Technical

❖Homogeneous Hydrogenation of Dienes with Rhodium Complexes

J.A. HELDAL[1] and E.N. FRANKEL,* Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, IL 61604

ABSTRACT

Different Rh complex catalysts were compared for the hydrogenation of methyl sorbate and linoleate in the absence of solvents. At 100 C and 1 atm H_2 the following complexes, $RhCl(Ph_3P)_3$ (Ph = phenyl), $[RhClNBD]_2$ (NBD = norbornadiene) and $RhH(CO)(Ph_3P)_3$, produced mainly methyl *trans*-2-hexenoate (34 to 56%). Their diene selectivity was not particularly high as they produced 14 to 41% methyl hexanoate. With $RhCl(Ph_3P)_3$ constant ratios between rates of methyl sorbate disappearance and formation of methyl *trans*-2- and *trans*-3-hexenoate indicate approximately the same activation energy for 1,2-addition of H_2 on the Δ4 double bond of methyl sorbate and for 1,4-addition to this substrate. In the hydrogenation of methyl linoleate with $RhCl(Ph_3P)_3$, the kinetic curves were simulated by a scheme in which 1,2-reduction was more than twice as important as 1,4-addition of H_2 via conjugated diene intermediates. Although the complexes $RhCl(CO)(Ph_3P)_3$ and $[Rh(NBD)(diphos)]^+PF_6^-$ (diphos = diphosphine) were inactive in the hydrogenation of methyl sorbate, they catalyzed the hydrogenation of methyl linoleate at 100 C and 1 atm. Catalyst inhibition apparently was caused by stronger complex formation with methyl sorbate than with the conjugated dienes formed from methyl linoleate.

INTRODUCTION

Extensive studies have been reported on the use of Rh complexes as homogeneous catalysts in various hydrogenation reactions. The mechanisms advanced for these reactions have been summarized by James (1,2) and Masters (3). The selectivity of these complex catalysts for the hydrogenation of polyunsaturated compounds has been reviewed by Frankel and Dutton (4). Mechanisms for the hydrogenation of carbon-carbon double bonds with Wilkinson's catalyst, $RhCl(Ph_3P)_3$, have been studied in detail, and the results have been summarized by Halpern (5).

The properties of cationic Rh complexes as catalysts have been studied by Schrock and Osborn (6-8). The application of this group of complexes in the hydrogenation of dienoic fatty esters (9) and soybean oil (10) showed high activity under ambient conditions and a low degree of isomerization. The Wilkinson's catalyst also has been reported to give low isomerization when it is presaturated with H_2 prior to hydrogenation (11-13). The activity of this catalyst for olefins depends both on the position and the configuration of the double bond, decreasing in the following order: 1-octene > *cis*-2-octene > *trans*-2-octene (14).

The selectivity calculated for diene and triene hydrogenation is compared for different Rh complex systems in Table I. Most of the research done on Rh complexes as catalysts has been carried out in the presence of different solvents. Solvents generally are implicated in the hydrogenation by forming ligands with the catalytically active complex (5). This interaction obviously will influence the degree of unsaturated coordinative bonds and the activity and selectivity of the catalyst. For practical hydrogenation of unsaturated fatty esters we were, therefore, interested in investigating these complexes in the absence of solvent. In the present work, different Rh complex catalysts were compared for the hydrogenation of methyl sorbate and linoleate at atmospheric pressure in the absence of solvent.

TABLE I

Selectivity of Various Rh Complexes for the Hydrogenation of Methyl Linoleate and Soybean Oil

Complex[a] (Condition)	Substrate/ solvent	S_{Lo}[b]	S_{Ln}[b]	Ref.
Py_3RhCl_3 (ambient)	Me Linoleate DMF	96.0		15
$RhCl(Ph_3P)_3$ (80 C, 1 atm)	Soybean oil Toluene	3.0	5.0	11
$[Rh(NBD)(Ph_3P)_2]^+PF_6^-$ (ambient)	Me Linoleate 2-propanol	55.1		9
$[Rh(NBD)(iBu_3P)_2]^+PF_6^-$ (ambient)	Me Linoleate 2-propanol	9.4		9
$[Rh(NBD)(diphos)]^+ClO_4^-$ (32 C, 1 atm)	Soybean oil Acetone	25.0		10

[a] Py = pyridine, NBD = norbornadiene, iBu = isobutyl, diphos = diphosphine, Ph = phenyl.

