

10,12-diketo esters had gained support on the basis of the Stork rule (2).

The reaction of V with a catalytic amount of p-toluene-sulphonic acid in benzene yielded ca. 60% methyl 9,12-epoxyoctadec-9,11-dienoate (VI). NMR gave the characteristic signal at 5.7s for



The formation of VI gave proof that oxymercuration-demercuration, followed by Jones's oxidation, of β - and γ -hydroxyacetylene, led to formation of the 1,4-diketo acids.

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❖ Comparison of Homogeneous and Heterogeneous Palladium Hydrogenation Catalysts

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ABSTRACT

Mechanistic and kinetic studies of Pd-catalyzed hydrogenation at atmospheric pressure and 30-100 C were carried out with methyl sorbate, methyl linoleate and conjugated linoleate. Homogeneous Pd catalysts and particularly Pd-acetylacetonate [Pd(acac)₂] were significantly more selective than Pd/C in the hydrogenation of sorbate to hexenoates, mainly *trans*-2-hexenoate. Relative rate constants for the different parallel and consecutive reactions, determined by computer simulation, indicated that the low diene selectivity of Pd/C can be attributed to a significant direct reduction of sorbate to hexanoate. The similar behavior of PdCl₂ to that of Pd/C suggests that Pd(II) was initially reduced to Pd(O). Valence stabilization of PdCl₂ by adding DMF or a mixture of Ph₃P and SnCl₂ increased the diene selectivity but decreased the activity. Stabilization of Pd(acac)₂ with triethylaluminum (Ziegler catalyst) resulted in increased activity but decreased selectivity. The kinetics of methyl linoleate hydrogenation showed that although Pd(acac)₂ was only half as active as Pd/C, their respective diene selectivity was similar (10.4 and 9.6). The much greater reactivity of conjugated compared with unconjugated linoleate toward Pd(acac)₂ suggests the possible formation of conjugated dienes as intermediates that are rapidly reduced and not detected in the liquid phase during hydrogenation.

INTRODUCTION

Homogeneous Pd complexes have been tried as catalysts to a very limited extent for the partial hydrogenation of unsaturated fatty esters and oils. The mixture of PdCl₂

(PPh₃)₃ and SnCl₂ has been used as a homogeneous catalyst for hydrogenation of simple alkenes (1) and soybean methyl esters (2). In the latter study, no significant formation of stearate was observed. When Pd(acac)₂ was used as catalyst for the continuous hydrogenation of soybean oil (3), relatively low triene (triene to diene) selectivity (max. 2.9) was obtained. In batch hydrogenation of soybean oil, the same Pd-complex produced a triene selectivity of ca. 4 (4). This selectivity is significantly higher than that of heterogeneous Pd catalysts. The latter normally ranges between 2 and 2.5 (5).

PdCl₂ has been used as precursor for the preparation of both homogeneous and heterogenized homogeneous catalysts. PdCl₂ alone, without any valence stabilization agent, is reduced rapidly in hydrogen atmosphere to metallic Pd. On the other hand, together with a conjugated diene and DMF, PdCl₂ forms complexes that prevent reduction of Pd(II) to Pd(O) (6,7). Similar valence stabilization has been obtained by adding metal ions to PdCl₂ (8). The dienes in the Pd-complex formed are reduced selectively to monoenes. When all dienes are hydrogenated, then Pd(II) is reduced to Pd(O), which catalyzes the hydrogenation and isomerization of monoenes (7).

In the present work, different homogeneous Pd-complexes have been used as catalysts for the hydrogenation of methyl sorbate, methyl linoleate and conjugated methyl linoleate. The results are compared with hydrogenations with a heterogeneous Pd/C catalyst.

