cis-Bond-Producing Hydrogenation of Polyunsaturates Catalyzed by Polymer-Complexed $Cr(CO)_3$ Catalysts

R.A. AWL, E.N. FRANKEL, J.P. FRIEDRICH, and E.H. PRYDE,
Northern Regional Research Center, Federal Research, Science and Education Administration,
U.S. Department of Agriculture, Peoria, Illinois 61604

ABSTRACT

cis-Bond-producing chromium carbonyl catalysts were prepared by complexing conventional or macroreticular, styrene-divinylbenzene copolymers or cross-linked poly(vinyl benzoate) with $Cr(CO)_6$. With one exception, these polymer-$Cr(CO)_3$ catalysts were as selective as the corresponding homogeneous arene-$Cr(CO)_3$ complexes for the formation of *cis*-monoenes from methyl sorbate and from conjugated, polyunsaturated fatty esters in cyclohexane. Although several of the polymer catalysts were very active when fresh, they all lost activity on recycling. They could not be recycled more than two times before a marked decrease in activity occurred due to loss of Cr, as shown by elemental analysis and infrared absorption in the recovered catalyst. Thermal analysis indicated instability of the polymer complexes at hydrogenation temperatures.

INTRODUCTION

As homogeneous hydrogenation catalysts, chromium carbonyl complexes are unique because they can convert polyunsaturates into *cis*-unsaturated products almost exclusively with no increase in saturates (1-4). The ability of these chromium complexes to minimize the formation of *trans* unsaturates and to avoid formation of saturated products makes them particularly desirable today (5). However, for practical, commercial use with edible products, it is necessary to remove the soluble catalysts and to recycle them. This requirement has not been realized with the homogeneous chromium catalysts because of their partial decomposition during hydrogenation and the difficulty in separating them from the product (1).

Recently, Pittman et al. (6) reported a "heterogenized" chromium carbonyl catalyst prepared from styrene-divinylbenzene (1%) copolymer complexed with $Cr(CO)_6$. This so-called anchored $Cr(CO)_3$ catalyst was as selective for the hydrogenation of methyl sorbate to 3-hexenoate as the homogeneous arene-$Cr(CO)_3$ complex catalysts (7,8). Pittman et al. (6) confirmed our previous observations (7,8) that on the basis of infrared the 3-hexenoate product has a *cis* configuration. Although the activity of the "heterogenized" catalyst was poor (total conversion required >10 hr), it could be recycled. This paper reports our extension of these studies aimed at achieving selective hydrogenation of polyunsaturated fats to *cis*-unsaturated products, separating catalyst from the product, and recycling the catalyst.

EXPERIMENTAL PROCEDURES

Materials and Methods

Sorbic acid (99+%) and 1,2-dimethoxyethane (99+%) were purchased (Aldrich Chemical Co., Inc., Milwaukee, WI). Methyl sorbate, prepared by esterification of sorbic acid with HCl and CH_3OH, was fractionally distilled. Soybean oil was commerciallyrefined and deodorized; its methyl esters, prepared by transesterification, were distilled and further purified by column chromatography on alumina (Fisher Scientific Co., Pittsburg, PA). Conjugated methyl linoleate was prepared by esterification of commerically conjugated (76%) linoleic acid (Pamolyn 380; Hercules Incorporated, Wilmington, DE) with HCl and CH_3 OH and was fractionally distilled.

For catalyst preparations spectroquality cyclohexane, petroleum ether, benzene, and 1,2-dimethoxyethane were dried over CaH_2 and distilled. Chromium hexacarbonyl (Strem Chemicals, Inc., Danvers, MA) and fresh sebacyl chloride (Eastman Kodak Company, Rochester, NY) were used as purchased. Benzoyl chloride was purified (9). Poly(vinyl alcohol) was Elvanol Grade 72-60 (DuPont, E.I. De Nemours and Company, Plastics Department, Wilmington, DE). Pyridine (reagent grade) was distilled from NaOH. Bio-Beads S-X1, 200-400 mesh, Bio-Beads SM-2, 20-50 mesh (Bio-Rad Laboratories, Richmond, CA), and Amberlite XAD-4, 20-50 mesh (Polysciences, Inc., Warrington, PA) are commercial polystyrene, cross-linked by copolymerization of styrene with divinylbenzene. To ensure purity and consistent history, all resins were extracted 4-8 hr in a modified Soxhlet extractor consecutively with the following solvents: (a) toluene-ethanol-water, a ternary azeotrope (10), (b) CH_3OH, and (c) CH_2Cl_2, and were dried in a vacuum oven.

