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Hydrogenation of Methyl Sorbate and Soybean Esters with Polymer-bound Metal Catalysts[1]

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ABSTRACT

New polymer-bound hydrogenation catalysts were made by complexing $PdCl_2$, $RhCl_3 \cdot 3H_2O$, or $NiCl_2$ with anthranilic acid anchored to chloromethylated polystyrene. The Pd(II) and Ni(II) polymers were reduced to the corresponding Pd(O) and Ni(O) catalysts with $NaBH_4$. In the hydrogenation of methyl sorbate, these polymer catalysts were highly selective for the formation of methyl 2-hexenoate. The diene to monoene selectivity decreased in the order: Pd(II), Pd(O), Rh(I), Ni(II), Ni(O). Kinetic studies support 1,2-reduction of the $\Delta 4$ double bond of sorbate as the main path of hydrogenation. In the hydrogenation of soybean esters, the Pd(II) polymer catalysts proved superior because they were more active than the Ni(II) polymers and produced less *trans* unsaturation than the Rh(I) polymers. Hydrogenation with Pd(II) polymers at 50-100 C and 50 to 100 psi H_2 decreased the linolenate content below 3% and increased *trans* unsaturation to 10-26%. The linolenate to linoleate selectivity ranged from 1.6 to 3.2. Reaction parameters were analyzed statistically to optimize hydrogenation. Recycling through 2 or 3 hydrogenations of soybean esters was demonstrated with the Pd(II) polymers. In comparison with commercial Pd-on-alumina, the Pd(II) polymers were less active and as selective in the hydrogenation of soybean esters but more selective in the hydrogenation of methyl sorbate.

INTRODUCTION

Polymer-bound catalysts have attracted much attention recently because they can offer the selectivity advantage of homogeneous catalysts and the ease of separation from products of heterogeneous catalysts (1-4). Bruner and Bailar (5,6) used a polymeric ligand containing diphenylbenzylphosphine complexed with either $PtCl_2$ or $PdCl_2$ to prepare heterogeneous catalysts that are analogs of the homogeneous catalysts $PtCl_2(Ph_3P)_2$ and $PdCl_2(Ph_3P)_2$. The $PdCl_2$ polymeric complex proved to be an active hydrogenation catalyst of soybean esters. Pittman et al. (7) prepared a crosslinked polystyrene complex with $Cr(CO)_3$ that was active as a stereoselective catalyst for the hydrogenation of methyl sorbate to *cis*-3-hexenoate. This type of stereoselectivity was previously observed with the homogeneous arene-$Cr(CO)_3$ complexes (8-10). Although the crosslinked polystyrene-$Cr(CO)_3$ was less active than the homogeneous analogs, it was reportedly recycled as often as 7 times. In our laboratory, depending on conditions, this same catalyst could be recycled from 2 (11) to 10 times with methyl sorbate (Friedrich et al., unpublished results). However, this catalyst lost its activity and could not be recycled when used with soybean oil esters at 180-200 C, the temperature necessary to hydrogenate the unconjugated fatty esters (9,12).

Our interest in more stable, active and recyclable catalysts for the selective hydrogenation of unsaturated fats led us to this investigation on new polymer-bound catalysts made by complexing $PdCl_2$, $RhCl_3$, or $NiCl_2$ with anthranilic acid anchored to chloromethylated polystyrene. The Pd(II) polymer-bound catalyst was active for the hydrogenation of alkenes, dienes, benzene, nitrobenzene and benzonitrile (13,14). The Rh(I) polymer-bound catalyst reduced olefinic and aromatic hydrocarbons and carbonyl, nitrile and nitro functional groups (15). Although hydrogenation of corn oil and soybean esters was indicated with these catalysts, no product analyses were made. In this report, Pd(II), Pd(O), Rh(I), Ni(II) and Ni(O) polymer catalysts were evaluated in the hydrogenation of methyl sorbate and soybean esters. The recyclability of the Pd(II) polymer catalyst also was tested.

