♣ Catalytic Behavior of Palladium in the Hydrogenation of Edible Oils

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Palladium supported on alumina was used to hydrogenate soybean and canola oil. Previous literature reports indicated that palladium forms more *trans* isomers than nickel. At 750 psig, 50 ppm palladium, and at 70 C, only 9.4% *trans* were formed when canola oil was hydrogenated to IV 74. In general, high pressure and low temperature favored low *trans* formation with no appreciable loss in catalyst activity. The effect of pressure, temperature and catalyst concentration on reaction rate, *trans* formation and selectivity is presented. A survey of various catalyst supports is discussed. Apparent activation energies of 6.3 to 8.9 kcal/mol were obtained; they are in good agreement with values reported in the literature.

Previous work (1) indicated that palladium black is a promising catalyst for the hydrogenation of canola oil. Its high activity and low level of geometrical isomerization make it a possible alternative to nickel, presently by far the most popular catalyst for industrial use. However, the higher cost of palladium relative to nickel precludes its use in industry even at a concentration of 150 ppm metal. Supporting the metal generally provides more efficient use of the catalyst. In this study we report on the reactivity of palladium on three supports: carbon, alumina and barium sulphate. The effect of temperature (50-110 C), pressure (50-750 psig), catalyst concentration (5-100 ppm) and starting oil (canola and soybean) on the reaction rate, *trans*-isomer formation and selectivity is presented. A review of palladium-catalyzed edible-oil hydrogenation has been presented previously (1). In general, it was found in the review that palladium forms more *trans*-isomers than nickel. Palladium black, however, when used in our laboratory at 560 ppm, produces a maximum of 14.1% *trans* isomers at IV 55. The operating pressure and temperature were 750 psig and 50 C, respectively (1). This *trans* content is about half of that obtained using commercially available nickel catalysts.

MATERIALS AND METHODS

The apparatus and experimental methods were as described earlier (1). Hydrogenations were carried out in a 300-ml Parr reactor using a charge of 100 g oil per run. Iodine values were calculated from GLC data. The rate constants reported, k, are the pseudo-first order rate constants obtained by assuming the rate of IV reduction to be first order with respect to IV.

Refined, bleached and deodorized soybean oil was supplied by Canada Packers Inc., Toronto. Palladium (5%) supported on carbon (1050 m^2/g), alumina (80-100 m^2/g), and barium sulphate (5 m^2/g), and 0.5% palladium-on-alumina pellets (1/8″ × 1/8″; 100 m^2/g) were purchased from Strem Chemicals Inc., Newburyport, Massachusetts.

Initially, a survey was done of the various supported palladium catalysts, from which a choice was made based on reactivity and degrees of geometrical isomerization. The chosen catalyst was then used in the hydrogenation of canola and soybean oils. Temperature, pressure and catalyst concentrations were the variables used in the subsequent study.

RESULTS AND DISCUSSION

Effect of catalyst support. Canola oil was first used in the hydrogenation runs for the screening of the catalysts. The runs were performed at 750 psig, 70 C and 90 C, and 50 ppm metal concentration. The results are shown in Figure 1A. The rates were almost identical for 5% Pd/alumina and 5% Pd/BaSO₄, the respective rate constants being 8.9 × 10^{-3} and 8.73 × 10^{-3} min^{-1} (Table 1). Palladium on carbon exhibited the slowest reactivity, with a rate constant of 3.43 × 10^{-3} min^{-1}. Catalyst Pd/C has the highest surface area, 1050 m^2/g, yet the lowest activity. A similar observation was made by Ahmad et al. in the study of the hydrogenation of soybean oil using charcoal-supported palladium catalysts (2). They measured the activity of four Pd/C catalysts (5% Pd) as a function of catalyst weight. It was found that the activity was related to the electron count obtained by ESCA, and therefore to the amount of palladium on the exterior surface. The catalysts with the higher surface area would have the metal deposited within the pores, thereby preventing easy access to the reactants. The above study was made at 120 and 160 C, and it was further observed that at 160 C the increased mobility of the molecules overcame, to some degree, the pore resistance. Clearly, diffusional effects are going to be more apparent at the lower (70 C) temperature used in this study, and this would result in a lower reaction rate.

Barium sulphate was chosen on the basis of a study in which it was observed that its use as a carrier, as compared with silica, alumina and carbon, suppressed isomerization without appreciably affecting activity or selectivity (3). However, in our work at approximately IV 75 Pd/alumina gave a linoleic selectivity of 2.7 and a triene content of 9.4, compared to the corresponding values for Pd/BaSO₄ of 4.5 and 14.4 (Table 1, runs 2 and 3; Fig. 1B). At 90 C a similar trend is observed (Table 1, runs 5,6). Thus, it can be concluded that under these conditions, the use of barium sulphate as a carrier enhanced isomerization and selectivity without appreciably affecting activity.

