Diene-to-Saturate Shunt in Fat Hydrogenation[1]

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ABSTRACT

In matching experimental data to kinetic models for hydrogenation of methyl *cis*-9,*cis*-15-linoleate, ethylene glycol diundecylenate and 1,7-octadiene with platinum or palladium catalysts, only if a diene-to-saturate shunt of 15- to 25% is included can a good fit be secured between the model and experimental composition. With nickel the shunt is much smaller or absent. Although the shunt might be attributed most readily to a liquid diffusion effect, its independence of temperature, viscosity and presence or absence of solvents and catalyst support suggests that some other factor is responsible. Evidence for similar shunts is found for other materials, including soybean triglycerides.

INTRODUCTION

In mathematical simulation of the kinetics of hydrogenation, several investigators have had to include "shunts" in their model to secure a good fit with experimental composition. Bailey (1) was probably the first to employ such a shunt with triglycerides when he considered linolenate going directly to monoene without stopping at the diene level. Later we found this same shunt necessary when studying the hydrogenation of methyl linolenate-linoleate mixtures with the aid of radioactive tracers (2). Albright and Wisniak (3) found a linoleate-to-stearate shunt necessary to fit data on hydrogenation of cottonseed oil at higher than usual pressures. In vapor-phase hydrogenation of methyl linolenate-linoleate mixtures at the Northern Laboratory, shunts were again needed to fit experimental data (4).

Two possible explanations of such shunts may be (a) an actual, rapid reduction of two double bonds while a molecule is adsorbed on the catalyst—possibly through a conjugated intermediate or (b) a liquid diffusion effect in which a molecule, once it is desorbed but still near the catalyst surface, tends to be adsorbed and reduced a second time before it can diffuse out into the main body of the liquid. One method of detecting such liquid diffusion effects and distinguishing between the two kinds of shunt is to study a compound with two double bonds located so that neither could interact to produce more rapid reduction of both. With such a compound in which conjugation is not possible and the double bonds are reduced by the same mechanism, their rates will be affected in the same way by factors such as catalyst characteristics, hydrogen concentration at the catalyst, etc. Ciola and Burwell (5) made such a study of diffusional control on nickel catalysts with 3,3-dimethyl-1,4-pentadiene. To obtain more information about the effect of liquid diffusion on fat hydrogenation, we applied a similar procedure with methyl *cis*-9,*cis*-15-linoleate, in which double bonds are separated by four methylene groups, and also with ethylene glycol diundecylenate and 1,7-octadiene as model compounds. Our results indicate the presence of a diene-to-saturate shunt with platinum and palladium catalysts but raise doubt that it is caused by liquid diffusion. With nickel catalysts the shunt effect was much smaller or absent.

EXPERIMENTAL PROCEDURES

Materials

Methyl *cis*-9,*cis*-15-linoleate was prepared by argentation countercurrent distribution of dienes from hydrazine-reduced linolenic acid (6). Ethylene glycol diundecylenate was prepared by esterification of ethylene glycol and 10-undecylenic acid with sulfuric acid as the catalyst. The product was ioslated by vacuum distillation. 1,7-Octadiene was supplied by Columbian Carbon Co., Princeton, N.J.

Hydrogenation

Samples were reduced in three different hydrogenators: (a) an Erlenmeyer flask with a magnetic stirrer as used in some of our earlier work (2); (b) the vibrating stirrer apparatus used for rate studies of methyl octadecenoates (7); and (c) the precision hydrogenator described by Rohwedder (8) but modified with a glass vessel so that samples could be removed during hydrogenation.

Hydrogenations with platinum, palladium and Raney nickel were run at 50 C, except one with platinum at 140 C and those of 1,7-octadiene which were run at 30 C. Other nickel hydrogenations were run at 140 C. The desired temperature was maintained in the hydrogenation vessel by immersing in a controlled temperature oil bath. All hydrogenations were at atmospheric pressure. From 0.15 to 0.3% platinum or palladium was used as a 5% metal on carbon catalyst. With platinum dioxide the amount of platinum was 3.5%. Approximately 1% of nickel was used, except for