EXPERIMENTAL

Materials and Methods

Preparation of the Pd(II) and Rh(I) polymer catalysts was described previously (13-15). One Pd(II) polymer preparation was sieved into 3 fractions of different mesh size: 20, 40 and higher than 100. The Ni(II) catalyst was prepared the same way by reacting anthranilic acid anchored chloromethylated styrene with $NiCl_2 \cdot 6H_2O$ in ethanol. The Ni(O) catalyst was prepared by treating the Ni(II) catalyst with excess $NaBH_4$ in ethanol (N. Holy, unpublished work). The Pd(O) catalyst was prepared similarly using a methanolic solution of $NaBH_4$. Methyl sorbate and soybean esters were prepared as described elsewhere (11). Methyl *cis*-3-hexenoate (98% pure plus 2% methyl 2-hexenoate by GC) was prepared by stereoselective hydrogenation of methyl sorbate with methyl benzoate-$Cr(CO)_3$ (10). Gas chromatographic (GC) analyses of hydrogenated methyl sorbate were carried out with a 72 x 1/8 in. column packed with 15% EGSS-X on Gas Chrom P 100/120 mesh (Applied Science Labs, State College, PA), programming between 80 and 130 at 2 C/min at 30 ml/min carrier flow rate; for analyses of hydrogenated soybean esters, a 10% DEGS column was used isothermally at 190 C. For kinetic studies with methyl sorbate, a more efficient GC column was used to separate 2-, 3- and 4-hexenoates: 10% SP2330 (68% cyanopropyl

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silicone) on 100/120 chromosorb W (Supelco, Inc., Bellefont, PA), run isothermally at 70 C for 25 min and then programmed to 130 at 4 C/min. Infrared (IR) analyses for *trans* unsaturation were done according to the AOCS method (Cd 14-61). Metal analyses of the polymer catalysts were performed by Galbraith Laboratories (Knoxville, TN).

Hydrogenations

Both magnetically stirred Magne Dash (Autoclave Engineers, Erie, PA) and Aminco rocker-type autoclaves were used with *n*-hexane as solvent. The rocking type autoclave also was fitted with a 6 10-ml compartment stainless steel insert (16), and the hydrogenations were carried out without solvent. After sealing and purging 3 times with H_2, the reaction mixtures were agitated and heated to reaction temperatures. After hydrogenation, the cooled reaction mixtures were filtered and solvent was removed partially by evacuation with a rotating evaporator. For recycling experiments, the used catalysts were recovered by filtration, washed several times with petroleum ether and air dried.

RESULTS

Hydrogenation of Methyl Sorbate

Hydrogenation parameters were first explored with methyl sorbate, which is a convenient substrate because the isomeric hexenoate products can be readily analyzed by GC. Hydrogenation data with different catalysts are summarized in Table I. The Pd(II) polymer catalysts are relatively selective for the hydrogenation of methyl sorbate to 2-hexenoate.

When a magnetically stirred autoclave was used, the activity of several Pd(II) polymer catalysts decreased and hydrogenation leveled off after ca. 6 hr with conversion ranging from 60 to 80%. When a hydrogenation was interrupted after 4 hr to introduce an additional 1% fresh catalyst, almost complete conversion was obtained compared to 79% for the equivalent hydrogenation with 2% catalyst (compare runs 3 and 4, Table I). Diene selectivity also was significantly increased. There was a loss of activity during hydrogenation that may have resulted from fragmentation of the polymer catalyst (14), or to decomposition, or to alteration of its structure. Increased activity and selectivity were obtained with the rocking autoclave, with which the agitation is less vigorous (compare runs 5 and 8, Table I). No relationship was apparent between relative catalytic activity and the Pd content of the polymers.

On the one hand, the reduced Pd(O) polymer catalyst was less active than the corresponding Pd(II) polymer catalyst (compare runs 11 and 18). On the other hand, the commercial Pd-on-alumina catalyst was somewhat more active than any of the Pd polymer catalysts but less selective than the Pd(II) polymer catalysts. The Ni(II) and Ni(O) polymer catalysts were the least active, whereas the Rh(I) polymer catalyst was more active but less selective than the corresponding Pd(II) polymer catalysts.

To elucidate the hydrogenation mechanism of the Pd(II) polymer catalysts, the progress of methyl sorbate reduction was followed by analyzing the products with an efficient

