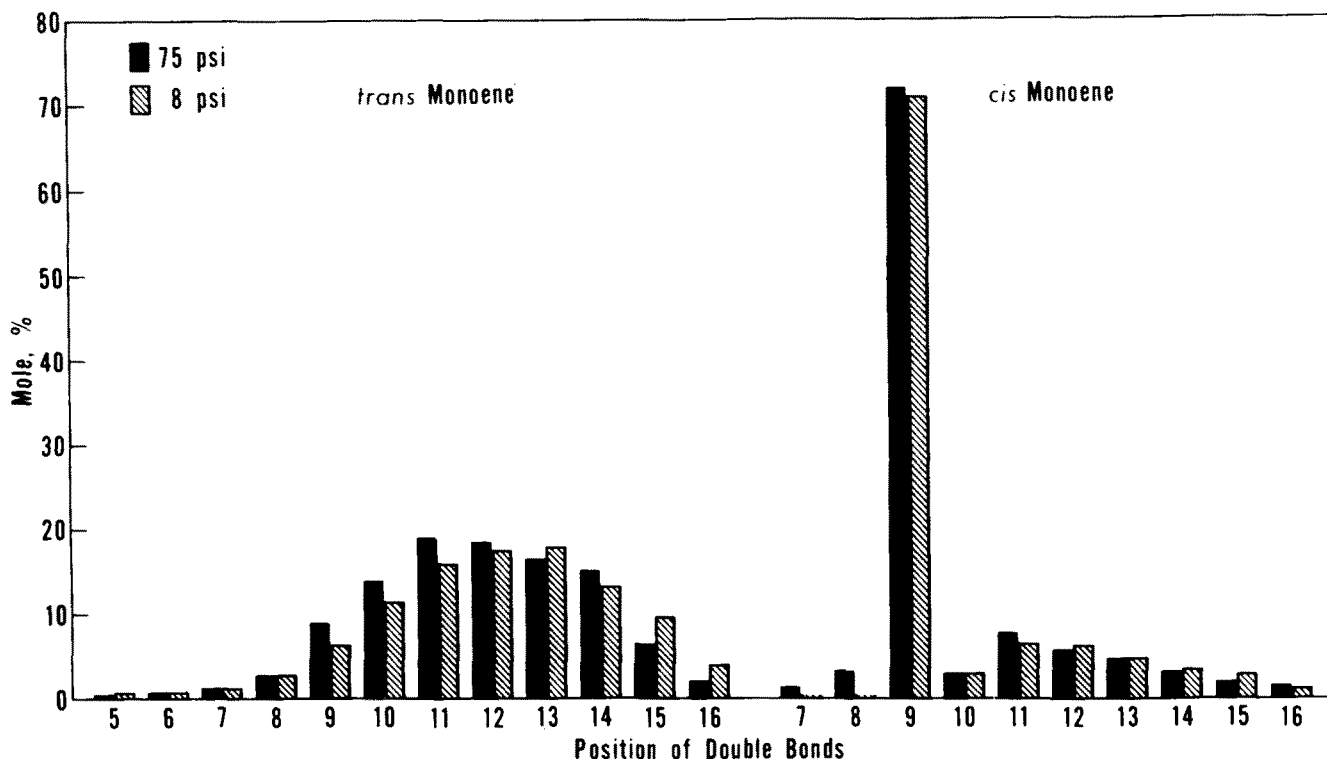
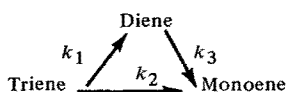


FIG. 7. Double bond distribution in *cis* and *trans* monoenes from hydrogenated linseed oils.

