Catalytic Behavior of Palladium in the Hydrogenation of Edible Oils II. Geometrical and Positional Isomerization Characteristics

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The geometrical isomerization characteristics of 5% Pd/alumina were investigated using response surface methodology. From the response surface, it was observed as expected that more *trans* isomers were formed at lower pressures and higher temperatures. A doubling of the metal concentration from 50 to 100 ppm resulted in a small increase in isomerization in soybean oil, while for canola oil the same increase had a larger effect, especially at lower pressures. Similarly, an increase in temperature increases geometrical isomerization, especially at lower pressures, but the effect is more pronounced for canola than for soybean oil. Positional isomers were determined by oxidative ozonolysis in BF_3-MeOH and subsequent GLC analysis. Higher pressures suppressed positional isomerization. The effect of various catalyst supports on positional isomerization was also investigated.

Based on the work reported in Part I (1), the mechanism of hydrogenation was studied by the analysis of positional isomers and by the application of response surface methodology to *trans*-isomer formation. The goal of the program is to develop industrially useful catalysts which have a high *cis* selectivity and an activity similar to that of nickel. We have shown that 5% Pd/Alumina is an active catalyst that hydrogenates canola and soybean oil forming less than half the *trans* isomers that nickel does (1). In this study we discuss the effects of process variables, namely temperature, pressure, catalyst concentration and type of starting oil on geometrical isomerization. The effect of pressure and catalyst support on positional isomerization is also discussed.

Palladium black, and palladium (5%) on alumina, carbon, and barium sulphate were used in this study. Palladium (5%) on carbon, together with nickel and platinum have been used in the hydrogenation of alkali-conjugated linoleate (2). The monoene isomer profiles obtained using nickel and palladium catalysts were indistinguishable, while isomerization of monoenes was suppressed with platinum (5%) on carbon at 80 psig. The deuteration of methyl linoleate using palladium, nickel, platinum and copper-chromite catalysts was also studied by Koritala et al. (3). It was observed that 51% of the linoleate was reduced via a conjugated intermediate for 5% palladium/C. The respective percentages for nickel and platinum were 59% and 23%. Copper catalysts reduce linoleate solely through a conjugated intermediate (3). Copper-chromite formed the highest amount of *trans* isomers, with palladium and nickel next, and platinum forming the least. In both studies (2,3), for palladium, the pressure used did not exceed 80 psig, while the temperature did not exceed 35 C. Pd/Carbon has also been used in the hydrogenation of soybean oil from which empirical models were developed that predicted the rate, *trans*-isomer formation and selectivity over a range of practical reaction conditions (4). It was observed that while palladium has a very high activity, and thus can be substituted for nickel at greatly reduced temperatures and catalyst concentrations, it offered no advantage over nickel in *trans*-isomer formation or selectivity.

MATERIALS AND METHODS

The hydrogenation procedure for canola and soybean oils was presented in Part I (1). Detailed results for all runs are not reproduced for the sake of brevity, but are readily available from the author. The ranges of temperature, pressure and catalyst concentration used for canola oil were 50–110 C, 50–750 psig, and 50–100 ppm Pd, while those used for soybean were 50–135 C, 50–750 psig, and 5–160 ppm Pd, respectively. The *trans* content was measured according to the standard AOCS method by using a Nicolet 60SX FTIR spectrophotometer. The percent *trans* at IV 70, calculated by linear interpolation, was used as the response in order to generate a response surface for the second order design chosen (5). The variables temperature (x_1), pressure (x_2) and catalyst concentration (x_3) were regressed with respect to the response percent *trans* to obtain the quadratic polynomial model

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$$

where

y = expected response (percent *trans*)
b_0 = intercept
b_i = linear coefficient of the i^th variable
$b_{i,i}$ = quadratic coefficient of the i^th variable
$b_{i,j}$ = interaction coefficient for the interaction of variables i and j