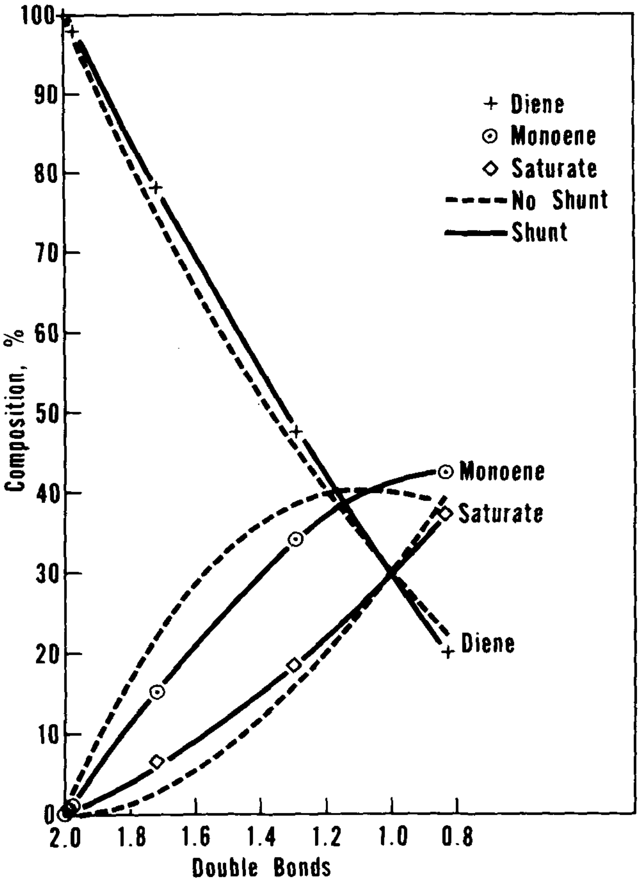

FIG. 1. Hydrogenation of methyl *cis*-9,*cis*-15-linoleate with platinum catalyst.

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TABLE I

Hydrogenation of Methyl *cis*-9,*cis*-15 Linoleate

Apparatus[a]	Catalyst	Shunt, %	Error term x 10^2	Error term x 10^2 no shunt
1	5% Platinum on carbon	16.1	0.04	2.36
1		19.5	0.52	1.97
1		13.4	3.95	4.17
1		19.3	1.40	4.23[b]
1		26.7	1.43	5.10[c]
2		16.0	1.20	2.17
2		20.0	1.72	2.30
3		26.1	0.38	4.46
3		18.2	0.42	3.66
3		16.1	0.22	2.79
3		15.4	0.72	3.62[d]
1	5% Palladium on carbon	15.7	0.84	2.02
1		18.7	1.60	4.24
2		14.5	1.76	3.59
1	Nickel G-70[e]	5.5	1.56	1.53
1		5.2	0.72	0.77
2		0.9	2.02	1.90
3	Nickel G-15[e]	0	0.83	0.79
3		0	0.75	0.72

[a] See text, Experimental Procedures. 1 = Erlenmeyer flask with magnetic stirrer; 2 = vibrating stirrer; 3 = precision hydrogenator.

[b] Run in ethyl acetate solution.

[c] Run in isooctane solution.

[d] Run at 140 C.

[e] Commercial catalyst provided by Girdler Catalysts Dept., Chemetron Chemicals, Louisville, Ky.

2.5 to 3.4% Raney nickel. After the catalyst was placed in the flask and the apparatus flushed with hydrogen, 300-400 mg of the material to be hydrogenated was added through a rubber septum. Hydrogenation times were generally from 15 min to 1 hr, after which time 0.2 to 1 double bond remained in the sample. Generally four to seven samples for analysis were removed through the septum with a hypodermic needle as hydrogenation proceeded.

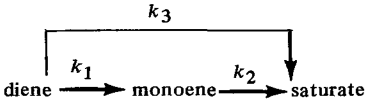
Analysis

Partially hydrogenated fatty esters were analyzed by gas chromatography on an EGSS-X column at 170 C. Samples from ethylene glycol diundecylenate reductions were analyzed on PPE 20 (poly-*m*-phenyl ether) at 223 C. Samples from 1,7-octadiene were analyzed on β,β'-oxydiproprionitrile at room temperature.

In the experiments with soybean triglycerides and soybean methyl esters, the triglyceride fractions were transesterified and gas chromatograms run using the microreactor technique (9). The methyl ester samples were analyzed with the same gas chromatograph.