TABLE II

Relative Rate Constants for Soybean and Linseed Oil Hydrogenation



Experiment	k_1	k_2	k_3
A	1.00	0.24	0.07
B	1.00	1.12	0.08
C	1.00	0.02	0.55
D	1.00	0.46	0.34
E	1.00	0.25	0.39
F	1.00	0.55	0.31

Refined oil and the catalyst were charged into a Parr hydrogenator and heated under vacuum while being stirred. At 5 C below the hydrogenation temperature, stirring was stopped and hydrogen introduced. Then the stirring was restarted and the progress of hydrogenation was measured by the drop in hydrogen pressure in an auxiliary hydrogen tank which fed the gas to the reactor. At every hydrogen pressure drop, corresponding to a drop of about four iodine value units for soybean oil and eight for linseed oil, hydrogen gas flow was turned off; stirring stopped; a 5 ml sample was removed from the reactor; and all pressure drops and times were carefully noted.

After having removed 7-10 samples (total iodine value drop for soybean oil ca. 40 units and for linseed oil 80 units), hydrogenation was stopped, hydrogen evacuated, and oil cooled under vacuum.

SOYBEAN OIL

Activity of Catalyst

Activities of the catalyst were evaluated by the decrease in iodine value as a function of time (Fig. 1).

Initial activities of catalyst in the high and low pressure hydrogenations were high during linolenate reduction but diminished quickly after linolenate dropped to Ca. 1%. Activity was greater at 75 psi pressure than at 30 psi.

Composition of Hydrogenated Soybean Oil

The change in fatty ester composition during hydrogenation as plotted by the computer is given in Figures 2 and 3. There are no significant differences between the results of the two experiments except that conjugated dienes content is higher at 30 psi. The results from 30 psi hydrogenation (Fig. 2) agree quite well with those obtained previously (9)

on a large scale hydrogenation under similar conditions.

Double Bond Distribution

Figure 4 illustrates the double bond distribution in *cis* and *trans* monoenes for the two hydrogen pressures. This analysis was made on the last sample at the end of hydrogenation.

At both pressures more than 70% of the *cis* monoene was true oleate. In the remaining 30% the double bond appeared along the carbon chain from the 6 to 16 position.

In the *trans*-monoene fraction the double bonds were more widely scattered, with Δ^{10} and Δ^{11} isomers predominating. The double bonds in *trans* monoenes from 30 psi hydrogenation were slightly more scattered than those in 75 psi hydrogenation. The percentage of true oleic acid in the hydrogenated oil calculated from the ozonolysis data and percentage *trans* in monoene was Ca. 24-26%, whereas the original soybean oil contained 25% oleate. Apparently, little true oleate, if any, was formed during hydrogenation of soybean oil.

LINSEED OIL

Activity of the Catalyst

Figure 1 shows the high activity of the catalyst in linseed oil compared to its activity for soybean oil hydrogenation. As with soybean oil, increasing pressure increased catalyst activity.

Composition of Hydrogenated Oils

The analytical data for the hydrogenation of linseed oil (Experiments C and D, Table I) at low and high pressure are given in Figures 5 and 6 as plotted by the computer.

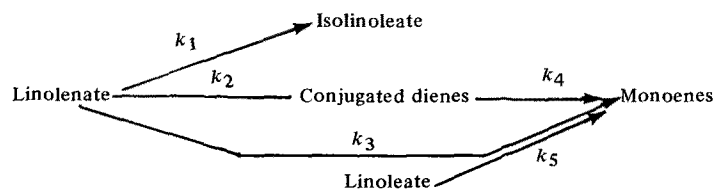
At both pressures linolenate reduction is accompanied by a concomitant increase in monoene. The reactive intermediate conjugated diene goes through a maximum. However the concentration of conjugated dienes is smaller at the higher pressure. Palmitate and stearate remain constant. Little, if any, linoleate is reduced during the reduction of linolenate. Isolinoate, which is not further reduced by the catalyst, accumulates during the reaction. The formation of isolinoate is favored at the higher pressure. When these experiments are repeated (Experiments E and F, Table I), there is reasonably good agreement between the duplicate runs except for isolinoate and linoleate, which are not measured with any accuracy.