The 0.5% Pd/alumina pellets, with a rate constant of 6.10 × 10^{-3} min^{-1}, had an activity between the 5% Pd/BaSO₄ and the Pd/carbon (Fig. 1A, Table 1). The *trans* formation and linoleic selectivity were similar to Pd/carbon (Fig. 1B; Table 1, runs 1,4). At 90 C, the reaction rate for the Pd/alumina pellets was lower than that for 5% Pd/alumina, yet the *trans* concentration and linoleic selectivity were higher (Table 1, runs 6,7).

The high activity and low *trans* isomerization of 5% Pd/alumina made it the obvious choice for further studies of the effect of the process conditions on the kinetics of hydrogenation.
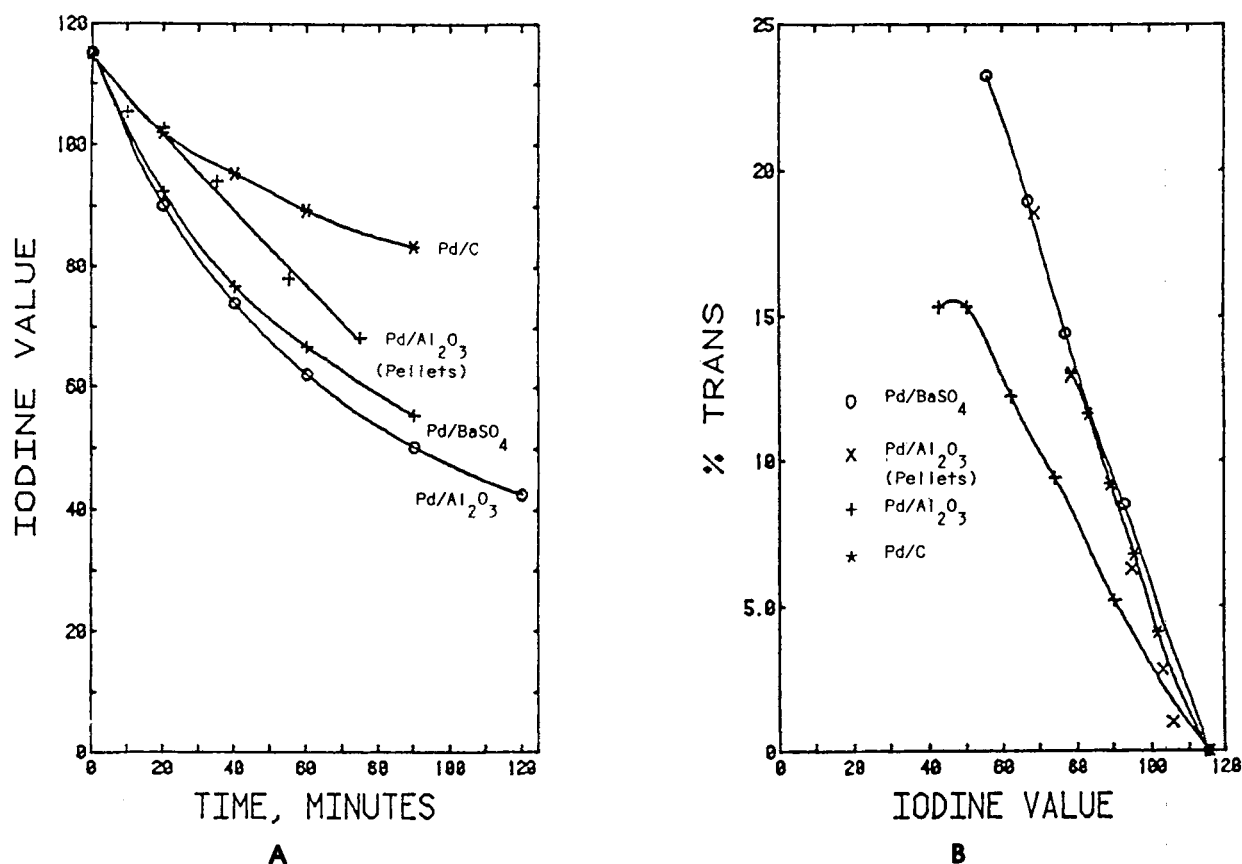
FIG. 1. Effect of catalyst support on canola oil hydrogenation at 750 psig, 70 C, 50 ppm Pd.

TABLE 1

Effect of Catalyst Support on Canola Oil

Run	Catalyst support	Temp °C	Press psig	Conc ppm	IV	Time min	% Trans	S(Ln)	S(Lo)	k × 1000 min^{-1}
1	Carbon	70	750	50	78.5	120	13.0	1.1	3.9	3.43
2	Alumina	70	750	50	73.9	40	9.4	1.0	2.7	8.90
3	BaSO₄	70	750	50	76.6	40	14.4	1.3	4.5	8.73
4	Alumina (pellets)	70	750	50	77.9	55	12.9	1.5	4.2	6.10
5	BaSO₄	90	750	50	70.9	20	19.7	1.5	5.0	16.70
6	Alumina	90	750	50	78.3	20	13.3	1.2	3.0	14.90
7	Alumina (pellets)	90	750	50	64.6	45	21.6	—	4.4	12.20