Methods for gas liquid chromatography (GLC) and infrared spectrometry (IR) were described previously (1,11). Methyl palmitate was employed as an internal standard for GLC of conjugated linoleate and its hydrogenation products. Elemental Cr analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Cross-linked Poly(Vinyl Benzoate)

Twenty grams of poly(vinyl alcohol) and 100 ml of pyridine were stirred under dry N_2 in a glass resin kettle and heated at 80-90 C for 1 hr. Benzoyl chloride (0.137 moles) in 25 ml of pyridine was then added dropwise, and the temperature was raised to 100-110 C. The initially heterogeneous reaction mixture became a yellow, viscous solution within an hour. Then sebacyl chloride (0.023 equivalents) was injected, followed by two injections (50 ml each) of pyridine at 15-min intervals. The sebacyl chloride caused almost immediate gelation in the hot solution. After another hour, more benzoyl chloride (0.429 moles) and pyridine (50 ml) were injected. Heating was continued for 6 hr. Then the reaction mixture was cooled and CH_3OH (200 ml) was added. The dark supernatant liquid was decanted and filtered. The dark resin was washed repeatedly with cold CH_3OH and finally with boiling CH_3OH or C_2H_5OH until the washes were colorless. The light-yellow resin was dried in a vacuum oven. Dry resin(67.5 g) was a tan, heterogeneous mass exhibiting dark brown, rubbery, or gelatinous areas, which were cut away from the tough solid portion. The solid fraction was ground and sieved to obtain a relatively homogeneous, 20-50 mesh fraction. The amount of cross-linking can only be estimated from the initial stoichiometry to be less than 5%. The IR spectrum was consistent with the expected structure showing a series of weak bands at 3100-3000 cm^{-1} (aromatic C-H stretching); a very strong, broad absorption at 1720 cm^{-1} (aromatic ester C=0); a broad, strong band at 1260 cm^{-1} (ester C-O-C stretch); and a weak absorption at 794 cm^{-1} (monosubstituted benzene).

TABLE I

Hydrogenation[a] of Methyl Sorbate Catalyzed by Polymer-Complexed Arenetricarbonylchromium

Experiment	Catalyst resin (conditions)[b]	Cycle	Catalyst Cr (%)[c]	Reaction time (hr)	Conversion (%)	Product distribution (%)[d]			
						Hexenoates			
						3-	2-	Hexanoate	Unidentified
1	Batch No. 1:								
	Bio-Beads S-X1,	1	9.06	2.5	100	88	11	1	—
	200-400 mesh	2	ND	7	99	91	8	1	—
	(14.9%, M_f, 160 C)	3	6.86*	16	100	86	12	2	—
	Batch No. 1:								
2	Bio-Beads S-X1,	1	9.06	22^e	100	93	6	1	—
	200-400 mesh	2	ND	22^e	100	94	5	0.6	0.4
	(16.7%, R, 150 C)	3	5.24*	22^e	100	95	4	0.4	0.6
	Batch No. 2:								
3	Bio-Beads S-X1,	1	5.39	9	100	95	5	0	—
	100-200 mesh	2	ND	19	98	93	5	0	2
	(15.7%, M, 160 C)								
	Batch No. 3:								
4	Bio-Beads S-X1,	1	3.49	6	100	93	6	0.5	0.5
	100-200 mesh								
	(15.7%, M, 160 C)								
5^f	Same as Expt. 4^f	1	3.49	10	100	94	5	1	—
		2	ND	18	99	93	6	1	—
	Batch No. 3:								
6	Bio-Beads S-X1,	1	3.49	16^e	100	94	4	1.5	0.5
	100-200 mesh	2	ND	16^e	95	94	6	0	—
	(15.7%, R, 160 C)	3	2.0*	24^e	82	93	6	1	—
	Batch No. 3:								
7	Bio-Beads S-X1,	1	3.49	16	95	95	4	0.6	0.4
	100-200 mesh	2	ND	24	95	96	3	0.5	0.5
	(15.7%, R, 150 C)	3	1.98*	24	70	95	4	0.6	0.4
8	Amberlite XAD-4,	1	6.38	10	98	92	8	0	—
	20-50 mesh^g								
	(15.9%, M, 160 C)								
9	Bio-Beads SM-2,	1	3.27	18	95	51	28	18	3
	20-50 mesh	2	ND	24	67	32	41	22	5
	(16.9%, M_b, 160 C)								
10	Poly(vinyl benzoate),	1	8.01	2	100	92	7	1	—
	20-50 mesh	2	ND	3	99	92	6	1	1
	(15.8%, M_f, 160 C)	3	5.7*	18	100	89	7	3	1

[a] Pressure, 500 psi H_2; solvent, cyclohexane.