EXPERIMENTAL

All hydrogenations were performed at 1 atm H₂ pressure,

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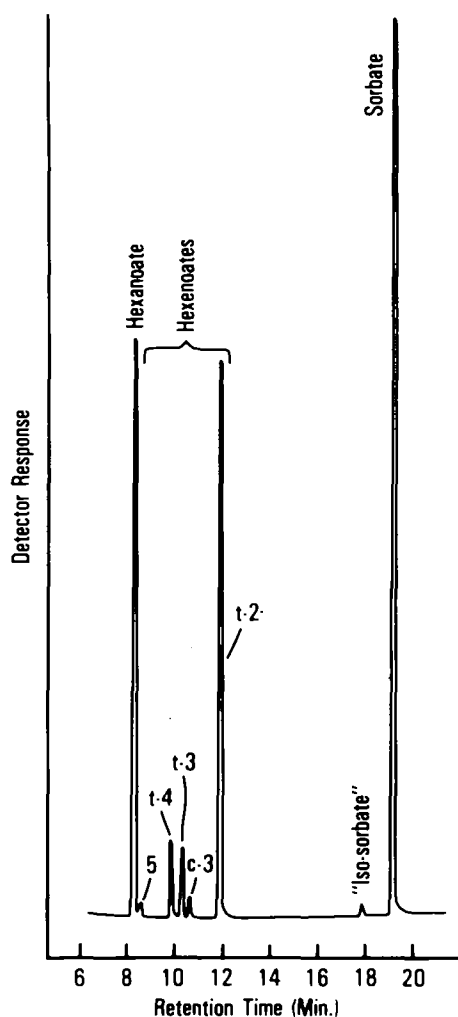


FIG. 1. Capillary chromatogram of methyl sorbate hydrogenated with Pd/C at 27 C, 1 atm, 10 min (Silar 10 CP, programmed 70-130 at 2 C/min). "Iso-sorbate" is an isomer of sorbate.

without solvents, in an all-glass apparatus (9). Methyl sorbate (10) was distilled and purified over activated alumina and stored under N_2 at -27 C. Methyl linoleate and alkali-conjugated methyl linoleate were prepared as described elsewhere (10), purified over activated alumina, and

stored under the same conditions as sorbate. The homogeneous Pd-catalysts (Strem Chemicals Inc., Newburyport, MA) and heterogeneous Pd/C (Engelhard, Newark, NJ) were purchased. The Pd-Ziegler was prepared in situ by adding 25% triethylaluminum in heptane to $Pd(acac)_2$ under hydrogen atm. (During hydrogenation of methyl sorbate with this catalyst, formation of ethyl esters was significant).

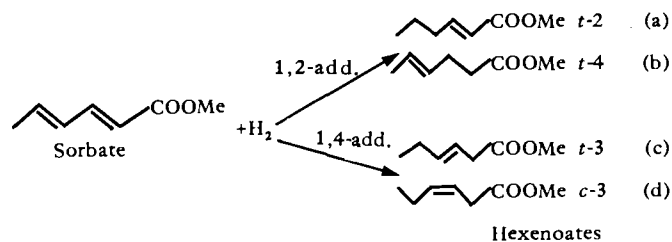
A typical hydrogenation was performed as follows. The catalyst was accurately weighed into the reactor, which was then connected to the hydrogenation apparatus. The whole apparatus was evacuated 3 times and filled with hydrogen. The temperature in the reactor was adjusted, 1 mL of substrate was injected through a septum into the reactor, and the magnetic stirrer was started.

The hydrogenations were followed by withdrawing samples from the reactor and analyzing products by gas liquid chromatography (GLC). The samples from the hydrogenation of methyl sorbate were diluted with isooctane and analyzed by capillary GLC (Silar 10 C, temperature programming 70-120 C, 2 C/min). A typical chromatogram is shown in Figure 1. Products from the hydrogenation of methyl linoleate were analyzed by GLC on a packed column (15% EGSS-X, isothermal at 190 C), and products from the hydrogenation of conjugated methyl linoleate by capillary GLC (Silar 10 C, isothermal 170 C).

RESULTS AND DISCUSSION

Hydrogenation of Methyl Sorbate

The results obtained with different homogeneous Pd catalysts and Pd/C on the hydrogenation of methyl sorbate are summarized in Table 1. The main intermediate product formed was in all cases *trans*(*t*)-2-hexenoate, the monoene with the double bond in conjugation with the carbonyl double bond. This result indicates that either the double bond in the 4 position is reduced by 1,2-addition, or 1,4-addition occurs followed by isomerization of methyl 3- to 2-hexenoate.