Effect of pressure. Palladium (5%) on alumina was used to study the effect of pressure on the reaction rate, selectivity and *trans* formation. For canola oil, at 90 C and at a palladium concentration of 100 ppm (Fig. 2A; Table 2, runs 1-3), an increase in pressure from 50 to 100 psig resulted in the rate constant increasing from 5.41 to 9.51 × 10^{-3} min^{-1}, an increase of 76%. At 750 psig, the rate constant was 4.71 × 10^{-2} min^{-1}. The overall increase in the rate constant, for 50 to 750 psig, was by a factor of 8.7, or almost an order of magnitude. For soybean oil, using 50 ppm metal at the same temperature (Table 2, runs 4,5), the increase in pressure from 50 to 750 psig, by a factor of 15, resulted in the rate constant increasing by a factor of 4, from 10.94 to 43.66 × 10^{-3} min^{-1}. The rate constants

for the two oils at the same temperature and pressure but at different catalyst concentrations (Table 2, runs 3,5) indicate that the type of starting oil affects reactivity, as soybean with only 50 ppm Pd reacts just as fast as canola with 100 ppm. The effect of the starting oil on the reaction rate, and the dependency of the rate constants on catalyst concentration, temperature and pressure, will be discussed later on.

The effect of pressure on *trans* formation is shown in Figure 2B. At IV 80, for example, for canola oil, the *trans* concentrations are 37, 34 and 9%, corresponding to pressures of 50, 100 and 750 psig, respectively. For soybean oil at the same IV the total *trans* was 31, and 14% for pressures of 50 and 750 psig, respectively. At 70 C and 100 ppm of Pd, the *trans* content decreases
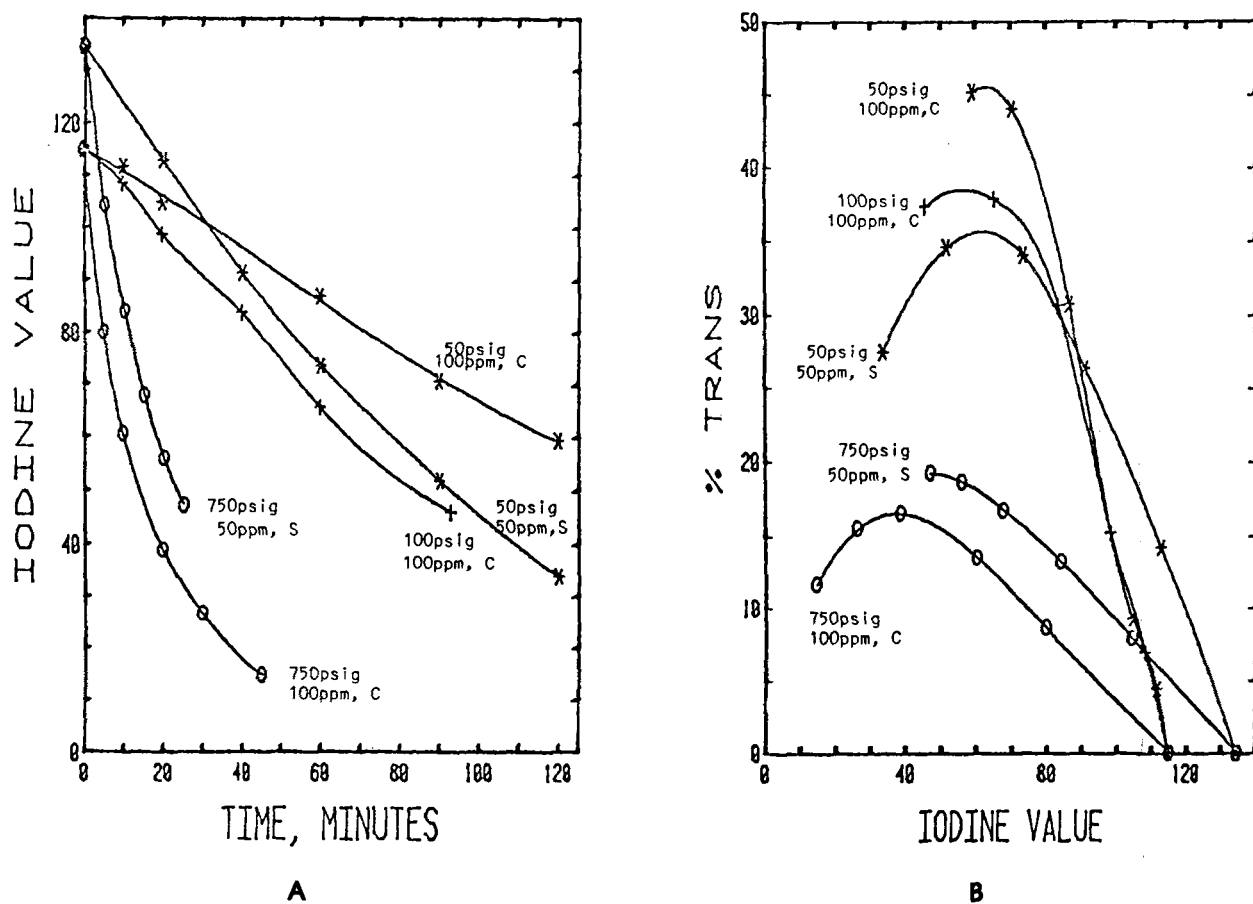
FIG. 2. Effect of pressure on hydrogenation of oil from canola (C) and soybean (S) with 5% Pd/Al$_2$O$_3$ (50,100 ppm) at 90 C.