[b] Percent of catalyst used (wt catalyst/wt substrate X100). Bio-Beads and Amberlite resins are commercial styrene-divinylbenzene copolymers. Autoclaves: M = 150 ml Magne Dash with sampling tube (no filter), M_f = 300 ml Magne Dash with 15 μ filter on sampling tube, M_b = 300 ml Magne Dash with sampling tube and basket (50 mesh, s.s.) on dasher, R = 300 ml. Aminco rocker-type. Hydrogenation temperature.

[c] Elemental analysis of dry catalyst. *Indicates values were determined on recovered catalyst. ND = not determined.

[d] Based on total conversion and determined by gas liquid chromatography.

[e] Since hydrogenations in the rocker autoclave could not be followed, the reaction time is not that required for complete conversion.

[f] Catalyst and solutions were exposed to air.

[g] Too friable during complexing, mesh size was reduced but catalyst was still retained by a coarse filter.

Catalyst Preparations

Airlessware glassware (Kontes Glass Co., Vineland, NJ) and Oxy-Traps (Alltech Associates, Inc., Arlington Heights, IL) were employed to provide an oxygen-free N_2 atmosphere. The procedure of Pittman et al. (6) was followed exactly to prepare a polystyrene-complexed $Cr(CO)_3$ as a reference catalyst equivalent to theirs. A mixture of sublimed $Cr(CO)_6$ and polystyrene beads cross-linked with 1% divinylbenzene in 1,2-dimethoxyethane is refluxed 48 hr under N_2 in a Strohmeier reactor. This reactor has a sophisticated condenser designed to ensure that all sublimed $Cr(CO)_6$ is continuously washed back into the reaction flask. The polymer-$Cr(CO)_3$ complex is collected by filtration under N_2, washed repeatedly with benzene and petroleum ether, and dried in vacuo. However, all other polymer catalysts were prepared by a modification of Pittman's procedure; i.e., an insulated Airlessware extractor and a West condenser were substituted for the Strohmeier reactor, and $Cr(CO)_6$ was placed in the extractor. This system was opened at the condenser several times during reaction, and sublimed $Cr(CO)_6$ was quickly scraped back into the extractor while a positive N_2 flow was maintained. A safety Hg bubbler and a pressure regulator (Airlessware) were adjusted to maintain 3-4 psi N_2 in the system. Catalysts were stored under N_2 in amber glass bottles.

Hydrogenations

In experiments where the progress of hydrogenation was followed, a stainless-steel Magne Dash autoclave (150 or 300 ml) with a sampling tube was used. A stainless-steel