For the determination of the positional isomers, the 18:1 fraction of the fatty methyl esters was initially separated before subsequent ozonolysis. The separation, on the basis of chain length and unsaturation, was performed by high performance liquid chromatography (HPLC). Chromatograms were run on a Hewlett Packard HP 1090 Liquid Chromatograph, using a 250 × 10-mm reverse phase C18/Silica semi-preparative column. The solvent used was purified acetonitrile (6). Detection was carried out by a refractive-index detector (HP 1037A) operated at 40 C. The C18 monoene fraction was checked for purity by GLC, using direct injection into a 30-m Supelcowax 10 column (Supelco Inc., Toronto, Canada). The purity ranged from 92–95%, with the rest being 16:0 which coelutes with the monoene. Though the separation can be further improved by changing the solvent, no attempt was made to do so as the 16:0 served as an internal standard for the subsequent ozonolysis.

The positional isomers were determined according to the method of Ackman (7), using 14% BF_3-MeOH. Purified hexane was used in place of methylcyclohexane. The resulting esters and diesters were analyzed by GLC using a Hewlett Packard 5890A Gas Chromatograph and 3392A Integrator. A 30-m Supelcowax 10 column was used under the following conditions: 120 C for four min, program at 25 C/min to 250 C, and hold. The esters and diesters from standards of Δ 6, Δ 9 and Δ 11 methyl-octadecenoate (Nu-Chek Prep Inc., Elysian, Minnesota) were used to confirm the retention times. The relative weight response in the FID was obtained by the calibration of known weights of 4:0 to 22:0 monocarboxylic methyl esters (Nu-Chek Prep Inc).

RESULTS AND DISCUSSION

Surface response methodology. The quadratic polynomial which resulted from the regression of the data for canola is given by the following equation:

$$\begin{aligned} y = {} & -39.6 + 0.711T + 0.0497P + 0.251\,C \\ & - 1.69 \times 10^{-3}T^2 + 1.30 \times 10^{-5}P^2 \\ & - 6.10 \times 10^{-4}TP + 8.76 \times 10^{-4}TC - 4.5 \times 10^{-4}PC \end{aligned} \qquad [I]$$

while for soybean the equation is

$$\begin{aligned} y = {} & -15.0 + 0.671T - 0.025P + 0.133\,C \\ & + 8.71 \times 10^{-4}T^2 - 1.79 \times 10^{-3}P^2 + 4.50 \times 10^{-5}C^2 \\ & - 2.60 \times 10^{-4}TP - 1.67 \times 10^{-3}TC - 1.60 \times 10^{-4}PC \end{aligned} \qquad [II]$$

The concentration quadratic term for canola oil was not included as only two concentrations were used. The plots of experimental value of percent *trans* versus that calculated from the above equations indicate a very good fit for both oils (Fig. 1A and 1B), with regression coefficients of 0.984 and 0.981 for canola and soybean oil, respectively. Fitted surfaces for 50 and 100 ppm catalyst are shown in Figure 2. Generally, surface response procedures are not designed to increase the understanding of the underlying system, but rather to optimize operating conditions or to define a region in space where certain operating specifications are met (8). In this case, however, as *trans* isomerization is the predicted response, one may use the surface to gain an understanding of the effect of process variables on isomerization.

In general, *trans*-isomer formation is favored at lower pressures. Doubling the catalyst concentration from 50 to 100 ppm also results in higher geometrical isomerization, especially at lower pressure. The effect of concentration on *trans* formation is more pronounced for canola (Fig. 2A) than for soybean oil (Fig. 2B). An increase in temperature results in an increase in the *trans* formation; however, this effect of temperature is lower at higher pressures. Qualitatively, these results agree with those reported previously (9), in which the isomerization was observed to vary with the dissolved hydrogen concentration near the catalyst surface. Process conditions which decrease the hydrogen concentration near the catalyst surface at the same time increase isomerization. High hydrogen coverage on the catalyst surface, due to a higher pressure, for example, will result in a high hydrogenation rate of the surface-bonded unsaturated fatty acids. Thus, isomerization will be low. Conversely, low hydrogen coverage, due to an increase in temperature or an increase in the catalyst concentration, will facilitate both geometrical and positional isomerization. The half-hydrogenated state (10) and the allyl intermediate (11) have both been used to explain isomerization during hydrogenation (12). Evidence for both mechanisms occuring simultaneously has been shown by different authors (13-15).