The product composition was simulated as a function of

TABLE I

Hydrogenation of Methyl Sorbate with Different Palladium Catalysts

Catalysts	Amount (%)	Temperature (C)	Time (min)	Methyl sorbate	Composition, rel. %				Methyl hexanoate	Diene selectivity ^b
					Methyl hexenoate ^a					
					<i>t</i> -2 (a)	<i>t</i> -3 (c)	<i>c</i> -3 (d)	<i>t</i> -4 (b)		
5% Pd/C	0.125	27	174	8.1	26.8	0.34	1.1	0.9	61.8	0.6
10% Pd/C	0.25	27	—	1.7	41.8	2.0	4.3	5.4	44.9	—
$PdCl_2$	0.45	27	178	1.1	42.4	3.9	7.2	11.3	34.1	1.8
$PdCl_2$:DMF (1:4)	0.45	27	300	42.2	33.6	4.3	8.0	8.5	3.1	18.0
$PdCl_2$:DMF (1:8)	0.45	27	300	32.1	34.8	3.3	9.1	11.8	3.9	19.1
$Pd(acac)_2$	0.125	100	190	2.5	64.8	4.9	12.4	13.7	0.6	49.0
Pd-Ziegler	0.125	27	124	9.7	66.0	1.1	4.4	5.3	10.5	7.5
$PdCl_2(PPh_3)_3 + SnCl_2$	0.146	100	300	76.7	16.0	0.6	1.9	2.1	1.3	15.6

^aSee text for structural designations.

^bCalculated from relative rate constants shown on scheme in Table II.

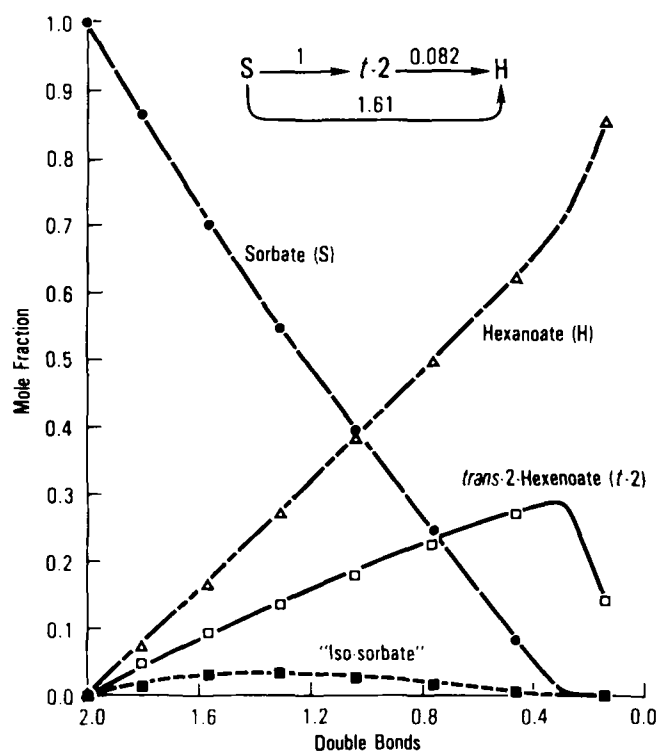


FIG. 2. Kinetic simulation of the hydrogenation of methyl sorbate with Pd/C (0.125% Pd, at 27 C, 1 atm).