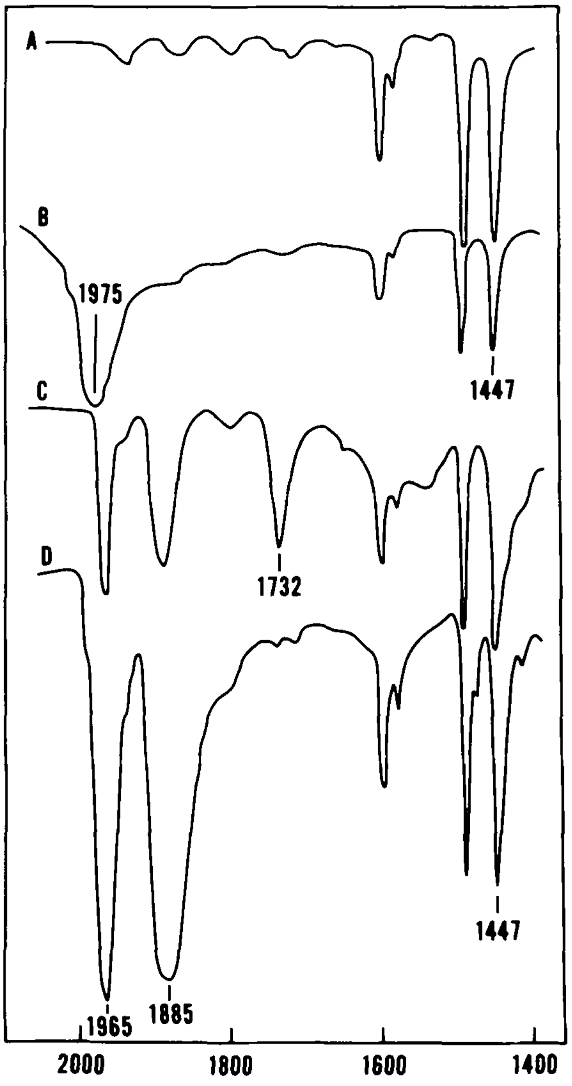

FIG. 1. Infrared spectra: (A) polystyrene (Bio•Beads S-X1); (B) mixture of $Cr(CO)_6$ + polystyrene (Bio•Beads S-X1); (C) recovered polystyrene-complexed $Cr(CO)_3$ catalyst (experiment 1, Table I); (D) fresh polystyrene-complexed $Cr(CO)_3$ catalyst (experiment 1, Table I).

solvent filter (15 μ; Waters Associates, Milford, MA) was connected to the sampling tube to permit filtration of product solution and to retain insoluble catalyst in the autoclave for recycling without air exposure. Hydrogenation was followed by periodic sampling and GLC analysis. Sampling times were based on the rate of hydrogen uptake monitored qualitatively by decrease in pressure. In experiments where hydrogenations were carried out for predetermined periods, an Aminco rocker-type autoclave without sampling tube was used.

For the initial hydrogenation cycle, either autoclave was purged with N_2 during addition of a cyclohexane solution of the substrate followed by the dry catalyst. The autoclave was then sealed and purged three times with H_2 before agitating and heating the contents. For catalyst recycling in the Magne Dash autoclave, the product solution was discharged under pressure through the sampling tube line. Catalyst was washed three times by successively evacuating the autoclave, charging it with cyclohexane, pressurizing with H_2, stirring, and discharging the wash. The autoclave was reloaded with fresh substrate solution through the sampling tube. For product recovery and catalyst recycling with the rocker-type autoclave, it was opened under slight H_2 pressure and quickly resealed with a rubber stopper containing an inlet and a filter tube to allow anaerobic transfer of product solution, solvent wash, or substrate solution between autoclave and airlessware.

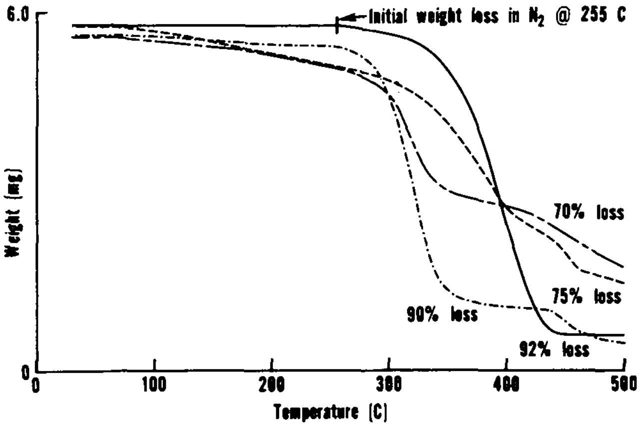

FIG. 2. Thermogravimetric curves of cross-linked polymers and their $Cr(CO)_3$ complexes in N_2 (35 ml/min) at 10 C/min from 27 C to 500 C. —— Polystyrene (Bio•Beads S-X1). --- Polystyrene-complexed $Cr(CO)_3$ (experiment 1, Table I). —•— Cross-linked poly(vinyl benzoate). – – – Poly(vinyl-benzoate)-complexed $Cr(CO)_3$ (experiment 10, Table I).