Positional isomerization. Migration of the double bond along the carbon chain occurs as a result of the hydrogenation mechanism. The determination of the positional isomers will give a measure of the extent of the migration and also whether or not the hydrogenation proceeded via a conjugated intermediate. Allen and Kiess (16) found that hydrogenation took place with equal ease in the 1,2 1,4 and 3,4 positions of the conjugated diene system of c10,c12-octadecadienoic acid.

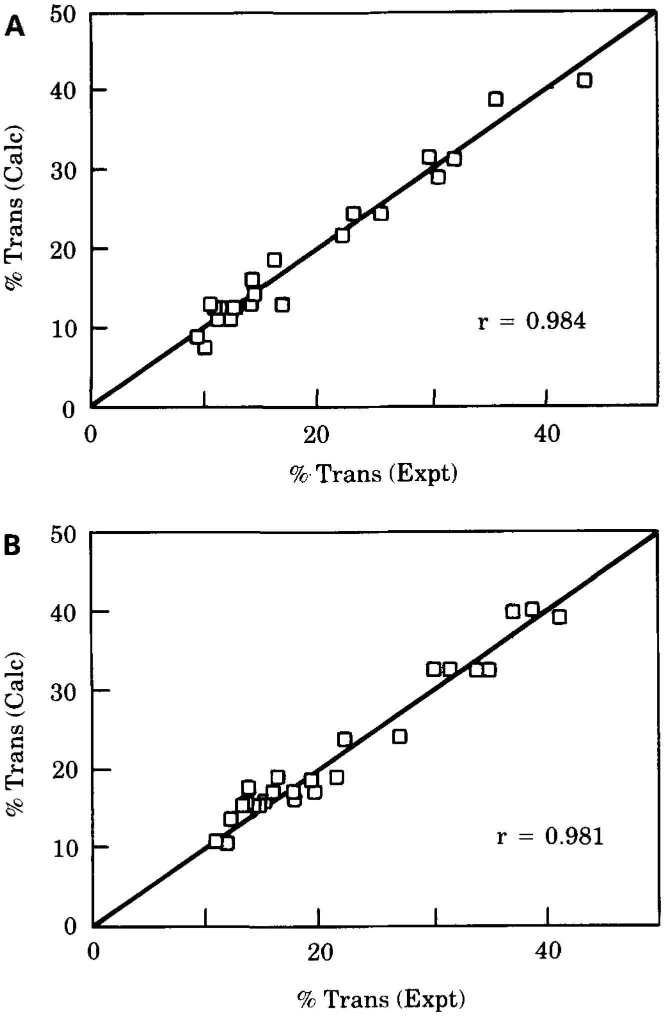

FIG. 1. Correlation of calculated vs experimental percent *trans* values for canola (A) and soybean oil (B).

Hence, if the 9,12 linoleic acid produced only 9,11 and 10,12 conjugated diene in equal amounts in the initial step of the reaction, addition of hydrogen should show twice as much Δ 10 or Δ 11 as Δ 9 or Δ 12. Hydrogenations even under drastic conditions did not show this ratio of positional isomers. Further work by Allen (17) on the hydrogenation of linoleate resulted in an experimental monoene distribution which was in good agreement with that expected from a nonconjugated hydrogenation. Itatani and Bailar (18) showed that conjugated dienes have IR absorption bands at 10.55 and 10.13 μm. All the samples analyzed in our laboratory failed to show these absorption bands. Only the *trans* double-bond absorption band at 10.36 μm was present, indicating the absence of conjugation during the hydrogenation. However, detection of the absorption bands is not a conclusive test for conjugation because the conjugated dienes react faster than the methylene interrupted dienes and thus would not accumulate in the products.