TABLE I

Hydrogenation of Methyl Sorbate with Polymer-bound Metal Catalysts

Run no.	Catalyst[a]	%	Autoclave[b]	Solvent	Temp. (C)	Pressure psi	GC analyses (%)				
								Hexenoates			
							Hexanoate	4+3–	2–	Sorbate	S_D[c]
1	Pd(II)-A	1	Magnetic	Hexane	150	500	2.7	12.7	54.3	30.3	18.0
2	Pd(II)-B	1	Magnetic	Hexane	150	500	2.3	12.3	41.0	44.4	10.8
3[d]	Pd(II)-B	2	Magnetic	Hexane	150	500	8.1	15.5	55.3	21.1	8.8
4[e]	Pd(II)B	1+1	Magnetic	Hexane	150	500	8.7	15.4	74.4	1.1	38.3
5	Pd(II)-B(20)	1	Magnetic	Hexane	150	500	11.3	11.1	37.7	39.9	2.5
6	Pd(II)-C	1	Magnetic	Hexane	150	500	18.3	7.6	37.2	36.9	1.6
7	Pd(II)-D	1	Magnetic	Hexane	150	500	9.4	10.8	39.7	40.1	2.2
8	Pd(II)-B(20)	1	Rocker	Hexane	150	500	8.8	17.0	70.5	3.5	25.7
9	Pd(II)-B(20)	5	Rocker	None	100	50	1.2	16.3	48.6	33.9	34.7
10	Pd(II)-C	5	Rocker	None	100	50	1.8	27.3	60.2	10.7	73.7
11	Pd(II)-D	5	Rocker	None	100	50	18.3	17.5	64.2	0	–
12	Pd(II)-B(20)	2	Rocker	None	150	50	0	9.9	20.4	69.7	–
13	Pd(II)-B(20)	1	Rocker	None	150	500	8.3	20.1	50.4	21.1	8.7
14	Pd(II)-B(20)	2	Rocker	None	150	500	29.5	16.1	54.1	0.4	12.9
15	Pd(II)-B(100)	1	Rocker	None	150	500	14.6	19.5	65.6	0.1	37.3
16	Pd(II)-B(100)	2	Rocker	None	150	500	34.9	11.6	53.4	0	–
17[f]	Pd(O)	2	Rocker	None	100	50	4.2	9.2	58.7	27.8	12.8
18[f]	Pd(O)	5	Rocker	None	100	50	3.6	8.2	65.6	22.6	19.3
19	Pd/Al	0.5	Rocker	None	100	50	2.1	12.5	44.8	40.5	14.4
20	Pd/Al	1	Rocker	None	100	50	51.0	6.6	42.5	0	–
21	Ni(II)	2	Rocker	None	100	50	0	6.4	3.7	94.7	–
22	Ni(II)	2	Rocker	None	150	50	0	1.9	5.7	92.4	–
23	Ni(II)	2	Rocker	None	150	500	4.8	14.5	48.0	32.7	8.9
24	Ni(O)	2	Rocker	None	100	50	0.9	4.0	12.0	83.1	1.7
25	Rh(I)	1	Rocker	None	100	50	2.5	20.3	37.7	39.5	12.6
26	Rh(I)	2	Rocker	None	100	50	7.0	34.1	58.9	0	–

[a] Pd(II)-A: 3.0% Pd, Pd(II)-B: 0.69% Pd, Pd(II)-B(20) = 20 mesh: 0.5% Pd, Pd(II)-B(100) >100 mesh: 1.1% Pd, Pd(II)-C: 0.58% Pd, Pd(II)-D: 0.38% Pd, Pd/Al = commercial 5% Pd-on-alumina (Engelhard, Newark, NJ), Ni(II): 2.0% Ni, Ni(O): 1.9% Ni, Rh(I): 0.9% Rh.

[b] Runs 1-8 with magnetically stirred autoclave-(300 ml Magne Dash): 10 g substrate, 90 ml solvent, 6 hr. Run 9 with rocking autoclave (300 ml): 10 g substrate, 90 ml solvent, 6 hr. Runs 10-27 with rocking autoclave fitted with a 6 10-ml compartment stainless-steel insert (16): 2 g substrate, no solvent, 6 hr.

[c] S_D = diene selectivity calculated by a computer method (17).

[d] See Fig. 1 for kinetic results.

[e] Mixture was first hydrogenated with 1% catalyst for 4 hr, then cooled, recharged with 1% fresh catalyst and hydrogenated 2 more hr.

[f] Derived from Pd(II)-D after $NaBH_4$ reduction.