RESULTS

Catalyst Preparations

A polystyrene-complexed $Cr(CO)_3$ catalyst (Table I, experiments 1 and 2) was prepared exactly according to the directions of Pittman et al. (6). Catalysts in experiments 3-10, however, were prepared by substituting a Soxhlet extractor for the Strohmeier reactor (12). Variations in the Cr content between fresh catalysts made from the same polymer (e.g., experiments 1, 3, and 4) were mainly due to a different reaction complexing period (i.e., 22 hr in experiments 3 and 4 vs. 48 hr in experiment 1), to variations in the rate of N_2 sweep through the system to remove generated CO, and to different mesh size. Furthermore, differences in the preparation of batch 2 catalyst (experiment 3) vs. batch 3 (experiments 4-7) may account for variations observed in their Cr content and activity. Preparation of the third batch differed from the second in that quantities of reagents were doubled, the N_2 sweep was intermittent, and refluxing was continuous for 23 hr instead of interrupted every 6 or 7 hr. Cr content of the other catalysts were also influenced by diversity in the physical nature (degree of cross-linking, porosity, rigidity, and surface area) and structure of the polymer supports.

The Cr content of our catalyst, prepared with cross-linked polystyrene according to Pittman et al. (6), is in excellent agreement with their reported value (9.06% vs. 8.89%). By reacting $Cr(CO)_6$ with a well-defined, linear polystyrene, Pittman et al. (13) realized a Cr content of 11.3%. In a different approach, they prepared the monomer styrenetricarbonylchromium but could not homopolymerize it. They were able to copolymerize it, however, with styrene or methyl acrylate to achieve Cr contents up to 11.2 and 13.3%, respectively. Their copolymerization studies suggested that Cr content in the polystyrene-$Cr(CO)_3$ complex may be limited by steric and other factors (13).

Because previous studies (8,14-16) have shown that catalytic activity of chromium carbonyl complexes is greatly influenced by the arene ligand (e.g., $C_6H_5COOCH_3$->C_6H_6>$C_6H_5CH_3$), we expected greater activity from a poly(vinyl benzoate) complex (experiment 10) compared

TABLE II

Hydrogenation[a] of Conjugated Methyl Linoleate by Polymer-Complexed Arenetricarbonylchromium

				Change (%)[d]		Distribution of unsaturates		
Experiment	Catalyst resin (conditions)[b]	Catalyst Cr (%)[c]	Reaction time (hr)	Monoenes	Conjugated dienes	Monoenes	Nonconjugated dienes	Conjugated dienes
1	Bio-Beads S-X1, 200-400 mesh (8.3%, M_f, 150 C)	9.06	0	—	—	24	10	66
			16	80	-78	76	9	14
2	Bio-Beads S-X1, 100-200 mesh (6.7%, M, 160 C)	5.39	0	—	—	26	11	63
			9	73	-73	72	11	17
3	Bio-Beads S-X1, 100-200 mesh (6.7%, M_f, 160 C)	3.49	0	—	—	23	10	67
			12	16	-17	34	11	55
4	Amberlite XAD-4 20-50 mesh[d] (6.6%, M, 160 C)	6.38	0	—	—	33	12	54
			11	74	-62	73	6	21
			19	94	-74	84	0	14
5	Poly(vinyl benzoate), 20-50 mesh. (8.8%, M_f, 150 C)	8.01	0	—	—	24	9	67
			16	78	-85	76	14	10
	Recycle (150 C)		8	24	-27	39	12	49
	(160 C)	ND	+8	60	-67	64	14	22
	Recycle (160 C)	ND	16	5	-8	27	12	61

[a,b,c]See Table I.

[d]Change (%) = $\frac{\text{\% difference (final-initial)}}{\text{\% initial conjugated dienes}} \times 100.$

[e]Determined by gas liquid chromatography.

to polystyrene complexes. The poly(vinyl benzoate) was prepared by reacting poly(vinyl alcohol) with benzoyl chloride in pyridine solution and crosslinking with sebacyl chloride. A more favorable distribution of cross-links was expected by crosslinking linear polymer in solution rather than performing a conventional copolymerization, as noted by Davankov et al. (17), in preparing macronet, isoporous gels from linear polystyrene. The Cr content of the poly(vinyl benzoate) complex (experiment 10) corresponds to ca. 44% of theoretical if all phenyl groups were complexed. For comparison, ca. 42% of the theoretical Cr content was found for the polystyrene catalyst in experiment 1.