TABLE 2

Catalytic Behavior of Palladium on Alumina

Run	Oil	Temp (° C)	Press (psig)	Conc (ppm)	IV	Time (min)	% trans	SII	S(Ln)	S(Lo)	k × 1000 (min)$^{-1}$
Effect of pressure											
1	Canola	90	50	100	70.8	90	44.0	97.8	0.9	17.8	5.41
2	Canola	90	100	100	65.7	60	37.8	75.4	0.9	12.4	9.51
3	Canola	90	750	100	60.5	10	13.5	26.9	1.4	2.4	47.10
4	Soybean	93	50	50	73.5	60	34.0	56.0	1.7	6.1	10.94
5	Soybean	90	750	50	67.7	15	16.7	25.1	1.5	1.9	43.66
6	Soybean	70	400	100	66.8	15	20.2	30.0	1.3	2.6	46.78
7	Soybean	70	750	100	72.2	15	14.1	22.7	1.2	1.6	60.66
Effect of temperature											
8	Canola	60	750	50	67.5	75	10.5	22.7	1.0	2.7	7.13
9	Canola	70	750	50	67.4	60	12.9	26.9	1.1	2.8	7.87
10	Canola	90	750	50	66.4	30	17.3	35.6	1.2	3.5	14.90
11	Soybean	50	750	100	75.5	20	11.5	19.6	1.2	1.6	27.00
12	Soybean	70	750	100	72.2	10	14.1	22.7	1.2	1.6	60.70
13	Soybean	90	750	100	64.1	7	18.8	26.8	1.4	2.1	101.40
14	Canola	50	100	100	60.1	100	19.0	37.5	1.3	4.4	5.92
15	Canola	90	100	100	65.7	60	37.8	75.4	0.9	12.4	9.51
Effect of concentration											
16	Soybean	70	750	5	107.6	120	6.1	22.9	1.3	1.1	1.79
17	Soybean	70	750	25	72.5	60	14.2	23.0	1.6	1.7	10.50
18	Soybean	70	750	50	70.5	27	14.6	25.0	1.4	1.7	22.00
19	Soybean	70	750	100	72.2	10	14.1	22.7	1.2	1.6	60.70
20	Soybean	90	750	25	75.3	30	15.5	26.3	1.6	1.7	19.60
21	Soybean	90	750	50	67.7	15	16.7	25.1	1.5	1.9	43.70
22	Soybean	90	750	100	64.1	7	18.8	26.8	1.4	2.1	101.40

from 20.2 to 14.1 for an increase in pressure from 400 to 750 psig (Table 2, runs 6,7). The dependency of *trans* content on pressure is further reflected in the Specific Isomerization Indices (SII), defined as [% *trans*/(IV$_0$-IV)] × 100. In general, the SII increases with decreasing pressure.

Linolenic selectivities varied between 0.9 and 1.4 for canola oil, over the pressure range of 50-750 psig. For soybean oil, the linolenic selectivity showed a variation of 1.7 to 1.2 (Table 2, runs 1-7). However, because of the inherent errors in calculating selectivities, these differences probably were not significant and the selectivities essentially remained constant. Linoleic selectivities showed a steeper change over the 50-750 psig range. For canola oil, the linoleic selectivity decreased from 17.8 to 2.4, a decrease of 87%, while for soybean the decrease was 69%, from 6.1 to 1.9 (Table 2). The general trend of the effect of pressure on selectivities (Table 2), or on composition (Fig. 3A,B), is almost identical to that of palladium black (1). Due to a higher surface concentration of hydrogen at a higher pressure, the polyunsaturated fatty acids may never reach the polybonded state (4) on the catalyst surface. Thus, the initial state (5) will be identical for the linolenic, linoleic and oleic fatty acids, and there would be an equal chance of reaction for all three adsorbed species. The magnitudes of the slopes of composition vs IV at 750 psig (Fig. 3A) are 0.18, 0.17 and 0.18 for linolenic, linoleic and oleic fatty acids, respectively, while for the stearate, the slope is

0.55, or approximately the sum of the three slopes of the unsaturates. At the lower pressure (Fig. 3B), the polybonded states will predominate and the triene and diene would hydrogenate to the monoene before further reduction to the saturate. The preferential adsorption of polyunsaturates as compared to monounsaturates (6) is further illustrated (Fig. 3B) by the steeper initial slope for the triene as compared with the diene.