It is generally accepted that the double bond farthest away from the carboxyl group has the highest reactivity. Allen et al. (19) observed that the Δ 12 bond in linoleic acid was hydrogenated faster than the Δ 9 bond. However, under conditions of poor hydrogen dispersion, both bonds were hydrogenated at the same rate. The pressures used in the above experiments were 5 psig and atmospheric, respectively. Thus, at 750 psig, a pressure typically used in our work, it can be reasonably assumed that the Δ 15 bond of the linolenic group will have the highest reactivity, with the Δ 12 having a higher reactivity than the Δ 9 bond. In fact, none of our hydrogenated samples had a Δ 15 monoene isomer.

The effect of pressure on positional isomerization is shown in Figure 3. Naturally occurring canola oil was found to contain octadecenoate positional isomers in the Δ9 and Δ11 positions, in agreement with the results of Ackman and Sebedio (20). The catalyst used was 5% Pd/alumina. At 50 psig, 100 ppm Pd were used, while at 750 psig, 50 ppm Pd were used. At 750 psig and IV

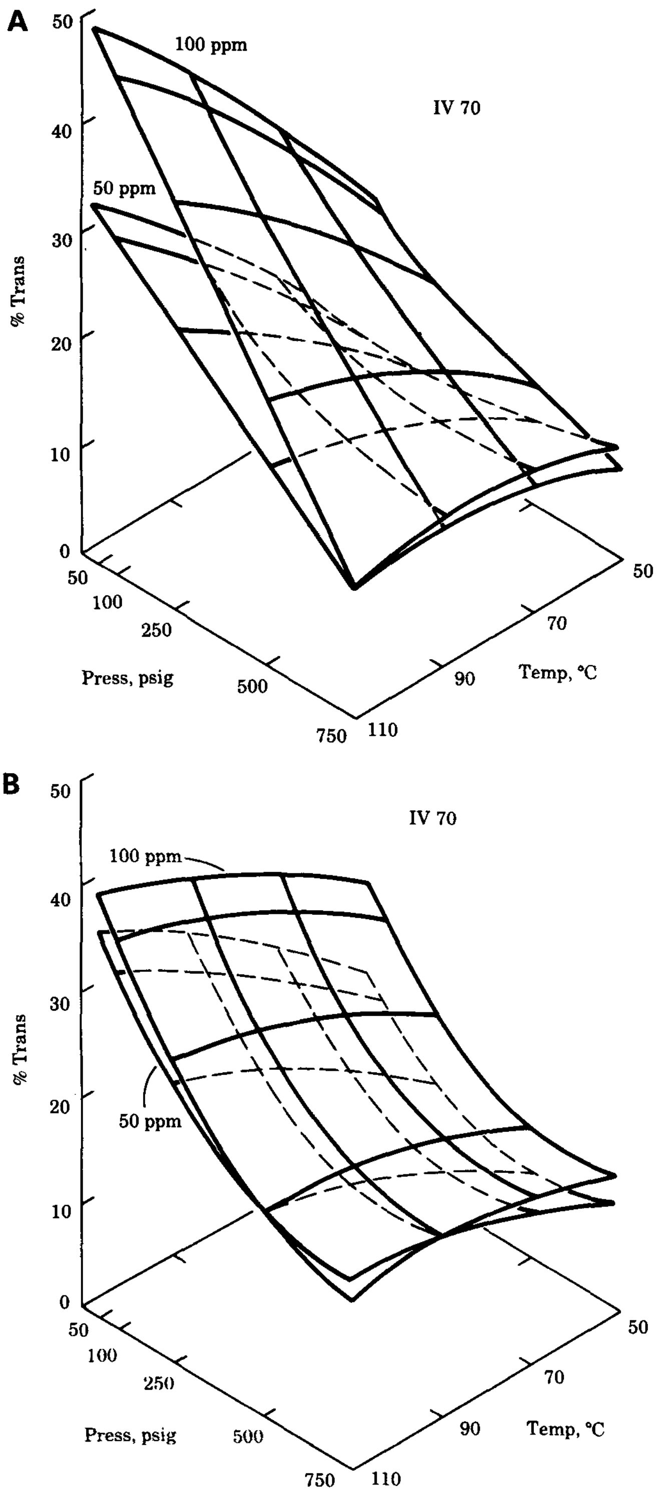

FIG. 2. Response surfaces generated by quadratic equation for canola (A) and soybean oil (B).