Catalyst Characterization

The IR spectrum of the polystyrene-Cr(CO)$_3$ catalyst (Table I, experiments 1 and 2) was compared with that of the uncomplexed resin and a mixture of this resin with Cr(CO)$_6$ (Fig. 1). The physical mixture of Cr(CO)$_6$ and the polystyrene resin gave only a single, broad band at ca. 1975 cm^{-1} for the carbonyl. The complexed polymer (curve D), however, exhibited bands due to Cr(CO)$_3$ at 1965 and 1885 cm^{-1} (6). These bands were observed to decrease in intensity in the recovered and recycled catalysts (cf. curve D vs. curve C). The ester carbonyl band at 1732 cm^{-1}, observed in the recovered Pittman catalyst but not in the fresh catalyst, may be due either to incompletely extracted 3-hexenoate or to sorbate bound to Cr. Unreacted methyl sorbate and 2-hexenoate absorbed (neat) at 1718 cm^{-1} and 1720 cm^{-1}, respectively, whereas 3-hexenoate and hexanoate absorbed (neat) at 1738 cm^{-1} and 1740 cm^{-1}, respectively. A rough estimate of the Cr content in the recovered catalysts could be made from the ratio of the carbonyl absorbances at either 1965 or 1885 cm^{-1} to that of the polystyrene at 1447 cm^{-1}.

The thermal stability of polymers and their Cr(CO)$_3$ complexes in Table I was examined by dynamic thermogravimetry (Fig. 2). The uncomplexed polymers were relatively stable up to or beyond 250 C but then rapidly lost 90% of their weight between 300-350 C. Except for the macroreticular complexes (Table I, experiments 8 and 9) which showed gradual weight losses below 100 C, the complexed polymers generally exhibited gradual losses (3-13%) from ca. 105 C up to 250 C where the rate accelerated sharply. However, overall weight losses for the complexed polymers were only 70-75%.

Hydrogenation of Methyl Sorbate

The polyester catalyst was just as selective for the formation of 3-hexenoate (Table I, experiments 1 and 10). However, analyses after 1 hr hydrogenation showed only 68% conversion with the polystyrene catalyst compared to 90% conversion with the polyester complex. Furthermore, the polystyrene catalyst required 7 and 16 hr for the second and third cycle, whereas the polyester catalyst required 3 and 18 hr. More rapid disappearance of Cr(CO)$_3$ from the plyester was also indicated by IR analysis of the recovered catalysts. Comparison of experiments 1, 3, and 4 suggests that the observed activity of the catalyst is not always in proportion to its Cr content. With the very active catalysts (experiments 1 and 10), hydrogen uptake began before reaction temperature was reached. However, with the less active catalysts an induction period of ca. 0.5-2.0 hr was observed at reaction temperatures. In experiment 5, air contact, during charging of the autoclave and filtration between cycles, appears to have reduced catalytic activity. A shorter hydrogenation time for experiment 4 relative to experiment 6 would be expected because of better agitation achieved with the Magne Dash autoclave than with the rocker. However, the rocker autoclave is more comparable to the Hoke bomb used by Pittman et al. (6). Their results indicated that more than 10 hr hydrogenation under similar conditions was necessary to attain complete hydrogenation of the sorbate. They also rationalized that the low activity of their polystyrene-Cr(CO)$_3$ catalyst may be caused by limited diffusion into the polymer beads because cyclohexane is a poor-swelling solvent. Since macroreticular polystyrenes are reportedly not affected as much by the solvent (18), Amberlite XAD-4 and Bio-Beads SM-2 (equivalent to Amberlite XAD-2) were complexed with $Cr(CO)_6$ and tried as catalysts. The XAD-4 complex was selective but less active than Pittman's type polystyrene catalyst (cf. experiments 1, 3, 4, and 8). The SM-2 catalyst (experiment 9) showed both poor selectivity and poor activity.

Since the results in Table I indicated that activity decreased considerably upon recycling the polymer complexes more than once or twice at 160 C, several hydrogenations (experiments 2 and 7) were tried at 150 C, the temperature Pittman et al. employed to recycle their catalyst six or seven times (6). Under these conditions, we found with recycling not only a decrease in the Cr carbonyl stretching frequencies at 1965 and 1885 cm^{-1} but also loss of Cr from the catalyst. The reported absorption at 1635 cm^{-1} (6) was either very weak or absent. Experiment 2 was conducted under conditions similar to those of Pittman et al. (6), and we found much less overhydrogenation to hexanoate. Experiments 6 and 7 also demonstrated that with polystyrene $Cr(CO)_3$ complexes having 3% or less Cr, the time required for complete hydrogenation of sorbate, a very reactive diene, would be impractical. All filtered products were yellow or green liquids, and their color may suggest the presence of solubilized Cr compounds. This problem is now under investigation.