Effect of temperature. The effect of temperature on reaction rate is shown (Fig. 4A) for canola oil, using 50 ppm palladium at 750 psig. A 10 C rise in temperature, from 60 to 70 C, increased the rate constant 10%, from 7.13 to 7.87 × 10^{-3} min^{-1} (Table 2). A further 20 C increase resulted in a 90% increase in the rate constant, to a value of 14.9 × 10^{-3} min^{-1}. As will be shown later, the rate constant exhibits an Arrhenius relationship to temperature, as is to be expected, and this fact was used to obtain a value for the overall activation energy. Geometrical isomerization increases with temperature (Fig. 4B). At IV 67 (Table 2, runs 8-10), the *trans* concentrations for 60, 70 and 90 C are 10.5, 12.9 and 17.3%, respectively. The SII shows a 57% increase over the 30 C range, from 22.7 to 35.6. As with pressure, temperature appears to have very little effect on linolenic selectivity for both canola and soybean oil (runs 11-13). Linoleic selectivities also do not change appreciably at the higher pressure. A maximum increase of 30% is observed for both canola and soybean. At 100 psig, however, for canola, the *trans*
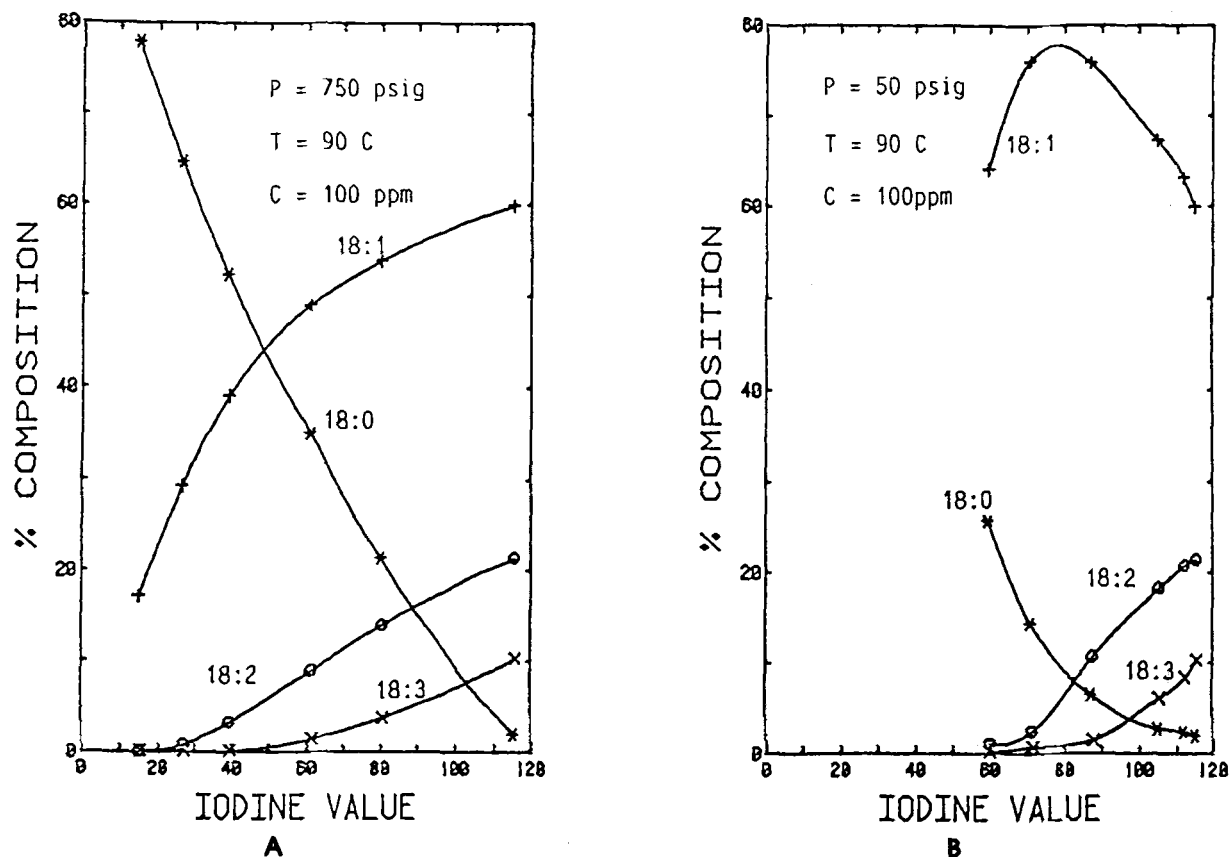

FIG. 3. Effect of pressure on composition of canola oil.

concentration almost doubles for a 40 C increase in temperature, while the linoleic selectivity increases threefold (runs 14,15).

Effect of catalyst concentration. Concentrations of 5, 25, 50 and 100 ppm palladium were used to study the effect on rate and isomerization for soybean oil. At 750 psig and 70 C, increasing the catalyst concentration from 5 to 100 ppm resulted in the hydrogenation rate of soybean oil increasing from 1.79 to 60.70×10^{-3} min^{-1} (Fig. 5A; Table 2, runs 16-19). A similar trend is observed at 90 C (Table 2, runs 20-22). A plot of the natural logarithms of the rate constants vs. concentration (Fig. 6). produced an excellent fit. Regression of the data produced a slope of 1.2, indicating that at these conditions of temperature and pressure, the hydrogenation rate is not limited by mass transfer.