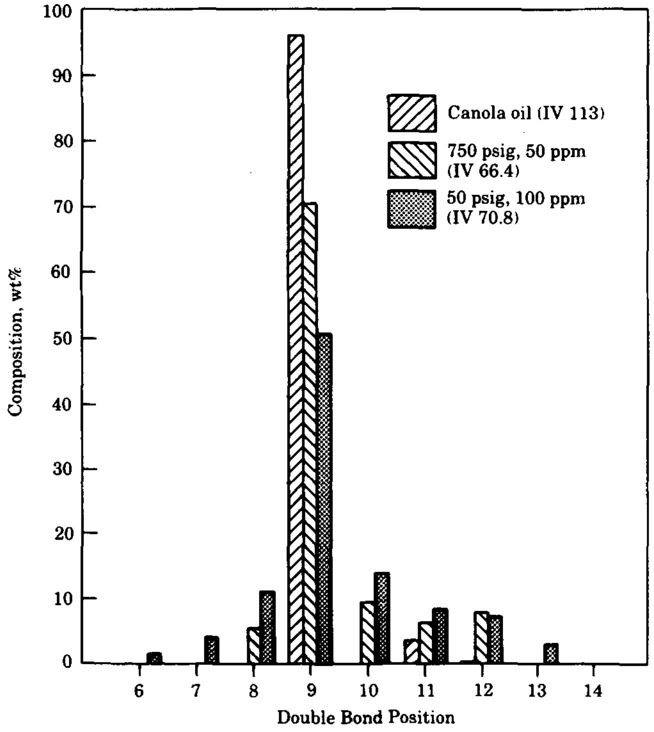

FIG. 3. Effect of pressure on positional isomerization for canola oil, at 90 C, 50–100 ppm Pd (5% Pd/alumina).

66.4, the monoenes are primarily in the Δ9 position, with less than 10% each in the Δ8, Δ10, Δ11 and Δ12 positions. At 50 psig and IV 70.8, 50.8% of the monoenes are Δ9, compared with 70.7% at 750 psig, and isomers exist from Δ6 to Δ13. For soybean oil hydrogenation using 5% Pd/alumina, somewhat different results were obtained (Fig. 4). Like canola, the starting oil has monoenes in the Δ9 and Δ11 positions. On hydrogenation at 750 psig, 90 C and 100 ppm catalyst, the isomers are distributed from positions Δ6 through Δ13 at IV 64.1. Unlike canola oil, soybean oil has about 50%, or 2.5 times as much linoleate. This difference, together with the doubling in the catalyst concentration, is most likely responsible for the wider distribution of monoenes in soybean than in canola oil. The difference in isomerization between the oils is readily explainable using the starting and final monoene concentrations. Canola oil has about 60% monoenes, while the partially hydrogenated sample has 55.6%. Soybean oil began with only 23.3% monoene but the final sample at IV 64.1 has 41.6% (Table 1). The isomeric monoenes in canola oil are essentially those from the starting monoene, with the rest being formed from the reduction of linolenate and linoleate. For soybean oil, however, due to the lower starting monoene concentration, the increase in the final monoenes is due primarily to the reduction of linoleate. The increase in the stearate content for the final soybean sample is almost 19%, while the total change in polyunsaturates (18:2 + 18:3) is a decrease of 42.7% (Table 1). For canola, the decrease in polyunsaturates is 21.6%, for a 25.5% increase in the stearate content. Thus, assuming the consecutive reaction scheme to be applicable, almost all the isomeric monoenes are due to the linoleate reduction. For nickel, a more realistic scheme for the hydrogenation of linoleate is one which includes a direct linoleate to stearate shunt (21). The ratio of the rate constants (k's) of linoleate to oleate, to that of linoleate to stearate was found to be approximately 24. If a similar shunt were found to be present in the reaction scheme involving palladium, the high k ratio would still validate the assumption that the monoenes are primarily from linoleate. Also, the higher starting IV of soybean oil relative to canola has resulted in the final soybean oil sample being hydrogenated to a higher degree, thus increasing the probability for isomerization.