Hydrogenation of Conjugated Linoleate

With polystyrene-$Cr(CO)_3$ catalysts, 70-80% of the conjugated dienes were hydrogenated in 9-16 hr at 150-160 C (Table II, experiments 1 and 2). Figure 3 shows the changes in composition with time to be in agreement with those observed with homogeneous $Cr(CO)_3$ complex catalysts (8). The *trans,trans*-conjugated diene was most reactive because it has the most favorable conformation for 1,4-addition; the *cis,cis*-conjugated diene was least reactive, as expected (8).

Neither condensation nor polymerication of the conjugated dienes was indicated by GLC as there were no noticeable changes in the weight concentration of the internal standard. The distilled product (Table II, experiment 2) was analyzed by GLC using a 20 ft x 4 mm glass column packed with 10% Silar 10 C to separate elaidate and oleate (19). Comparison of the starting material and product showed that percentage of *cis*- monoene increased 45.7%, but that of *trans*-monoene only 0.8%. IR was not considered reliable for the *trans* analysis in the presence of conjugated dienes.

Results of experiment 3 suggest that with conjugated linoleate relatively little catalytic activity may be expected if the Cr content is 3.5% or less. The macroreticular catalyst in experiment 4 exhibited good activity and caused hydrogenation of the nonconjugated diene fraction. At 150 C, the polyester-$Cr(CO)_3$ catalyst converted 80% of the conjugated dienes to monoenes in 16 hr (experiment 5), and the recovered catalyst was still fairly active. However, because the hydrogenation rate with the once recycled catalyst was considerably slower at 150 C, the temperature was increased to 160 C after 8 hr. By the second recycle, this catalyst was relatively inactive, and a significant decrease (ca. 93% relative to the ester carbonyl bond) in the Cr carbonyl absorption was determined by IR analysis of the recovered catalyst.

Hydrogenation of Soybean Oil and Esters

Selective conjugation and hydrogenation were attempted with the polystyrene-$Cr(CO)_3$ catalyst at 175 C and 500 psi H_2, as previously achieved with the homogeneous $Cr(CO)_3$ complexes (1,2). With soybean methyl esters, 11% of the polyunsaturates were hydrogenated in 12 hr at 180 C, but with the oil no hydrogenation was detected after 8 hr. With the polyester $Cr(CO)_3$ catalyst, no hydrogenation was detected after 9 hr at 170 C, but 44% of the polyunsaturated esters were selectively hydrogenated after first conjugating them with alkali in a separate step. With the exception of one macroreticular catalyst, the polymer $Cr(CO)_3$ complexes apparently were not active conjugation catalysts below 180 C. At higher temperatures, they were expected to be too thermally unstable to recycle.

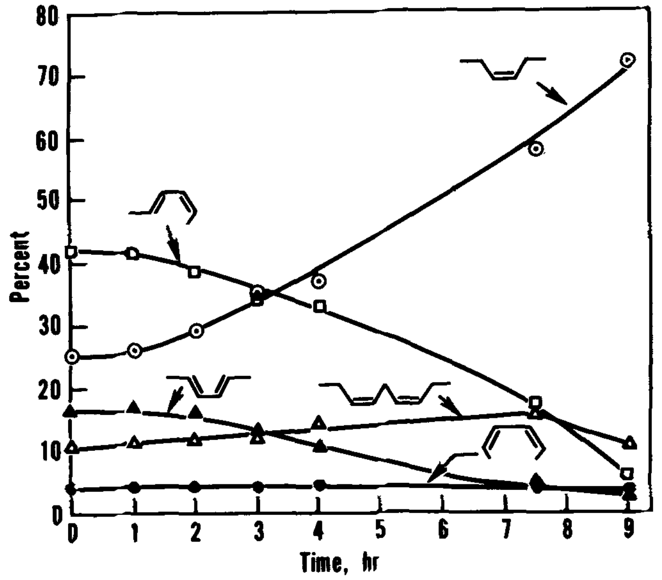

FIG. 3. Hydrogenation of conjugated methyl linoleate catalyzed with polystyrene-complexed $Cr(CO)_3$ (experiment 2, Table II).