Over the catalyst range studied, the SII's showed almost no variation at 70 and 90 C. This is also illustrated in Figure 5B, where the percent of *trans* shows no variation with concentration for the runs at 70 C. Linolenic selectivity appears to remain relatively constant at 1.4 for the runs at 70 C.

Linoleic selectivity increases 55%, from 1.1 to 1.7 (Table 2, runs 16-19), due to a fivefold increase in the catalyst concentration for runs 16 and 17, but remains constant for the subsequent increases. At 90 C, linolenic selectivities did not change significantly (Table 2, runs 20-22).

Effect of type of oil. In general, it was observed that the rate constant was higher for soybean oil than for canola at identical conditions of temperature, pressure and catalyst concentration. The pressure in all these cases was 750 psig. The SII values remained essentially the same for both oils except for the run at 90 C and 50 ppm palladium (Table 3), where the SII was 25% higher for canola than for soybean. Absolute values of percent of *trans* cannot be used in this comparison, as the compositions of the two oils are different. The results are summarized in Table 3. The ratio of the rate constants for soybean to canola vary from 2.16 to 2.93, with an average value of 2.62. The linolenic selectivities for soybean and canola, averaged over 15 runs for each, are 1.2 and 1.1, respectively. Therefore, the rate of reduction of linolenic acid is the same as for linoleic acid. Because the reaction scheme involves a first order dependency of linolenic and linoleic acid concentrations, any change in either of the fatty acids will be reflected in the overall rate. The ratio of trienes in soybean to that in canola is 0.88, but the ratio of dienes is 2.43. Thus, it is most likely that this difference in the starting oil composition is responsible for the higher hydrogenation rate constant of soybean oil.

ACTIVATION ENERGIES

The overall rate constant values at different temperatures were used to calculate an apparent activation
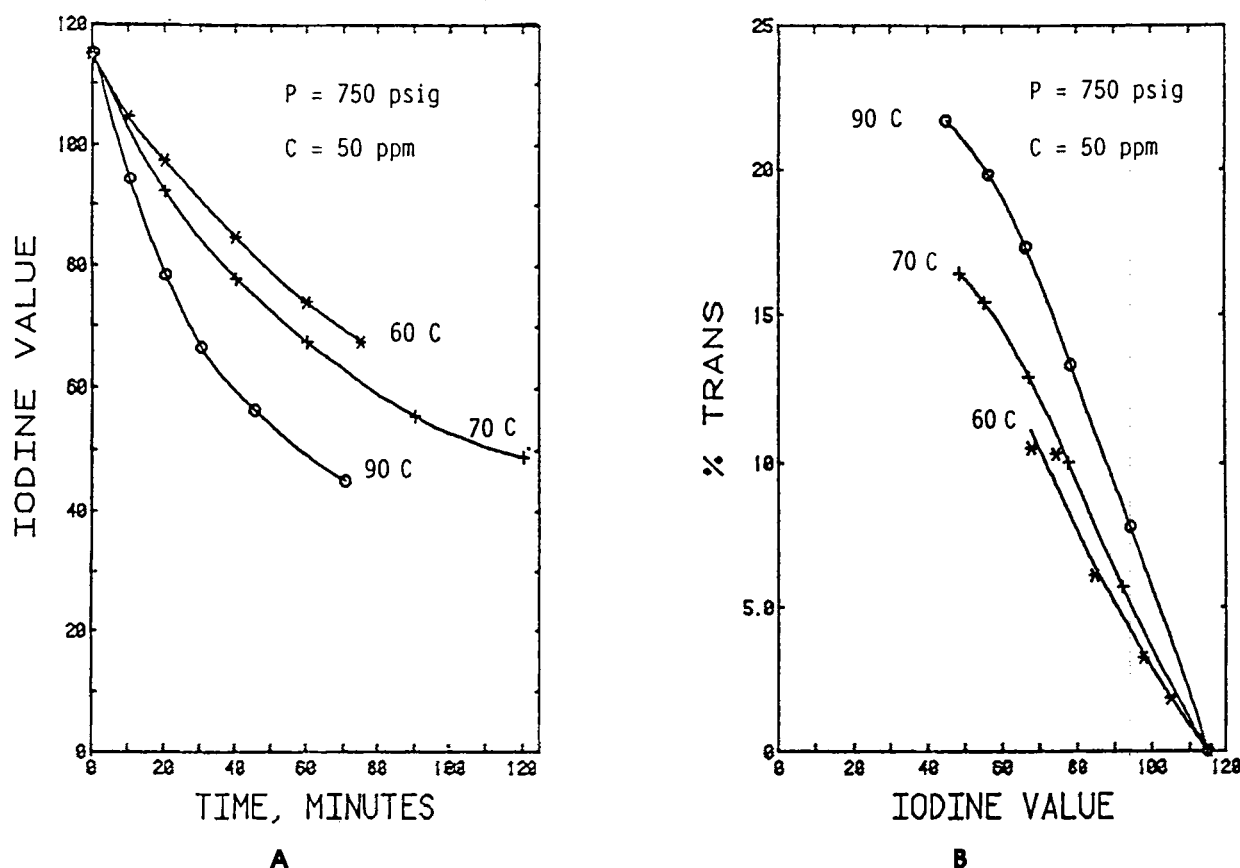