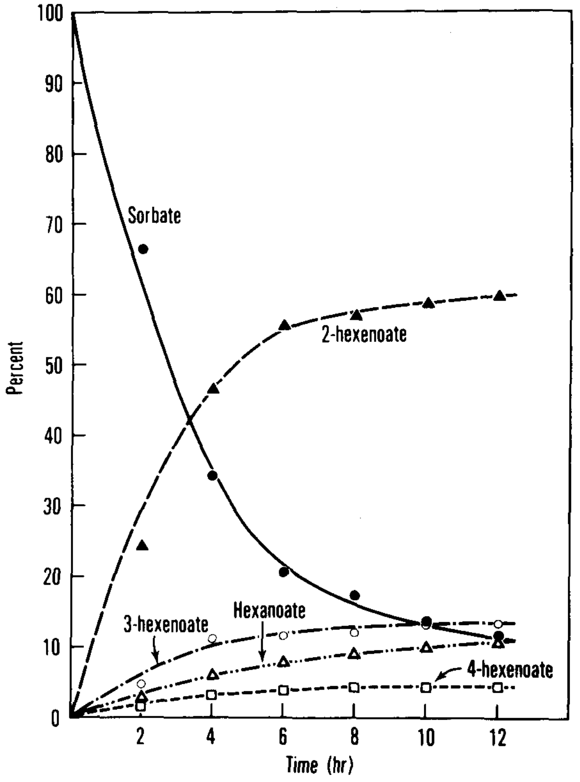

FIG. 1. Hydrogenation of methyl sorbate with Pd(II) polymer catalyst. (Conditions: see run 3, Table I).

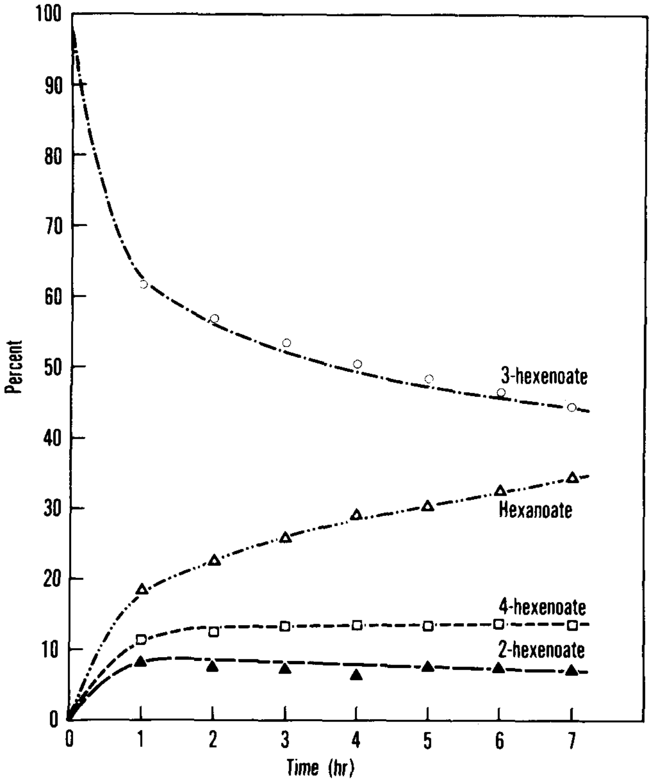

FIG. 2. Hydrogenation of methyl *cis*-3-hexenoate with Pd(II) polymer catalyst. (Conditions: 1 g substrate, 5% catalyst, 50 ml hexane, 100 C, 100 psi).

GC column (68% cyanopropylsilicone). Figure 1 shows that formation of methyl 2-hexenoate as the initial and most important product is accompanied by small amounts of 3- and 4-hexenoates and hydrogenation to methyl hexanoate. In another kinetic experiment, methyl *cis*-3-hexenoate (98% pure + 2% 2-hexenoate) was hydrogenated with the same Pd(II) polymer catalyst. Figure 2 shows that methyl *cis*-3-hexenoate is isomerized to 2- and 4-hexenoate with significant formation of methyl hexanoate. The relatively low level of 2-hexenoate indicates that it is readily hydrogenated to hexanoate. This high reactivity of 2-hexenoate is expected because its double bond is activated by conjugation with the ester carbonyl. However, in the presence of methyl sorbate, which is more reactive, methyl 2-hexenoate accumulates and the formation of hexanoate becomes relatively minor (Fig. 1).

Hydrogenation of Soybean Methyl Esters

Three Pd(II) polymer catalysts were examined under different conditions (Table II). At temperatures of 50-100 C and pressures of 50-100 psi, the linolenate content of soybean esters was reduced to levels ranging from 1.2 to 4.3% and the *trans* was increased to 9.8-25.7%. Linolenate selectivity ranged between 1.6 and 3.2 and linoleate selectivity between 4.7 and 20.6. As in the hydrogenations of methyl sorbate, there was no apparent relationship between catalytic activity and Pd content of the polymer. At 50 C and 50 psi, catalyst Pd(II)-D (0.38% Pd) produced a significantly lower *trans* level for a given IV drop than catalyst Pd(II)-B (0.50% Pd) (runs 27 and 31). Generally, high linolenate selectivities were correlated with high *trans* unsaturation (compare runs 32, 33 and 36, Table II).