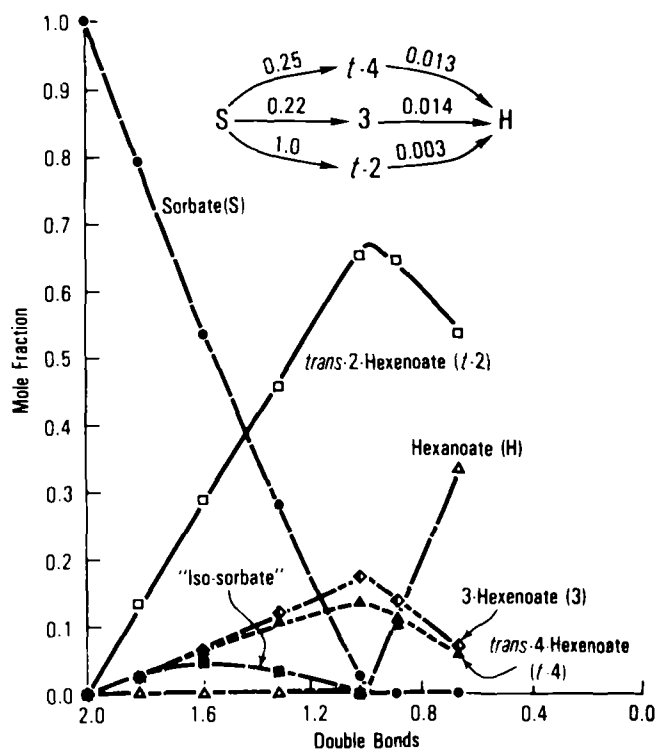


FIG. 4. Kinetic simulation of the hydrogenation of methyl sorbate with Pd(acac)₂ (0.125% Pd, at 100 C, 1 atm).

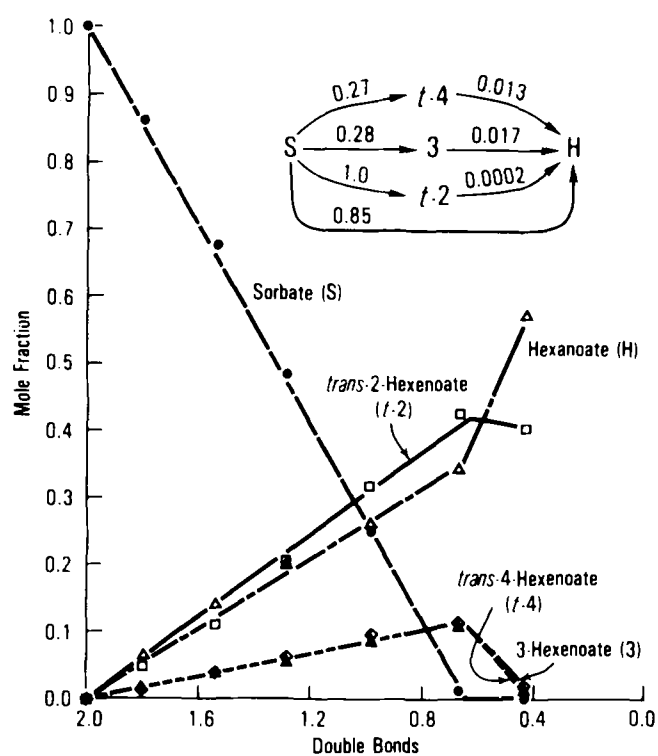


FIG. 3. Kinetic simulation of the hydrogenation of methyl sorbate with PdCl₂ (0.45% Pd, at 27 C, 1 atm).

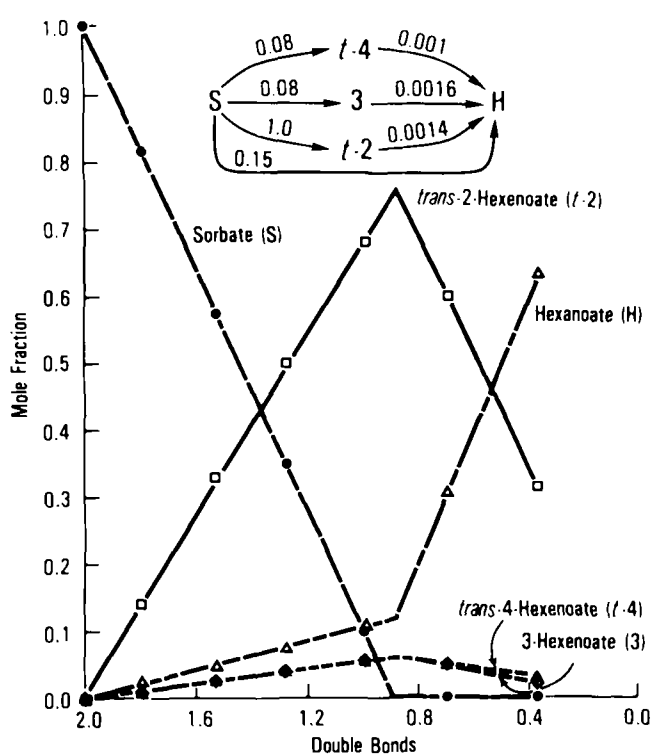


FIG. 5. Kinetic simulation of the hydrogenation of methyl sorbate with Pd-Ziegler catalyst (0.125% Pd, at 27 C, 1 atm).