RESULTS AND DISCUSSION

Relative reaction rates were calculated with a digital computer program described previously (10) and models both with diene-to-saturate shunt



and without the shunt diene $\xrightarrow{k_1}$ monoene $\xrightarrow{k_2}$ saturate. The percentage of diene that reduced directly to saturate by way of the shunt is $(k_3/[k_1 + k_3]) \times 100$.

The principle of the computer calculation is illustrated in Figure 1. The composition of each sample removed from the hydrogenating mixture is plotted against its extent of reduction as represented by the remaining double bonds. The computer chooses ratios of rate constants k_1/k_2 or $k_1/k_2/k_3$, such that the sum of the squares of the distances from each point to its corresponding calculated curve is a minimum. In most instances as in the figure the better fit with the shunt is evident upon visual inspection of the curves. A quantitative measure of the goodness of fit is obtained by comparing the summed squared errors with and without the shunt. Since the number of samples removed during the hydrogenation varied, an error term was calculated from the summed squared error with degrees of freedom as follows:

$$\text{Error term} = \sqrt{\frac{\text{Summed squared error}}{\text{Number of experimental points - number determined by initial conditions - number determined by difference - number of independent rate ratios.}}}$$

For example in Figure 1, there are 12 experimental points. The three corresponding to the starting diene are determined by initial conditions. Since the composition must total 100%, there are only two independent values in each set of three composition points. With the shunt there are two independent rate ratios, k_1/k_2 and k_1/k_3; without the shunt there is one, k_1/k_2. Then with the shunt there are 12-3-3-2 or 4 degrees of freedom; without the shunt there are 5. The error term has the characteristics of a standard deviation, and a statistical comparison of results with and without the shunt can be made by calculating approximate F values from the squared error term (11).

Results for hydrogenations with methyl *cis*-9, *cis*-15-linoleate are compiled in Table I. For all the platinum runs the error term is less with the shunt. Calculated F values showed a significantly better fit with the shunt for all runs except the third, where both error terms are large. An F value for pooled data on the palladium runs showed a significantly better fit at the 99% level with the shunt.

TABLE II

Hydrogenation of Ethylene Glycol Diundecylenate

Apparatus[a]	Catalyst	Shunt, %	Error term x 10^2	Error term x 10^2 no shunt
1	5% Platinum on carbon	24.7	0.78	4.06
2		16.5	0.96	2.98
3		14.5	1.54	2.77
3	Platinum dioxide	21.9	0.71	4.02
3		25.0	1.62	4.43
2	Nickel G-15[b]	3.6	1.33	1.82
3		0	0.64	0.58
3		1.9	0.81	0.80
3	Rufert nickel[c]	1.6	0.38	0.45
3		7.5	0.72	1.51
3		0	3.51	3.37
3	Raney nickel	10.5	1.21	2.24
3		0.4	2.34	2.25
3		0	5.72	5.29

[a] See footnote a, Table I.

[b] See footnote e, Table I.

[c] Commercial catalyst from Harshaw Chemicals, Cleveland, Ohio.

Pooled data for Nickel G-70 and G-15 showed no significant difference with or without the shunt.

Hydrogenations of ethylene glycol undecylenate and 1,7-octadiene were run for several reasons. With these compounds any effect upon the calculations of differing reduction rates of the 9- and 15-double bonds in the ester (7) is eliminated. Also some isomerization was observed in gas chromatographic curves of samples taken near the end of 9,15-linoleate hydrogenations. Although there was no evidence that isomerization was great enough to affect the results, it was considered desirable to compare the values for 9,15-linoleate with those for other compounds that should undergo less isomerization. Since terminal double bonds hydrogenate much faster than internal double bonds (7), their isomerization might be less, but some was still detected in the gas chromatographic curves. Finally the shunt might be affected by differences in physical properties of the three compounds; in particular, if it were related to liquid diffusion it might be affect by viscosity. Hydrogenations with ethylene glycol diundecylenate are given in Table II and those with 1,7-octadiene, in Table III.

With platinum, *F* values from pooled data showed significant differences at the 99% level between models with and without the shunt both for ethylene glycol diundecylenate and for 1,7-octadiene. With nickel, the *F* value from pooled data in Table II indicated no significant difference although the individual runs with Rufert nickel 7.5% shunt and Raney nickel 10.5% shunt did show significant differences.