DISCUSSION

The polystyrene catalysts examined in this study showed more loss of activity with recycling than catalyst in similar experiments described by Pittman et al. (6). The reason for this difference has not been determined. Our findings on loss of activity are consistent with the decreases of elemental Cr and IR absorption due to $Cr(CO)_3$. Perhaps, in our experiments, arene-$Cr(CO)_3$ complexes were leached as they were destroyed due to better agitation, different actual hydrogenation temperatures, catalyst pretreatment, and other experimental conditions. More catalyst activity was shown initially by the poly(vinyl benzoate) complex than by the polystyrene complex of $Cr(CO)_3$. All but one polymer catalyst (Bio-Beads SM-2) showed very good selectivity for the hydrogenation of methyl sorbate to 3-hexenoate. For practical purposes, none of the catalysts was recyclable more than twice. Conjugated dienes were hydrogenated selectively to *cis*-monoenes by $Cr(CO)_3$ complexed to cross-linked polystyrene or poly(vinyl benzoate) at 150-160 C and 500 psi. However, these catalysts were relatively unstable to air and heat.

For commercial use, more stable, active, and recyclable catalysts are needed. We are now examining more promising polymeric ligands and reevaluating reaction parameters. The question of whether complete (7) or partial (16) dissociation of $Cr(CO)_3$ occurs during homogeneous hydrogenation catalyzed by arene complexes has not been resolved yet (3). More basic research should be carried out to answer several important questions: (a) does $Cr(CO)_3$ remain bound to the phenyl moiety of the polymer during hydrogenation, (b) is partial or complete dissociation necessary for hydrogenation, and (c) if dissociation occurs is reassociation of $Cr(CO)_3$ possible for recycling. A more complete characterization of the heterogenized-$Cr(CO)_3$ catalysts is required for a fuller appreciation of the potential of this approach to stereoselective hydrogenation of polyunsaturated fats.

ACKNOWLEDGMENT

The authors thank R.L. Reichert for hydrogenations.

REFERENCES

1. Frankel, E.N., JAOCS 47:11 (1970).
2. Frankel, E.N., U.S. Patent 3,542,821 (1970).
3. Frankel, E.N., Rev. Fr. Corps Gras 24:241 (1977).
4. Coenen, J.W.E., JAOCS 53:382 (1976).
5. Symposium on Nutrition Effects of *trans* Fatty Acids. Papers presented at the AOCS Meeting, Chicago, IL, September 26-29, 1976. Abstracts 146-150, 159-164, JAOCS 53:466A-468A (1976).
6. Pittman, C.U., Jr., B.T. Kim, and W.M. Douglas, J. Org. Chem. 40:590 (1975).
7. Frankel, E.N., E. Selke, and C.A. Glass, J. Am. Chem. Soc. 90:244 (1968).
8. Frankel, E.N., and R.O. Butterfield, J. Org. Chem. 34:3930 (1969).
9. Oakwood, T.S., and C.A. Weisgerber, Org. Synth. Coll. Vol. 3:113 (1955). Note 3.
10. Gould, R.F., ed., "Azeotropic Data-II, " Adv. Chem. Ser. 35:61 (1962).
11. Mabrouk, A.F., H.J. Dutton, and J.C. Cowan, JAOCS 41:153 (1964).
12. Cais, M., D. Fraenkel, and K. Weidenbaum, Coord. Chem. Rev. 16:27 (1975).
13. Pittman, C.U., Jr., P.L. Brube, O.E. Ayers, S.P. McManus, M.D. Rausch, and G.A. Moser, J. Polym. Sci. Part A-1, 10:379 (1972).
14. Cais, M., E.N. Frankel, and A. Rejoan, Tetrahedron Lett. 1968:1919.
15. Frankel, E.N., and F. Little, JAOCS 46:256 (1969).
16. Cais, M., and A. Rejoan, Inorg. Chim. Acta 4:509 (1970).
17. Davankov, V.A., S.V. Rogoshin, and M.P. Tsyurupa, J. Polym. Sci., Symp. No. 47, 95 (1974).
18. Technical Notes, "Amberlite XAD-4," November 1974 and "Amberlite XAD-2," August 1975, Rohm and Haas Co., Philadelphia, PA.
19. Gas-Chrom Newsl. 17(4):4 (1976). Applied Science Laboratories, Inc., State College, PA.

[Received January 31, 1978]