[b] S_{Lo} = linoleate selectivity, S_{Ln} = linolenate selectivity, calculated by the method of Butterfield and Dutton (16).

EXPERIMENTAL

Hydrogenations were performed in a glass manometric apparatus (17) at 1 atm H_2 without solvents. In a typical hydrogenation 11.15 mg $RhCl(Ph_3P)_3$ (1.22×10^{-5} mol) was weighed into a 125 ml Erlenmeyer flask with side arm sealed by a rubber septum. The flask was then connected to the manometric apparatus, evacuated three times and filled with hydrogen. The temperature in the reactor was adjusted, 1 ml of methyl linoleate (3.02×10^{-3} mol) was injected into the reactor and magnetic stirring was started. At 100 C the reaction mixture turned brown and homogeneous. Samples were withdrawn from the reactor, and the progress of hydrogenation was followed by gas liquid chromatography. The Rh complex catalysts were purchased from Strem Chemical Inc. (Newburyport, Massachusetts). Methyl sorbate and linoleate were purified by methods described previously (18). The same procedures also were used for analyzing the samples during hydrogenation (18).

RESULTS AND DISCUSSION

Hydrogenation of Methyl Sorbate

The results of hydrogenation of methyl sorbate with different Rh complex catalysts are summarized in Table II. None of the complexes tested showed particularly high diene selectivity in the hydrogenation of methyl sorbate. *trans*-2-Hexenoate was the main monoene product in all cases. $RhH(CO)(Ph_3P)_3$ was the only complex that produced any significant amount of *cis*-3-hexenoate. Neither $RhCl(CO)(Ph_3P)_2$ nor $[Rh(NBD)(diphos)]^+PF_6^-$ were active for the hydrogenation of methyl sorbate. Because it was found later that both of these complexes are

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[1] Visiting scientist, Laboratory of Industrial Chemistry, University of Trondheim, Trondheim, Norway.

*To whom correspondence should be addressed.

TABLE II

Hydrogenation of Methyl Sorbate with Different Rh Complexes at 100 C and 1 atm Pressure (0.15 mole % Rh)

		Composition (Rel. %)						
			Methyl hexenoate[b]					
Catalyst	Time[a] (min)	Methyl sorbate	*t*2	*t*3	*c*3	*t*4	Methyl hexanoate	T.N.[c] (min^{-1})
$RhCl(Ph_3P)_3$	39	31.3	33.7	3.5	0.5	7.9	18.4	14.0
$RhCl(CO)(Ph_3P)_2$	NR							0
$[RhClNBD]_2$	64	11.5	38.5	4.4	1.3	3.4	40.7	13.4
$RhH(CO)(Ph_3P)_3$	280	4.5	54.5	7.0	10.0	5.8	14.2	2.5
$[RhNBD(diphos)]^+PF_6^-$	NR							0

[a] NR = no reaction.

[b] *t*2 = *trans*-2-, *t*3 = *trans*-3-, *c*3 = *cis*-3-, *t*4 = *trans*-4-hexenoate.

[c] T.N. = turnover number, mol double bonds hydrogenated/mol catalyst, min.

active catalysts for the hydrogenation of methyl linoleate, it appears that these catalysts are inactivated in methyl sorbate by stronger complex formation with its conjugated triene system, –C = C–C = C–C = O, that involves the ester carbonyl group.