In Tables I-III replicate runs appear generally in fairly good agreement, although an occasional run differs greatly. No differences were found that could be related to differences in agitation or other physical characteristics of the three hydrogenators.

TABLE III

Hydrogenation of 1,7-Octadiene with a 5% Platinum-on-Carbon Catalyst

Apparatus[a]	Shunt, %	Error term x 10^2	Error term x 10^2 no shunt
1	21.8	0.28	4.02
2	18.6	1.25	1.23
2	15.1	0.59	2.40
2	5.3	1.24	1.43
3	15.4	1.91	3.34
3	22.5	2.72	4.88

[a] See footnote a, Table I.

There is generally a 15 to 25% shunt with platinum or palladium catalysts for methyl *cis*-9,*cis*-15-linoleate. With nickel the shunt is much smaller or completely absent. The conslusion that the shunt effect is real, and that the better fit with the shunt is not caused simply by allowing additional pathways for reduction, is confirmed by the consistent differences between results with platinum or palladium and with nickel. The shunt is also found for ethylene glycol diundecylenate with platinum but not with nickel, and it is present for 1,7-octadiene with platinum. In addition to these results and the data following on soybean oil, we are finding the same difference between platinum and nickel in studies now in progress on relative hydrogenation rates of dienoic isomers.

There is no obvious explanation for the difference between platinum and palladium on the one hand and nickel on the other. It is apparently not caused by differences in isomerization, since nickel lies between platinum and palladium in promoting this reaction. We thought differences in liquid diffusion might be caused by differences in viscosity at the lower temperature used for platinum and palladium and the higher temperature used for nickel. However, in two methyl *cis*-9,*cis*-15-linoleate runs with platinum, and a solvent to lower the viscosity, and also in the run at 140 C, the shunt is still present. The shunt also remains small with Raney nickel at the temperature used for platinum and palladium, and it is not significantly different for the three model compounds hydrogenated, although they differ greatly in viscosity. The shunt was not affected by support of the catalyst. It was the same with unsupported platinum oxide as with platinum on carbon and the same for unsupported Rufert nickel and Raney nickel as for supported G-70 and G-15. These results do not explain the difference between platinum or palladium and nickel; instead they raise doubts as to whether the shunt is actually the result of a liquid diffusion effect or of some other cause.

Although the cause of the shunt is unknown and we cannot explain the difference between platinum or palladium and nickel, the shunt is obviously real and should be considered in interpretation of kinetic data. For example, in hydrogenations of methyl linolenate-linoleate mixtures with nickel we have found a linolenate-to-monoene shunt (2). Since shunts are small with nickel when double bonds cannot interact, this shunt is probably caused by triene conjugation of linolenate followed by rapid reduction of two double bonds rather than by the effect considered here.

To compare the results from model compounds just discussed to those from a mixture of more immediate interest, soybean oil triglycerides and methyl esters were hydrogenated with 5% platinum on carbon and with nickel in the modified Rohwedder apparatus. Shunts were calculated from a model that considers all pathways that can be distinguished by gas chromatographic analysis:

$$\begin{tikzcd}
\text{Linolenate} \arrow[r] \arrow[rr, bend left] & \text{Diene} \arrow[r] \arrow[rr, bend right] & \text{Monoene} \arrow[r] & \text{Stearate}
\end{tikzcd}$$

Unfortunately in this model changes in relative rate constants are rather insensitive to changes in the experimental fatty acid composition. Also linolenate in soybean oil is too low to be measured with an accuracy as high as that for linoleate or oleate. Nevertheless, in agreement with previous results, a diene-to-stearate shunt of 50% was found for soybean triglycerides with platinum compared to 9% with nickel. The linolenate-to-monoene shunt—where triene conjugated esters may be an intermediate—was 32% for platinum compared to ca. 50% for nickel. With platinum, differences also occurred between triglycerides and methyl esters. The diene-to-stearate shunt decreased from 50% for triglycerides to 24% for methyl esters, while the linolenate-to-monoene shunt increased from 32% to ca. 46%. With nickel, no differences were observed between methyl ester and triglyceride for the diene-to-stearate shunt; for the linolenate-to-monoene shunt the spread of values for methyl esters with nickel was too great to allow a good comparison.

ACKNOWLEDGMENTS

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