FIG. 4. Effect of temperature on hydrogenation of canola oil.
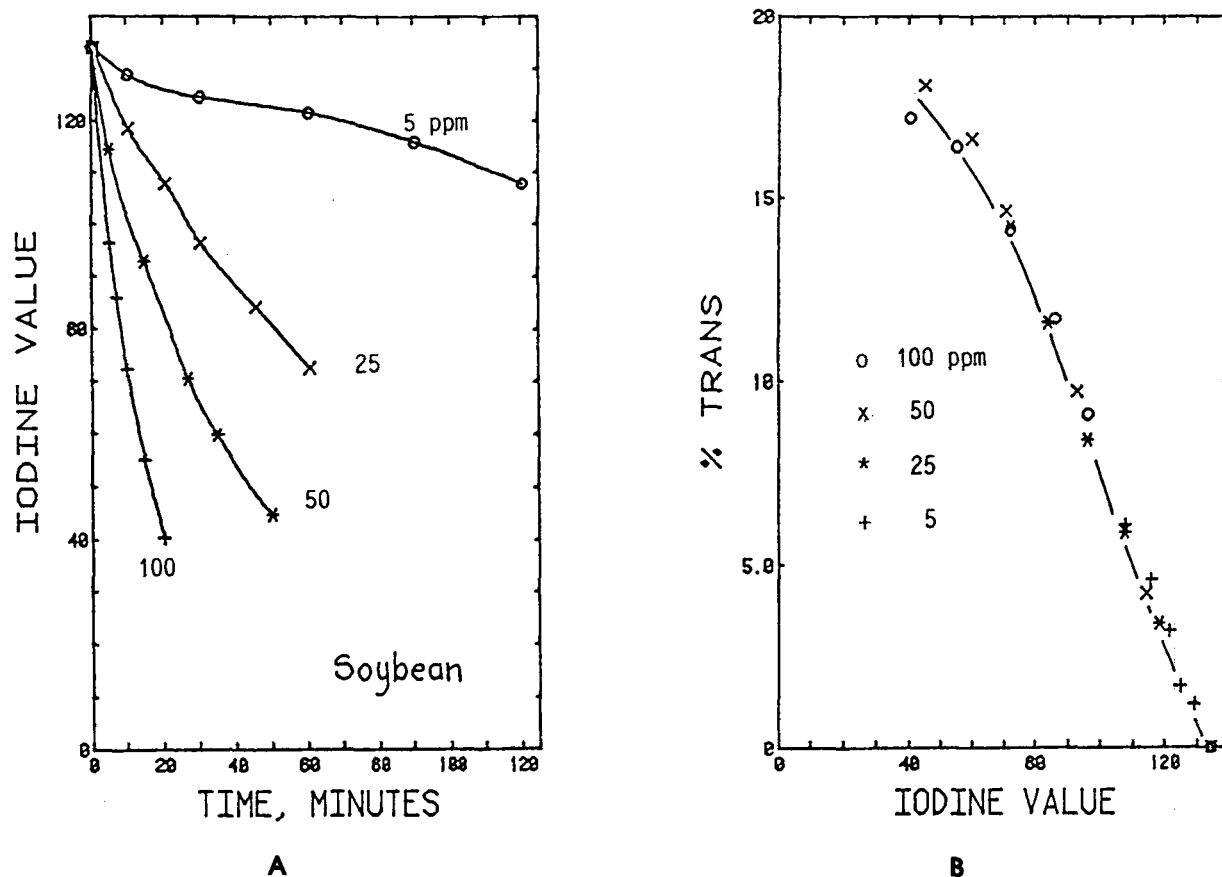
FIG. 5. Effect of catalyst concentration on hydrogenation of soybean oil at 750 psig, 70 C.
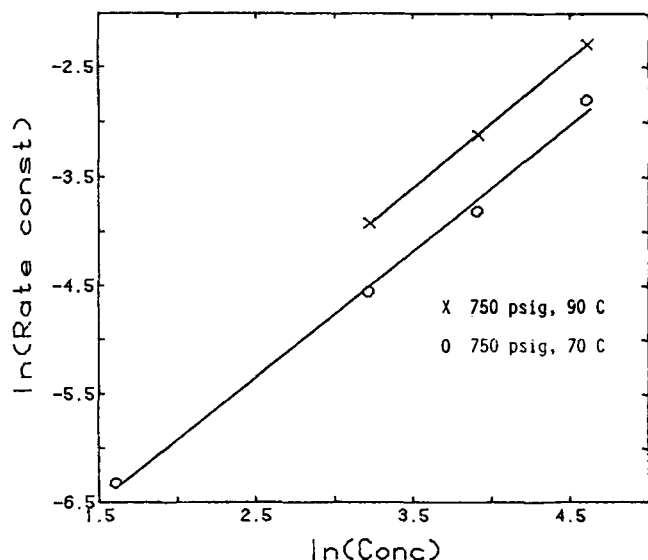