To explain the formation of methyl *trans*-2-hexenoate as the major monoene from methyl sorbate with $RhCl(Ph_3P)_3$, the relative rates of hydrogenation (R_H) and isomerization (R_I) of different methyl hexenoate isomers were compared. Under ambient conditions, no significant isomerization of methyl *trans*-2-hexenoate was observed. The ratio between initial R_H for methyl *cis*-3-hexenoate and R_I was about 5.5. The R_H for methyl *trans*-2-hexenoate was 3.1×10^5 and, for methyl *cis*-3-hexenoate, 4.5×10^5 mol/min. To determine the relative competitive rates of hydrogenation between methyl *cis*-3-hexenoate and methyl sorbate, a 1:1 mixture of these substrates was hydrogenated under ambient conditions. The results in Figure 1 show that methyl *cis*-3-hexenoate is hydrogenated at a rate about 2.7 times higher than methyl sorbate. The low accumulation of methyl *cis*-3-hexenoate during hydrogenation apparently is due to the higher reactivity of this monoene than of methyl sorbate.

Methyl sorbate hydrogenation approximated zero order kinetics initially in the temperature range between 30 and 100 C (Fig. 2). Linear regressions of these kinetic curves gave a set of pseudo zero order rate constants, k_s (Table III). An Arrhenius plot of these rate constants deviated somewhat from linearity (Fig. 3). This deviation from linearity may be due to thermal decomposition of the catalyst decreasing the rate at high temperatures. At lower temperatures strong complex formation between the catalyst and methyl sorbate may inhibit hydrogenation. The initial formation of methyl *trans*-2-hexenoate and *trans*-3-hexeno-

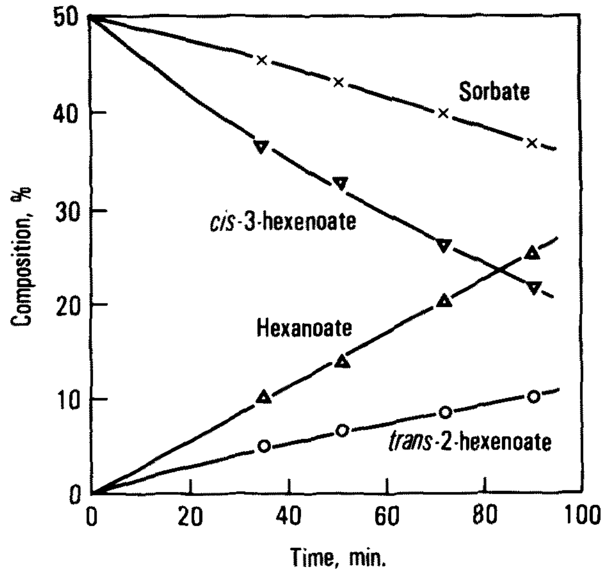


FIG. 1. Hydrogenation of a 1:1 mixture of methyl sorbate and *cis*-3-hexenoate with $RhCl(Ph_3P)_3$ (0.15% Rh) at 30 C and 1 atm.

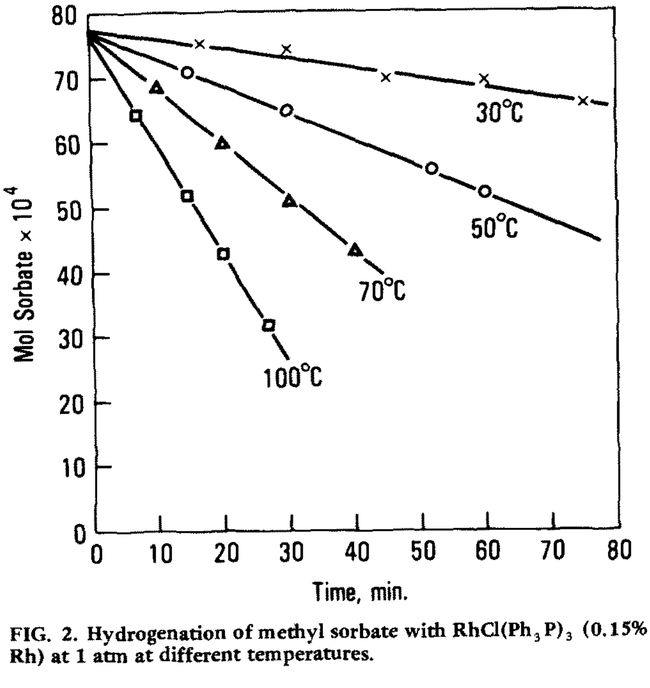


FIG. 2. Hydrogenation of methyl sorbate with $RhCl(Ph_3P)_3$ (0.15% Rh) at 1 atm at different temperatures.