In order to hydrogenate the linolenate in soybean esters below 3%, a level generally used commercially to achieve acceptable flavor and oxidative stability (18), it was necessary to raise either the catalyst concentration (run 29) or the temperature to 100 C (runs 33-35). Better conversions were obtained in the recycling experiments carried out on a larger scale (runs 36 and 37). Recycling of 2 Pd(II) polymer catalysts of different mesh particles was demonstrated through 2 and 3 hydrogenations. Initially, the 100 mesh catalyst was more active and selective than the 20 mesh catalyst. Although on recycling the activity diminished with both catalysts, the 20 mesh polymer retained more activity than did the 100 mesh polymer.

The filtered products were analyzed for Pd to determine if diminished activity after recycling might be caused by leaching of the metal from the polymer catalyst during hydrogenation. However, atomic absorption analyses of the hydrogenated samples showed that any Pd was below the limit of detection of 0.8 ppm. Therefore, diminished activity on recycling may be caused by partial disintegration of the polymer beads by abrasion during agitation.

In contrast to the hydrogenations of methyl sorbate, in the hydrogenations of soybean esters run at lower conversions, the Pd(O) polymer catalyst was as active or more active and more selective than the corresponding Pd(II) polymer catalyst (compare runs 38 and 41 with runs 31 and 35, Table II). The Pd-on-alumina catalyst was again quite active and its linolenate selectivity was in the same order as the Pd(II) polymer catalysts (run 42). The Ni(II) polymer catalyst required a temperature of 75 C to reduce the linolenate content of soybean esters below 3%. The corresponding Ni(O) polymer catalyst was less active. Finally, the Rh(I) polymer catalyst required a temperature of 100 C to reduce linolenate below 3% and produced the most *trans* unsaturation per unit IV drop (1.8) (run 47, Table II).

Hydrogenation runs were made with Pd(II) polymer catalysts of 3 mesh sizes in all combinations of 3 temperatures, 2 pressures and 2 concentrations. Data were analyzed

TABLE II

Hydrogenation of Soybean Esters[a] with Polymer-bound Metal Catalysts

Run no.[b]	Catalyst[c]	%	Temp.(C)	Pressure psi	GC analysis [d](%)				IV[e]	*Trans*(%)	Selectivity[f]	
					S	M	D	T			Lo	Ln
27	Pd(II)-B	1	50	50	4.0	36.8	45.3	4.3	121	14.1	–	2.1
28	Pd(II)-B	1	50	100	5.2	42.5	38.5	3.5	112	16.2	8.4	1.7
29	Pd(II)-B	2	50	100	7.7	49.9	30.2	2.3	101	20.6	7.1	1.6
30	Pd(II)-C	1	50	50	5.6	34.8	41.5	3.5	110	11.3	5.5	2.5
31	Pd(II)-D	1	50	50	8.3	38.1	35.6	3.4	103	9.8	3.3	1.6
32	Pd(II)-B	1	75	50	4.0	38.8	43.7	3.4	118	16.5	20.6	2.5
33	Pd(II)-B	1	100	50	4.3	45.5	37.1	2.7	110	21.4	17.4	2.0
34	Pd(II)-C	1	100	50	5.1	45.6	33.4	1.2	100	25.7	21.0	3.2
35	Pd(II)-D	1	100	50	5.2	42.7	35.2	2.2	104	20.5	15.3	2.4
	Recycling											
36[g]	Pd(II)-B(20)	1										
	Cycle 1		50	100	8.3	56.6	24.2	0.8	92.8	23.4	9.1	2.2
	Cycle 2		50	100	6.0	47.5	34.5	2.0	106	20.9	8.4	2.3
	Cycle 3		50	100	6.2	46.7	35.3	2.0	106	19.6	8.3	2.3
37[h]	Pd(II)-B(100)	1										
	Cycle 1		50	100	5.2	47.1	35.8	1.7	107	14.7	12.2	2.7
	Cycle 2		50	100	6.2	42.1	39.2	2.2	110	18.9	5.5	2.7
38	Pd(O)	1	50	50	5.7	42.8	38.7	2.0	109	17.3	3.8	3.0
39	Pd(O)	2	50	50	6.4	50.8	31.7	0.7	101	25.3	6.1	3.4
40	Pd(O)	1	75	50	6.1	45.9	36.1	1.3	106	25.1	4.6	3.1
41	Pd(O)	1	100	50	6.0	55.8	27.7	0	96.0	–	–	–
42	Pd/Al	0.1	50	50	5.8	41.6	40.1	2.4	112	11.4	3.9	2.8
43	Pd/Al	0.5	50	50	7.3	70.2	12.0	0	81.2	–	–	–
44	Ni(II)	1	75	50	4.2	40.7	37.9	2.6	108	19.0	–	2.6
45	Ni(O)	1	75	50	4.4	32.8	43.9	4.3	116	8.1	26.6	2.4
46	Rh(I)	1	75	50	4.3	34.2	42.6	4.2	114	30.9	–	2.2
47	Rh(I)	1	100	50	4.8	53.4	30.8	0.9	101	42.9	23.5	3.0