double bonds on a computer program according to Buttefield (11) for hydrogenation with Pd/C (Fig. 2), PdCl₂ (Fig. 3), Pd(acac)₂ (Fig. 4), and Pd-Ziegler (Fig. 5). The conversion with the other Pd-complexes used was too low to be

simulated on the computer. The simulated curves show, in all cases, good agreement with the experimental values. A simulation as a function of time gave very poor correlation with the experimental values, mainly because the reaction

TABLE II

Relative Reaction Constants for the Hydrogenation of Methyl Sorbate

Catalysts	k_2	k_3	k_4	k_5	k_{10}	k_{11}	k_{12}
PdCl ₂	0.27	0.28	1	0.85	0.013	0.017	0.0002
Pd/C	—	—	1	1.61	—	—	0.082
Pd-Ziegler	0.08	0.08	1	0.15	0.0011	0.0016	0.0014
Pd(acac) ₂	0.25	0.22	1	—	0.013	0.014	0.003

order of the different parallel and consecutive reactions was not established. Accordingly, calculating the absolute rate constants for these reactions was not possible. However, relative rate constants were calculated for the reaction pattern shown in Table II. These relative rate constants show that the very poor diene (diene to monoene) selectivity of Pd/C is caused by a high amount of direct reduction, k_5 (shunt), between sorbate and hexanoate. Similar studies on the hydrogenation of conjugated linoleate and conjugated trienes with a Pd/C catalyst (12) show that the direct shunt between conjugated diene and stearate is low compared with the reduction via monoenes, whereas the hydrogenation of conjugated trienes shows a very high amount of direct shunt between the trienes and monoenes. These results indicate that methyl sorbate behaves like a conjugated triene system with Pd/C, and the carbonyl double bond in some way participates in the adsorption of sorbate on the catalyst surfaces, permitting double hydrogenation of the double bonds.

Hydrogenation with PdCl₂ shows much the same activity and diene selectivity as Pd/C and indicates that Pd(II) is reduced initially to Pd(O). PdCl₂ is known to be very easily reduced under these conditions (13). The addition of small amounts of DMF caused the activity to decrease and the diene selectivity to increase in the hydrogenation with PdCl₂. Sisak et al., (7) have reported that DMF together with conjugated dienes stabilized PdCl₂ against reduction to Pd(O). This effect may be explained by the formation of a strong complex between DMF and the conjugated diene that is not reduced under ambient conditions.

Pd-Ziegler shows both high activity and diene selectivity in the hydrogenation of methyl sorbate. The precursor to Pd-Ziegler, Pd(acac)₂, shows a very high diene selectivity but a lower activity than Pd-Ziegler. Almost no activity was observed with Pd(acac)₂ at ambient temperatures and H₂-pressure. Activity was observed only when the temperature was raised to 100 C.

The absolute reaction rate was calculated for the hydrogenation of sorbate with different Pd catalysts (Table III). The absolute rate for the hydrogenation of *t*-2-hexenoate could be calculated after sorbate was completely reduced. These rate constants show that on both Pd/C and Pd(acac)₂, *t*-2-hexenoate is reduced at a higher rate than sorbate when all sorbate is removed from the system. With Pd-Ziegler, the reduction of sorbate is more rapid than the reduction of *t*-2-hexenoate, and the activity with this catalyst is higher than that with Pd/C. This very high diene selectivity and the large difference in the reaction rate between sorbate

TABLE III

Reduction Rates (mol/min) of Sorbate (S), and of *t*-2-Hexenoate (*t*-2) after Disappearance of S with Pd Catalysts^a

Catalyst	Temperature (C)	$-r_s \cdot 10^4$	$-r_{t-2} \cdot 10^4$
Pd(acac) ₂	100	0.520	1.497
Pd/C	27	0.313	0.432
Pd-Ziegler	27	0.731	0.481

^aHydrogen at 1 atm H₂-pressure and 0.15% Pd.