There was no evidence of a Δ15 isomer in all the samples, indicating that the linolenate is reduced initially only to the linoleate. The half-hydrogenated intermediate state (10) can be used to explain the observed positional isomer distribution. Consecutive movements of the double bond along the carbon chain during the hydrogenation-dehydrogenation process will account for the formation of positional isomers. Clearly this migration of the double bond along the chain will be more apparent at a low surface coverage of hydrogen. This may be caused by a higher reaction temperature, a lower pressure, a higher catalyst concentration, a lower degree of agitation, a higher degree of unsaturation of the oil, or combinations of these variables. For both oils, a lower pressure results in an increase in the positional isomerization. A higher linoleate content, as for soybean oil, would increase the probability of migration occurring during the adsorption-desorption sequences.

The effect of various catalyst supports on positional

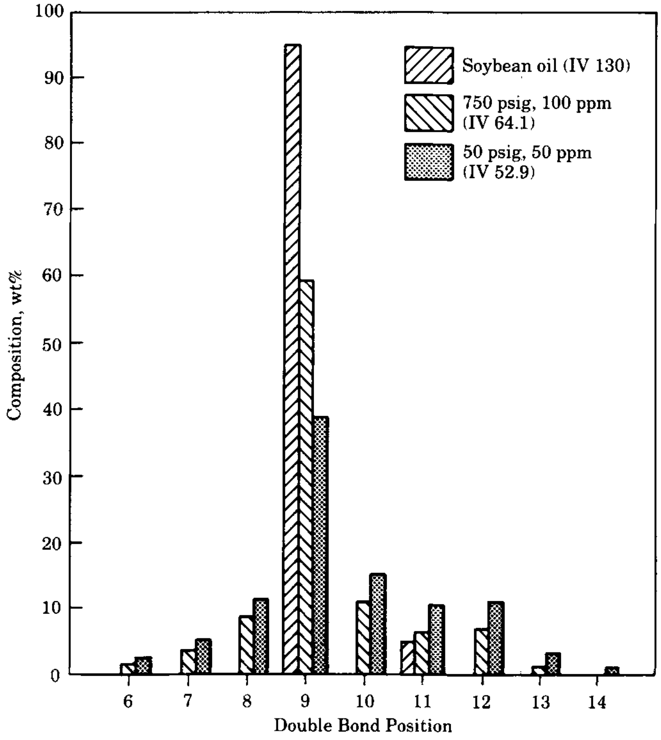

FIG. 4. Effect of pressure on positional isomerization for soybean oil, at 90 C, 50-100 ppm Pd (5% Pd/alumina).

TABLE 1

Fatty Acid Composition of Original Oil and Oil Hydrogenated Using 5% Pd/Alumina

	Cat conc (ppm)	Press (psig)	Temp (C)	IV	18:0	18:1	18:2	18:3
Canola				115.0	1.9	59.8	21.3	10.2
	50	750	90	66.4	27.4	55.6	8.2	1.7
Change in composition					25.5	-4.2	-13.1	-8.5
	100	50	90	70.8	14.3	76.0	2.3	0.6
Soybean				129.0	3.2	23.3	49.8	8.7
	100	750	90	64.1	22.1	41.6	14.6	1.2
Change in composition					18.9	18.3	-35.2	-7.5
	50	50	90	52.9	26.0	54.3	3.6	0.0