[a] Composition of starting material for runs 27-29, 32-33, 36-43, 47: 10.0% palmitate, 3.7% stearate, 23.5% oleate, 55.5% linoleate, 7.5% linolenate (IV = 136); for runs 30-31, 34-35, 44-46: 14.6% palmitate, 4.2% stearate, 24.4% oleate, 50.1% linoleate, 6.7% linolenate (IV = 125).

[b] Runs 27-35 and 38-49 with rocking autoclave fitted with a 6 10-ml compartment stainless-steel insert (16): 2 g substrate, no solvent, 6 hr. Runs 36 and 37 were run with the same autoclave without insert: 40 g substrate, no solvent. See footnotes g and h for reaction times.

[c] See footnote a in Table I.

[d] Abbreviations: S = stearate; M = monoene; D = diene; T = triene.

[e] Calculated on the basis of GC analysis.

[f] Linoleate (Lo) and linolenate (Ln) selectivities calculated by a computer method (17).

[g] Catalyst recovered by filtration between each cycle. Reaction time for cycle 1: 5.3 hr; cycle 2: 6.25 hr; cycle 3: 7 hr.

[h] Reaction time for cycle 1: 0.5 hr; cycle 2: 7.5 hr.

statistically (19) to examine main effects and interactions between factors. Table III shows the means for levels of different factors computed on the basis of 36 runs. Increasing catalyst concentration from 1 to 2% had a significant effect on total hydrogenation as measured by change in iodine value (ΔIV), in stearate (ΔSt), in oleate (ΔOl), in linoleate (ΔLo) and in linolenate (ΔLn); it had no significant effect on the ratio of % *trans* to ΔIV and linoleate (S_{Lo}) and linolenate (S_{Ln}) selectivities. Increasing the temperature from 50 to 100 C increased significantly ΔLn and S_{Ln}. *Trans*/ΔIV was significantly increased with any increase in temperatures. Pressure increase from 50 to 100 psi influenced all measurements significantly except the *trans* and S_{Ln}; it significantly decreased S_{Lo}. Mesh size was a particularly important factor. In going from 20 to 100 mesh and from 40 to 100 mesh, hydrogenation was significantly increased and the *trans*/ΔIV was significantly decreased; the increase in linolenate selectivity was significant but not that of linoleate selectivity.

Significant interactions included catalyst concentration-mesh size (CM), temperature-pressure (TP) and temperature-mesh size (TM) (Table III). Concentration had a more significant effect on ΔIV and ΔLn with the 20 mesh than with the higher mesh catalysts. The effect of temperature on *trans* was much greater at 100 psi than at 50 psi. Accordingly, a lower *trans* level was attained at 50 C and 100 psi than at 50 C and 50 psi. Finally, the effect of temperature on S_{Ln} was greater with the higher mesh catalysts than with the 20 mesh catalyst. From Table III, it is concluded that the highest linolenate selectivity was obtained at 100 mesh and 100 C and the lowest *trans* at 50 C and 100 psi.

DISCUSSION

The selectivity of Pd(II) polymer-bound catalysts in producing 2-hexenoate from methyl sorbate is entirely different than that of the $Cr(CO)_3$ complex catalysts (8-11) that produce 3-hexenoate from methyl sorbate. Formation of methyl 2-hexenoate can be explained either by selective 1,2-reduction of the Δ 4 double bond in methyl sorbate or by 1,4-reduction producing 3-hexenoate that is isomerized to 2-hexenoate. The kinetic results in Figures 1 and 2 support 1,2-reduction to form initially methyl 2-hexenoate, which is isomerized and reduced as follows:

$$\begin{tikzcd}\text{Sorbate} \arrow[r] & \text{2-hexenoate} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d] & \text{3-hexenoate} \arrow[r, phantom, "\rightleftharpoons"] & \text{4-hexenoate} \\ & \text{hexanoate} & & \end{tikzcd}$$

Although 1,4-reduction of sorbate to 3-hexenoate or 1,2-reduction of the Δ2 double bond to form 4-hexenoate (followed by isomerization) are not ruled out by the kinetic data, they are minor paths.