and *t*-2-hexenoate obtained with Pd(acac)₂ might be explained by a strong complex formation between Pd(acac)₂ and sorbate. This complex formation probably prevents reduction of Pd(II) to Pd(O) and also reduction of monoenes to hexanoate. When all sorbate is reduced to monoenes, Pd(II) is reduced to Pd(O), which is a more active catalyst and the latter reduces monoenes at a higher rate than the starting Pd(II) complex. The reaction solution is initially clear, colorless and remains homogeneous until all sorbate is reduced; then a black precipitate appears that is presumed to be metallic Pd. No such reduction to Pd(O) was observed with Pd-Ziegler.

Hydrogenation of Linoleate and Conjugated Linoleate

Two different catalysts, Pd/C and Pd(acac)₂, were used to hydrogenate methyl linoleate under the same conditions used for methyl sorbate. The formation of monoenes and stearate was monitored as a function of time by GLC analyses of withdrawn samples. The results were simulated on a computer (11), and relative rate constants were calculated. The simulated curves and relative rate constants are shown in Figures 6 and 7. In the proposed reaction scheme for reduction of linoleate, conjugation before reduction is not included. Linoleate may possibly be reduced via conjugated dienes, but only a trace of conjugation was detected by GLC analyses of the samples. Koritala et al., (12) have previously shown that conjugated dienes are reduced 10-18 times faster than linoleate on Pd/C. This result indicates that conjugated dienes, possibly formed as intermediates, would be reduced very rapidly to monoenes before they desorbed into the liquid bulk phase.

Some significant differences between Pd/C and Pd(acac)₂ are evident, but the differences are much less than those observed with the hydrogenation of methyl sorbate. On Pd/C, the direct shunt between diene and stearate is ca. 2

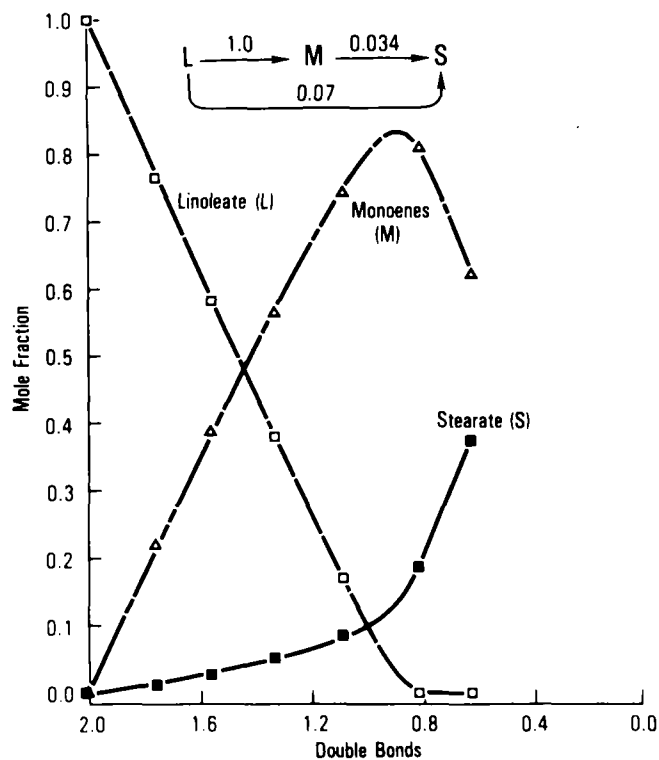


FIG. 6. Kinetic simulation of the hydrogenation of methyl linoleate with Pd/C (0.15% Pd, at 100 C, 1 atm).