Double Bond Distribution

The composition of monoene isomers formed during hydrogenation of linseed oil is plotted in Figure 7. As in the

TABLE III

Relative Rate Constants for Soybean and Linseed Oil Hydrogenation



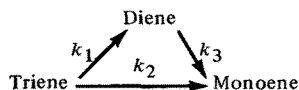
Experiment	k_1	k_2	k_3	k_4	k_5
A	1.00	1.25	0.00	1.22	0.16
B	1.00	0.37	0.23	0.29	0.11
C	1.00	4.12	0.00	9.34	0.01
D	1.00	1.41	0.51	5.77	0.17
E	1.00	2.16	0.22	5.51	0.29
F	1.00	1.69	0.00	10.98	0.12

soybean oil experiments the *cis*-monoene fraction contained more than 70% oleate. In the *trans*-monoene fraction the double bond is largely scattered between the 6 and 16 position with the 9 to 15 position predominating. The double bonds in *trans* monoenes were slightly more scattered at the lower pressure than at the higher pressure. Ozonolysis of the total methyl esters with palmitate as the internal standard showed 1.7% Δ^{17} monoene at 8 psi pressure and 0.3% at 75 psi.

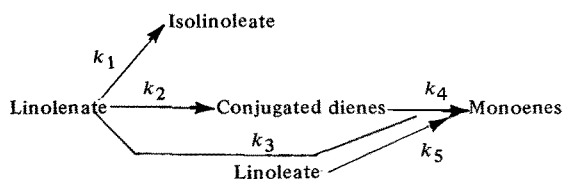
The percentage of true oleic acid in the oil calculated from ozonolysis data and percentage *trans* in monoene is Ca. 21% at 8 psi and 23% at 75 psi, whereas the original linseed oil contained 20% of oleate. Therefore little true oleate is formed during hydrogenation of linseed oil.

Relative Rate Constants

The rate constants were calculated at first according to the following simple scheme:



The calculated rate constants listed in Table II indicate that increasing the pressure enhances the Le→M shunt. On the basis of this simplified scheme the soybean oil runs fit quite adequately, whereas the linseed oil data fit poorly. A more complex reaction sequence is needed to explain that data. In the soybean oil reaction the fit was due to the low content of linolenate, which produced only minor amounts of isomeric dienes. In an attempt to describe the kinetics more realistically, the following scheme was used:



The relative rate constants obtained for different experiments are shown in Table III.

Excellent fits of the experimental values were obtained in all runs as can be seen in Figures 2, 3, 5 and 6. The

Le→M shunt appears to be enhanced at the higher pressure for soybean oil hydrogenation; however in duplicate runs on linseed oil the results are quite contradictory. Several factors probably contributed to this discrepancy. Due to the exothermic nature of this reaction, the temperature changed considerably during the initial period of reaction and may have changed the kinetics of the reaction. Experimentally, linoleate and isolinoleate values are subject to errors because of the limited nature of the methodology, and this will contribute errors to the determination of k_1 , k_3 and k_5 .

From the relative rate constants it appears that linolenate reduced primarily through a conjugated intermediate, and that this intermediate is desorbed less readily from the catalyst at the higher pressure. Consequently at the higher pressure, more linolenate is reduced either to isolinoleate or to monoene through a shunt.

In soybean oil, linolenate is reacting 13-15 ($k_1 + k_2 + k_3/k_5$) times faster than linoleate. In linseed oil, values of 12-22 (except Experiment C) are definitely higher. These higher values should be discounted because linoleate did not react sufficiently to establish k_5 precisely.

In linseed oil, conjugated dienes are reacting faster than linolenate ($k_4 > k_1 + k_2 + k_3$), which strongly implies conjugation mechanism for linolenate hydrogenation. In soybean oil, because of the small amount of conjugation formed, no definitive conclusions can be reached. Nevertheless at low pressure most of the linolenate disappears through the formation of conjugated dienes.

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