In previous work, the loss of activity of the Pd(II) polymer-bound catalyst for the hydrogenation of 1,3-cyclooctadiene on recycling was explained by changes in the

TABLE III

Hydrogenation of Soybean Esters with Pd(II)-Polymer Catalysts—Mean Values for Various Conditions[a]

Factors	ΔSt	ΔOl	ΔLo	ΔLn	ΔIV	*Trans*/ΔIV	S_{Lo}	S_{Ln}
Catalyst conc.[b] (C)								
(C_0)	1.49	25.11	21.26	5.38	29.24	0.83	17.42	2.38
(C_1)	2.31	29.11	25.29	6.13	34.76	0.79	16.52	2.38
LSD	0.52	3.84	3.86	0.60	4.61	0.05	2.97	0.22
Temperature (T)								
50 C (T_0)	1.96	25.00	21.88	5.22	29.58	0.66	16.03	2.14
75 C (T_1)	1.74	27.24	23.30	5.70	31.75	0.84	18.88	2.23
100 C (T_2)	2.01	29.07	24.94	6.35	34.68	0.93	16.01	2.76
LSD	0.64	4.70	4.73	0.74	5.72	0.06	3.63	0.26
Pressure (P)								
50 psi (P_0)	1.25	24.39	20.14	5.45	28.14	0.82	20.42	2.48
100 psi (P_1)	2.55	29.86	26.41	6.06	35.86	0.80	13.53	2.28
LSD	0.52	3.84	3.86	0.60	4.67	0.05	2.97	0.22
Mesh size (M)								
20 (M_1)	1.88	24.26	21.02	5.18	29.05	0.81	14.87	2.14
40 (M_2)	1.71	26.07	22.34	5.42	30.39	0.82	18.12	2.17
> 100 (M_3)	2.12	31.00	26.48	6.68	36.57	0.74	17.93	2.83
LSD	0.64	4.70	4.73	0.74	5.72	0.06	3.63	0.26
S	0.74	5.44	5.47	0.86	6.61	0.08	4.20	0.31

Interactions

	ΔLn			ΔIV		
CM	M_1	M_2	M_3	M_1	M_2	M_3
C_0	4.27	4.97	6.90	21.75	28.38	37.58
C_1	6.08	5.87	6.45	36.35	32.38	35.55
LSD		1.05			8.10	

	trans/ΔIV		S_{Ln}	
TP	P_0	P_1	P_0	P_1
T_0	0.73	0.58	2.47	1.82
T_1	0.83	0.85	2.17	2.30
T_2	0.88	0.97	2.80	2.72
LSD	0.09		0.38	

	S_{Ln}		
TM	M_1	M_2	M_3
T_0	1.90	1.67	2.85
T_1	2.25	2.38	2.08
T_2	2.25	2.45	3.53
LSD		0.46	

[a] Abbreviations: ΔSt = increase in % stearate; ΔOl = increase in % oleate; ΔLo = decrease in % linoleate; ΔLn = decrease in % linolenate; ΔIV = decrease in iodine value (calculated by GC); S_{Lo} = linoleate selectivity; S_{Ln} = linolenate selectivity; LSD = least significant difference (95% level); S = standard deviation.

[b] Catalyst concentrations were adjusted for Pd concentrations in the 3 catalysts used as follows: M_1 (20 mesh); 0.5% Pd, M_2 (40 mesh); 0.5% Pd, M_3 (>100 mesh); 1% Pd, C_0 = 1% for M_1 and M_2 and 0.5% for M_3 ; C_1 = 2% for M_1 and M_2 and 1% for M_3.

beads and conversion from the anchored anthranilic carboxylate to the free acid (14). Similarly, the bead integrity of the corresponding Rh(I) polymer catalyst was important, and activity was severely reduced by fragmentation during derivatization (15). Our results showing diminished activity on vigorous agitation and recycling can also be explained by bead fragmentation with a resulting change in the nature of the anthranilic ligand. Another possibility may be the replacement or reorganization of the ligands or insertion in a benzene C-H bond.

From the use of nonswelling solvents in the preparation of the Rh(I) polymers and the low metal contents, it was previously presumed that the metal is more likely to be concentrated at or near the surface of the macroreticular bead structure (15). The greater activity of the fine mesh Pd(II)-polymer catalysts in this work can be explained on the same basis. The lack of relation between activity and total metal concentration can be explained by assuming that surface metal concentration is more important.