TABLE III

Rate Constants[a] for the Hydrogenation of Methyl Sorbate with $RhCl(Ph_3P)_3$

Temp. (C)	$k_s \times 10^4$	$k_{t2} \times 10^4$	$k_{t3} \times 10^4$	k_{t2}/k_s	k_{t3}/k_s
30	0.150	0.092	0.008	0.61	0.053
50	0.417	0.241	0.020	0.58	0.048
70	0.857	0.517	0.044	0.60	0.051
100	1.672	0.955	0.085	0.57	0.051

[a] k_s: pseudo zero order rate constant for the disappearance of methyl sorbate (Fig. 2), k_{t2}: pseudo zero order rate constant for the initial formation of *trans*-2-hexenoate, k_{t3}: pseudo zero order rate constant for the initial formation of *trans*-3-hexenoate.

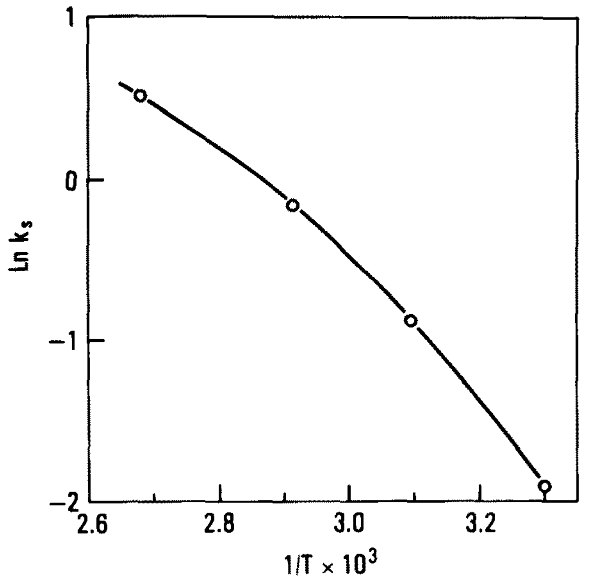
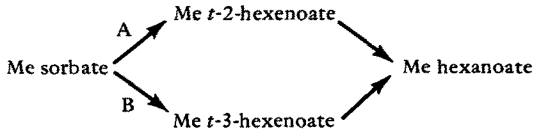


FIG. 3. Arrhenius plot of rates of hydrogenation of methyl sorbate with $RhCl(Ph_3P)_3$. Data from Fig. 2.

ate shows the same zero order kinetics at different temperatures as the disappearance of methyl sorbate. Assuming that further reduction of these monoenes is negligible at the early stages of the reaction, pseudo zero order rate constants can be calculated for these two monoenes, k_{t2} and k_{t3} (Table III). An Arrhenius plot of these rate constants gave a curved line similar to that for methyl sorbate. The data in Table III show that the ratio between the different rate constants is approximately constant between 30 and 100 C. The result indicates that the activation energy for 1,2-addition (A) of H_2 to the Δ4 double bond of methyl sorbate is approximately the same as that for 1,4-addition (B) of H_2 to methyl sorbate in the transoid configuration.