FIG. 6. Effect of catalyst concentration on rate constant for soybean oil.

energy assuming an Arrhenius relationship. The data for palladium black, based on work previously published (1), has been included for comparison (Table 4). The regression coefficient, near unity, for each set of runs confirms the Arrhenius relationship of tempera-

ture to the rate constant. As expected, the average apparent activation energy of 7.7 kcal/mol did not vary significantly between each set as the reacting species and the metal site has not been changed, even though the catalyst support and the oil are different. There have been no values for the apparent activation energy reported for palladium. However, values reported for the nickel-catalyzed hydrogenation of palm oil are 8 to 12 kcal/mol (7). As palladium is more active than nickel, a lower value for the activation energy is expected.

Modelling of rate constant. The data of both oils were used to obtain an empirical relationship for the rate constant with respect to pressure, temperature and catalyst concentration. The rate constant k, defined from the rate expression as

$$\text{Hydrogenation rate} = -\,d(IV)/dt = k\,(IV) \qquad (1)$$

was expressed in the following form

$$k = ae^{b/T}\,P^cC^d \qquad (2)$$

where k = rate constant in min^{-1}, P = hydrogen pressure in psig and C = concentration of catalyst in ppm. Equation 2 assumes that there are interactions among the variables T, P and C, and this is known to occur.

TABLE 3

Effect of Type of Oil on Hydrogenation by Pd/Alumina

Press (psig)	Temp (C)	Conc (ppm)	K_s(1/min) Soybean	k_c(1/min) Canola	K_s/k_c	SII Soybean	SII Canola
750	90	50	0.0437	0.0149	2.93	24.6	30.7
750	70	100	0.0607	0.0211	2.87	22.0	22.6
750	70	50	0.0220	0.0079	2.80	25.2	25.7
750	90	100	0.1014	0.0471	2.16	26.7	25.9
750	50	100	0.0270	0.0115	2.35	19.0	21.4
Average linolenic selectivity:						1.21	1.08

TABLE 4

Activation Energies Calculated From Rate Data

Catalyst Oil	Press (psig)	Conc (ppm)	Temps (°C)	Ea (kcal/mol)	$\ln(k_0)$	Regr coeff
Pd black canola	750	566	50-90	6.3	6.7	0.99
Pd black canola	250	566	50-90	7.5	7.7	0.97
Pd black canola	750	150	50-90	7.5	7.6	0.99
Pd/alumina canola	750	100	50-90	8.1	8.2	0.99
Pd/alumina canola	750	50	60-90	6.6	5.0	0.95
Pd/alumina soybean	750	100	50-110	7.2	7.7	1.00
Pd/alumina soybean	750	50	50-90	8.6	8.4	1.00
Pd/alumina soybean	750	25	50-90	7.8	6.9	1.00
Pd/alumina canola	500	50	50-90	8.1	7.1	1.00
Pd/alumina canola	250	50	70-110	8.9	8.0	1.00
Avg (S/dev)				7.66	(0.78)	

A multiple linear regression was used to evaluate the constants for each oil. The results of the regression are

$$k_{soy} = 0.050 \ e^{(-3000)/T} \ P^{0.6} \ C^{1.1} \qquad (3)$$

$$k_{can} = 0.407 \ e^{(-3300)/T} \ P^{0.5} \ C^{0.6} \qquad (4)$$

The regression coefficients for equations 3 and 4 are 0.980 and 0.782, indicating a much poorer fit for canola oil than for soybean. While the exponents for T and P are similar for the two oils, there is a significant difference between the C term and the constant a_0. The difference is most likely due to the exclusion of the agitation term, as there will certainly be a quantitative relationship between this term and T, P and C. The constant a_0 implicitly contains this term, as agitation was kept constant for each run. The assumption that all the reactions were operating under surface-controlled conditions may thus be invalid for certain runs of canola, especially under low pressure and high temperature conditions. The low-pressure (50,100 psig) and high-pressure (500,750 psig) runs for canola

were regressed individually, and the corresponding exponents for C were 0.51 and 1.14. Thus, regression of kinetic data is an acceptable way of generating kinetic models as long as the reaction-controlling conditions are the same for all runs used.

From this work, it can be concluded that 5% palladium-on-alumina may be a viable industrial hydrogenation catalyst which produces less than half the amount of trans isomers at elevated pressures than nickel does at conditions under which it is normally used. Furthermore, when compared with palladium black (1), an order of magnitude less palladium is used for the hydrogenation due to the enhanced reactivity as a result of the catalyst support. Pilot plant studies have been carried out with 5% palladium-on-carbon (8,9). Hydrogenation of a single batch of 15,500 lb of soybean oil to produce margarine was carried out with 775 g of 5% palladium-on-carbon corresponding to 5.5 ppm palladium (8).

In another study by Zajcew using palladium catalysts, the catalyst was reused repeatedly (9). The high activity of palladium, and its previously demonstra-

ted ability to be recycled, may offset its much higher cost than nickel. More studies on the behavior of palladium will be published at a later date.

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