In a comparison with Pd-on-alumina, the Pd(II) polymers were less active and showed similar selectivity in the hydrogenation of soybean esters but superior diene selectivity in the hydrogenation of methyl sorbate. The polymer catalyst might be advantageous if recycling can be achieved without bead disintegration. A continuous fixed bead system might prove beneficial in maintaining bead integrity. This work is now being extended to such continuous systems.

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Effect of Amino Acids on the Autoxidation of Safflower Oil in Emulsions

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ABSTRACT

Oxygen absorption rates were measured on liquid emulsions containing safflower oil and various amino acids. The antioxidant effects of the several amino acids were quite variable depending on the type of emulsifier used, the pH of the system and the presence of added sugar. Preliminary tests with Maillard reaction products obtained by heating dextrose with lysine showed little stabilizing effect. In freeze-dried emulsions, methionine, threonine, lysine and histidine all exhibited antioxidant activity. With sodium caseinate as the matrix, methionine was much better than any of the other amino acids. The inclusion of sugar enhanced the rate of oxidation. Porosity measurements on the freeze-dried powders revealed that oxygen diffusion was not rate-determining. When xanthan gum was used to replace caseinate in these dried emulsions, oxidation rates increased.

INTRODUCTION

The literature contains conflicting observations on amino acids as antioxidants for fats (1-6). Marcuse et al. tested a number of amino acids with linoleate (1,2). Tryptophan and histidine were very functional whereas glycine and alanine showed weak activity. Sliwick and Siechowsky found methionine and cysteine to have antioxidant effects in soybean oil whereas cystine was a weak prooxidant (3). Recently Farag et al. studied the effects of various amino acids in oil-in-water emulsions, in oils and in freeze-dried systems (4-6). The amino acids tested were all prooxidants in liquid emulsion and in oils. This effect was attributed to the NH_3R group. But in the dried systems the amino acids, with the exception of cysteine, all proved to be antioxidants. A number of reasons have been offered to explain these variations in behavior including differences in temperature, trace metal content, lipid concentration, emulsifier type and pH.

In our laboratory, we studied the influence of sugars and polyols on the oxidation of safflower oil in liquid emulsions (7). It was found that oxidative stability improved as the level of added sugar or polyol was increased. It was suggested that these compounds do not behave as actual antioxidants. They increase the viscosity of the aqueous phase which results in improved resistance to phase separation. A lower concentration of oxygen in the aqueous phase when sugar is present and a slower diffusion of the gas through the oil-water interface were suggested as causes for the better oxidative stability.

The objective of the work reported here was to determine the autoxidation rates of safflower oil in liquid emulsions containing added amino acids. The studies were subsequently extended to include freeze-dried emulsions with sodium caseinate or xanthan gum as matrices. Preliminary results with Maillard reaction products in liquid emulsions also are reported.

EXPERIMENTAL PROCEDURES

Materials

Refined safflower oil was obtained from the Pacific Vegetable Oil Co., San Francisco, CA. This oil contained no added antioxidants. Sodium stearoyl-2-lactylate (Artodan SP50), distilled monoglycerides (Dimodan TH), polyglycerol esters of fatty acids (Triodan 55) and citric acid esters of monodiglycerides (Acidan BC) were obtained from Grindsted Products, Inc., Kansas City, MO. Sodium caseinate was a product of the New Zealand Dairy Board. Xanthan gum (Keltrol) was from Kelco Co., Clark, NY. Sucrose, dextrose monohydrate and lactose were all from Mallinkrodt, Inc., St. Louis, MO. L-methionine, and ℓ-threonine were from ICN Pharmaceuticals, Inc., Cleveland, OH. L-histidine was obtained from Nutritional Biochemicals Co., Cleveland, OH, and ℓ-lysine hydrochloride was from J.T. Baker, Phillipsburg, NJ. Crystal Springs Water, Pine Hill Crystal Spring Co., Bronx, NY was used.

Methods

Oil-in-water emulsions were prepared by dissolving amino acids and sugar (where indicated) in spring water, dispersing anionic surfactant and adjusting pH in some cases with 5% NaOH or 0.1 N HCl. Dimodan TH or Triodan 55 were dissolved in safflower oil at 50 C and added to the water phase. The mixture was homogenized for 2 min using a Tekmar Probe at maximal speed (Model SD45N from Tekmar Co., Cincinnati, OH). Emulsion temperatures increased to 50-60 C during homogenation.

Oxygen absorption rates were measured on 20-g samples (5 g oil) in duplicate at room temperature following the