The cisoid configuration required for the formation of methyl *cis*-3-hexenoate can be ignored because of the small amount of this monoene found with $RhCl(PH_3P)_3$ (Table II). Similar calculations based on the formation of methyl *trans*-4- and 5-hexenoate were not possible because further reduction of these monoenes to hexanoate was significant even in the early stages of hydrogenation of methyl sorbate (Fig. 4). These kinetic curves indicate that the reactivity of the different monoenes increases with increasing distance between the double bond and the carboxyl group. Figure 4 shows that the activity of $RhCl(Ph_3P)_3$ levels off during hydrogenation, a phenomenon observed during all hydrogenations with this catalyst. Similar inactivation of Wilkinson's catalyst has been reported by others (13,19). This catalyst inactivation may be similar to the so-called aging phenomenon observed with the homogeneous catalyst pentacyanobaltate and attributed to the formation of a hydride intermediate complex (20,21).

Hydrogenation of Methyl Linoleate

In the hydrogenation with $RhCl(Ph_3P)_3$, the kinetic curves simulated fairly well a scheme in which methyl linoleate was either reduced directly or via a conjugated diene intermediate that was reduced at a lower relative rate (k_{CD} of 0.55) (Fig. 5). According to this scheme, methyl stearate is

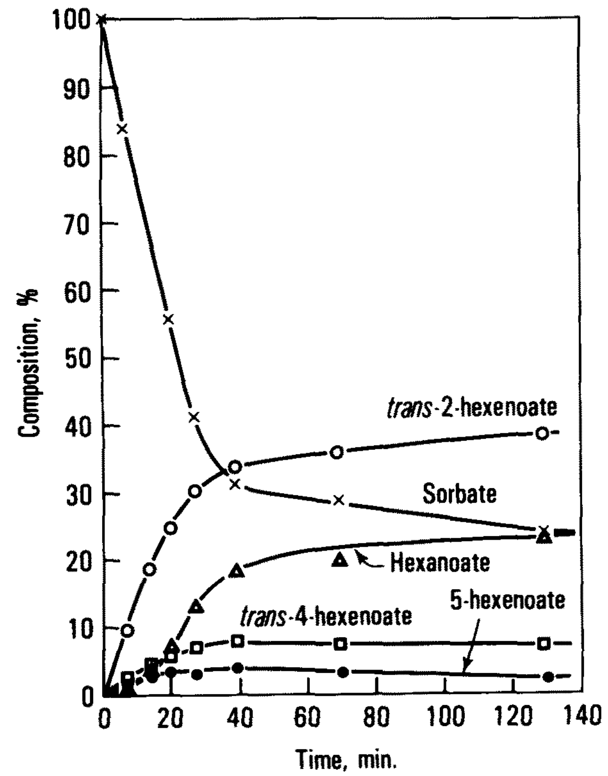


FIG. 4. Hydrogenation of methyl sorbate with $RhCl(Ph_3P)_3$ (0.15% Rh) at 100 C and 1 atm.

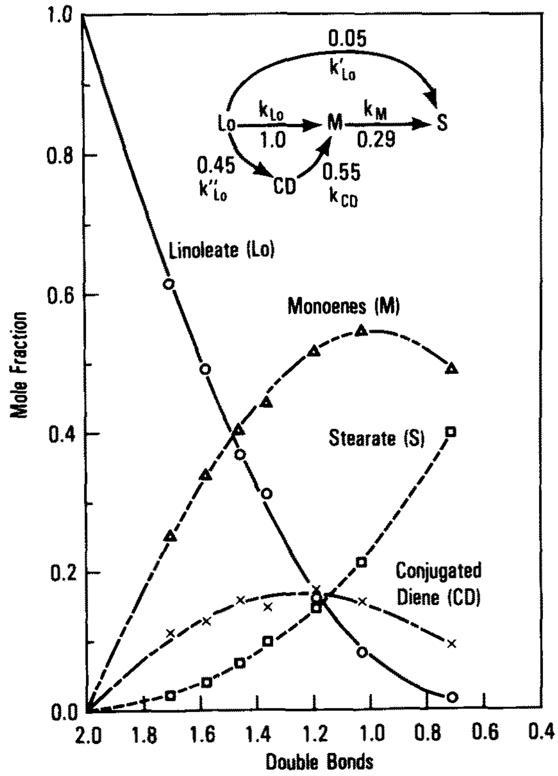


FIG. 5. Hydrogenation of methyl linoleate with $RhCl(Ph_3P)_3$ (0.4 mole % Rh) at 100 C and 1 atm. Relative rates simulated by computer method (22).