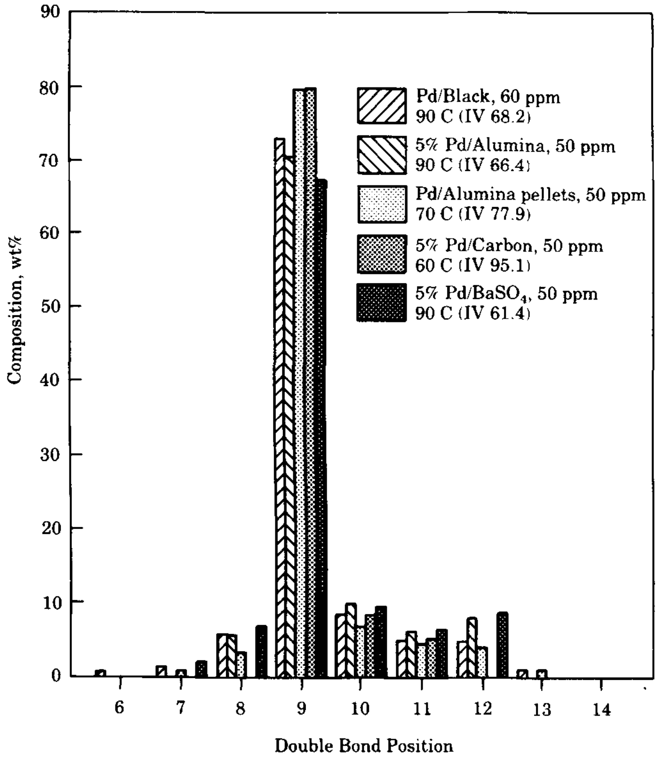

FIG. 5. Effect of catalyst support on positional isomerization for canola oil, at 750 psig, 60-90 C, 50-61 ppm Pd.

isomerization was also investigated. Considerable activity for double-bond migration on alumina-supported metal catalysts was observed in the absence of hydrogen at 100 C (22). When the same catalysts were used without the support, little or no activity was observed. Hence, it was assumed that the hydrogen necessary to form the half-hydrogenated intermediate originated from the support by migration of adsorbed hydrogen atoms from this support to the metals (21). Under the conditions used in our study, 750 psig, 60-90 C and 50-100 ppm palladium, there was no significant difference between unsupported palladium [Data from Ref. (23)] and palladium supported on alumina (Fig. 5). Also, the Pd/alumina pellets and Pd on carbon and on barium sulphate supports there appears to be no change in the positional isomers (Fig. 5), even though of all these catalysts palladium-on-alumina had the lowest level of geometrical isomers (1). This possibly indicates the absence of the π-allyl mechanism at high pressure, as such a mechanism only allows a geometrical isomerization via a positional isomer (14).

The complexity of the hydrogenation reaction and the inadequacy of models that fully describe the hydrogenation mechanism make it difficult to draw general conclusions. At pressures of 750 psig, 5% Pd/alumina produces only about 10-15% *trans* isomers, and does not promote positional isomerization to any large extent. A typical monoene distribution for canola oil would be Δ8 to Δ12, while for soybean the distribution is Δ6 to Δ13. For both oils, the main monoene isomer is Δ9, the content of which is six to seven times as much as the next isomer, Δ10. Most of the published research on positional and geometrical isomerization of methyl linoleate and methyl oleate has been performed at much lower pressures and using other catalysts, mainly nickel. Extrapolation of previous work to higher pressures, such as used in this study, and to different catalysts is not possible, at least not quantitatively. Hydrogenation of pure compounds, for example methyl linoleate, using a 5% Pd/alumina at elevated pressures and lower temperatures is necessary for a further understanding of the basic catalystic behavior of supported palladium in edible oil hydrogenation. Given the present analytical techniques for the identification and quantification of geometrical and positional isomers, such a goal can be readily achieved.

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