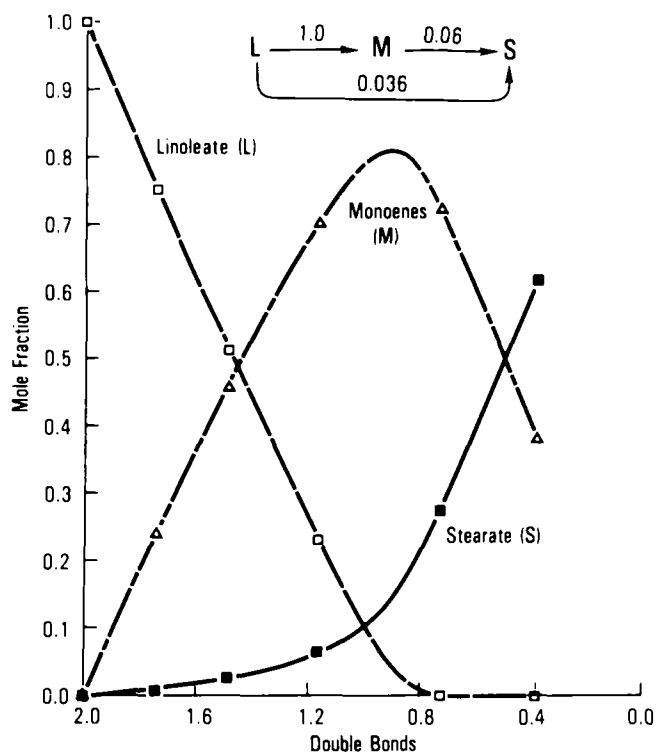


FIG. 7. Kinetic simulation of the hydrogenation of methyl linoleate with Pd(acac)₂ (0.15% Pd, at 100 C, 1 atm).

times higher than with Pd(acac)₂, but the diene selectivity is nearly the same with the 2 catalysts, 10.4 and 9.6 respectively for Pd(acac)₂ and Pd/C. This result indicates that the same complex formation between Pd(acac)₂ and substrate

TABLE IV

Reduction Rates (mol/min) of Linoleate (18:2), and of Monoenes (18:1) after disappearance of 18:2 with Palladium Catalysts^a

Catalyst	$-r_{18:2} \cdot 10^4$	$-r_{18:1} \cdot 10^4$
Pd/C	1.470	1.765
Pd(acac) ₂	0.748	0.779

^aAt 100 C, 1 atm H₂-pressure and 0.15% Pd.

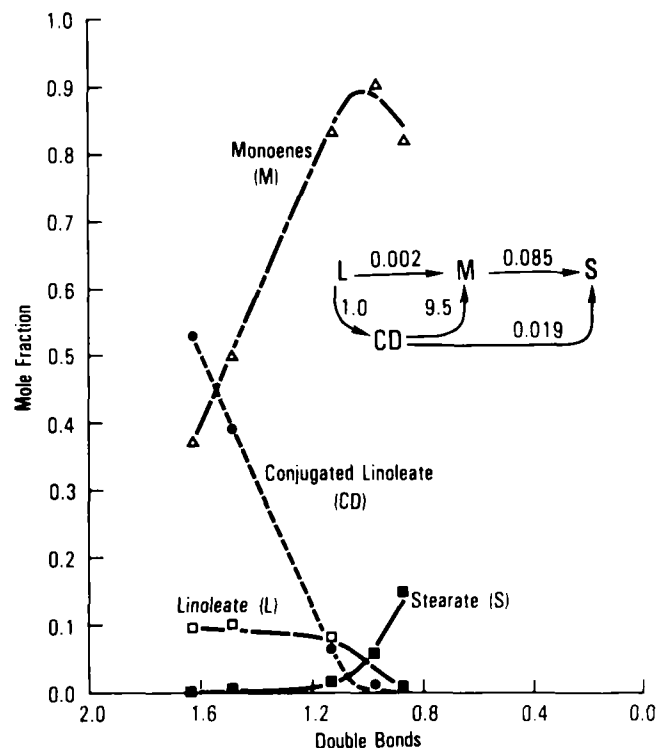


FIG. 8. Kinetic simulation of the hydrogenation of a mixture of methyl linoleate and conjugated methyl linoleate with Pd(acac)₂ (0.15% Pd, at 100 C, 1 atm).

postulated for the hydrogenation of sorbate does not occur during hydrogenation of linoleate.

The absolute rate constants calculated for the reduction of linoleate and monoenes when all linoleate is reduced are shown in Table IV. These figures show that Pd/C is ca. 2 times more active than Pd(acac)₂ on the hydrogenation of linoleate. As observed with sorbate, when no dienes are left in the system, monoenes are reduced at a higher rate than diene.