TABLE IV

Hydrogenation of Methyl Linoleate with Different Rh Complexes at 100 C and 1 atm Pressure (0.4 mole % Rh)

Catalyst	Time (min)	Composition (Rel. %)^a					T.N. (min^{-1})
		Lo	CD	M	S	S_{Lo}	
$RhCl(CO)(Ph_3P)_2$	320	37.7	5.2	42.8	14.1	2.0	0.57
$[RhNBD(diphos)]^+PF_6^-$	200	32.2	4.2	54.7	8.9	4.4	0.79
$RhCl(Ph_3P)_3$	47	8.3	15.6	54.8	21.3	4.5	5.18

^{a}Lo = methyl linoleate, CD = conjugated dienes, M = monoenes, S = methyl stearate.

formed either from monoene (k_M 0.29) or directly by double reduction from linoleate (k'_{Lo} 0.05). The 1,2-addition route (k_{Lo} 1.0) producing *cis* monoenes is more than twice as important as the 1,4-addition route via conjugated diene intermediates (k''_{Lo} 0.45). This pathway may explain the formation of low *trans*-unsaturation in a similar system (11). The accumulation of conjugated dienes is significant (Table IV), however, because further hydrogenation of these intermediates is slow compared to the direct reduction of methyl linoleate.

Although the complexes $RhCl(CO)(Ph_3P)_2$ and $[Rh(NBD)(diphos)]^+PF_6^-$ were completely inactive in the hydrogenation of methyl sorbate (Table II), they both catalyzed the hydrogenation of methyl linoleate (Table IV). The turnover numbers for these two complexes were, however, rather low compared to that of the Wilkinson's catalyst. With all these complexes, the accumulation of conjugated dienes was rather high and the linoleate selectivity rather low. Apparently the complex formation between these catalysts and the conjugated triene system of methyl sorbate is much stronger than that with the conjugated dienes formed with methyl linoleate. In methyl sorbate, such complex formation causes complete inactivation of the catalyst. In methyl linoleate, this complex formation results in a slower reduction (k_{CD} 0.55) than that of methyl linoleate (k_{Lo} 1.0) (Fig. 5). The linoleate selectivity values obtained in this study in the absence of solvent are significantly lower than those reported previously in the presence of polar solvents (Table I). Therefore, catalyst solvation may play a key part in the linoleate selectivity of Rh complexes.

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Sunflower Oil Diesel Fuel: Lubrication System Contamination

C. REWOLINSKI, Union Oil Company, Kenai, AK 99611, and **D.L. SHAFFER**, Chemical Engineering Department, Montana State University, Bozeman, MT 59717

ABSTRACT

Diesel lubrication oil contaminated with sunflower oil fuel was exposed to conditions simulating an engine crankcase environment to quantify and elucidate the mechanisms of loss of alkalinity and oil mixture thickening. Oxygen was found to be a dominant factor in both phenomena as was the presence of metallic copper catalyst. Triglyceride polymerization causing oil thickening does not appear causally related to alkalinity loss, but rather seems governed by a separate free radical mechanism.

INTRODUCTION

In recent years the escalating price of diesel fuel and the uncertainty of its availability have spurred research to develop alternate fuelstocks. Seed oils such as sunflower oil show promise as substitute diesel fuels and ultimately may prove acceptable, but problems of oilseed fuel contamination of engine lubrication oil must be overcome. Severe lubrication oil thickening and loss of alkalinity are encountered commonly when plant oils are substituted directly for standard diesel fuel in extended engine testing (1,2).

Thickening of lubrication oil contaminated with oilseed fuel probably is due to addition polymerization at points of unsaturation in the plant oil. As with drying oils, this polymerization might be expected to be accelerated by the presence of oxygen and certain metals (3). Such results, along with a strong relationship between the extent of plant