Hydrogenation of a mixture of conjugated linoleate, linoleate and monoenes with Pd(acac)₂ as catalyst is shown in Figure 8, and the results were simulated on a computer. The relative rate constants indicate that the hydrogenation of linoleate goes almost entirely via conjugated dienes and that the hydrogenation rate of conjugated dienes is about 10 times as large as the conjugation rate. If the same scheme holds for pure linoleate, where no significant amount of conjugated dienes was observed during the hydrogenation, the ratio of linoleate to monoene disappearance in Figure 8 ($1.0 + 0.002/0.085 = 11.8$) should correspond to that in Figure 7 ($1.0/0.06 = 16.7$). The difference observed can be caused either by experimental error or the competing effect of conjugated dienes (Fig. 8)

for the catalyst reaction sites. More kinetic studies may further clarify the mechanism.

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Optimization of Parameters for the Analysis of Triglyceride by Reverse Phase HPLC Using a UV Detector at 210 nm

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ABSTRACT

Factors affecting the quantitative analysis of triglycerides from natural oils were investigated on reverse-phase HPLC columns. The organic solvent used to dissolve the triglycerides greatly determined the extent to which the solute molecules interacted with the mobile phase and hydrocarbonaceous ligand. Chloroform-dissolved triglycerides resulted in better resolution and detection of the solute matrix of all the organic solvents used. Also, ethanol was superior to methanol as the polar organic modifier in the mobile-phase composition. Ballistic temperature programming significantly reduced analysis time and column temperature, when raised high enough, can reverse the elution of some solutes. Possible mechanisms of triglyceride solute retention on reverse-phase columns are advanced in conjunction with the various parameters used in the investigation.

INTRODUCTION

Ca. 80% of all the separations made by high performance liquid chromatography (HPLC) have been made using reverse-phase columns. The analysis of triglycerides has not been an exception. Even though reverse phase is the most popular mode of HPLC used at the present time, the mechanism of solute retention is complex and is the least understood method (1). The exact topography of the bonded hydrocarbonaceous ligand is not known, which leads to complications in attempts to interpret solute retention and solute interactions with the mobile phase and bonded support. Interaction of the mobile phase with solute molecules is generally considered the dominant force in reverse-phase chromatography (2) and the nature of this reaction is the driving force for solute distribution. In reverse-phase systems, when water is used as the primary solvent, solute retention is caused by the "hydrophobic effect" whereas, with the nonaqueous solvents, the "solvo-

phobic theory" has been applied to solute retention (2).

Triglycerides are relatively large solute molecules that are very hydrophobic in character, and of low polarity (3). This class of lipids is soluble in such organic solvents as hexane, acetone, benzene, chloroform, methylene chloride, dioxane and tetrahydrofuran, but they have limited solubility in water. Earlier work in the HPLC analysis of oilseed triglycerides used a differential refractometer as the detector and used acetone as one of the solvents (4). The UV cutoff of this solvent negates the use of the more sensitive UV detector at 210 nm because of the optical windows of this solvent. Even though water has been used in the analysis of triglycerides (4), it was not considered in the present study because of the low solubility of triglycerides in water. A nonaqueous phase, consisting of solvents compatible with the UV detector at 210 nm, was used.

The objectives of this study were to investigate the various parameters necessary to optimize conditions for the analysis of triglycerides on reverse-phase columns and to provide information about triglyceride solute retention by hydrocarbonaceous ligands.

EXPERIMENTAL PROCEDURES

Triglycerides were analyzed using a Varian 5000 HPLC unit equipped with a 10 μ L loop automatic valve injector. The detector was a Vari Chrom variable wavelength detector operated at 210 nm with an 8 μ L cell. All analyses were performed on a MCH-10 (Varian) reverse-phase column (C-18 bonded). Methanol, ethanol and acetonitrile used in the mobile phases were HPLC-grade solvents.

Peanut oil was obtained by homogenizing the seeds 3 times with chloroform/methanol (2:1), filtering and removing the solvent by rotary evaporation. Coconut oil, which was used as a source of saturated triglycerides, was obtained commercially. The 2 triglycerides of known composition used as solute probes (glycerol-2-oleate, 1,3 dipalmitate and glycerol-2-oleate, 1,3-distearate) were obtained from