

# Hydrogenation of Canola Oil Using Chromium Catalysts

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Homogeneous, supported and precipitated chromium catalysts were prepared from chromium hexacarbonyl in an attempt to selectively hydrogenate canola oil. These chromium compounds showed low activity, lowering the iodine value of the oil by only 10 IV units. The concentration of *trans*-isomers, however, was very low (<1% for most runs). Infrared spectroscopy revealed the presence of a  $\text{Cr}(\text{CO})_3(\text{diene})\text{PPh}_3$  complex in two of the hydrogenated oils. The selectivity and the mechanism by which chromium catalysts hydrogenate unsaturates are discussed.

Chromium carbonyl compounds can selectively hydrogenate unsaturated vegetable oils to *cis*-monoenes (1). This selectivity is desirable in the processing of edible oils. Examples of such chromium catalysts are  $\text{Cr}(\text{CO})_6$ , benzene- $\text{Cr}(\text{CO})_3$  and many other tricarbonyl species. These compounds, however, act as homogeneous catalysts and pose a problem in removing various toxic chromium species from the oil.

There has been considerable interest in the preparation of polymeric and supported analogs of known homogeneous catalysts in the hope that these compounds would have limited solubility characteristic of the polymer or support and yet retain the catalytic activity of the monomer (1-6). The goal of this research was to chemically bond chromium hexacarbonyl to silica, an inert insoluble support. This was accomplished by replacing the hydrogen atoms of the surface hydroxyl groups on silica with a phosphine group. These phosphines were then used as ligands to bind chromium carbonyl to the support. Homogeneous and precipitated chromium catalysts were also prepared to further study the hydrogenation reaction.

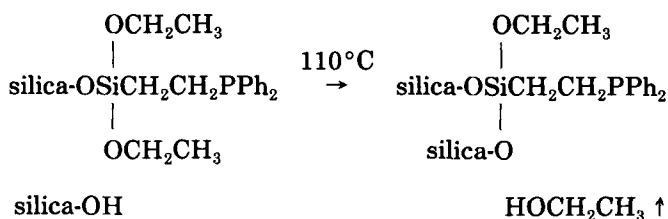
## EXPERIMENTAL

The silica was supplied by Cabot Carbon of Canada Ltd., 99.8%,  $200 \pm 25 \text{ m}^2/\text{g}$ , and the canola oil was supplied by Canada Packers Ltd., Toronto, Ontario. Triethylamine was dried over  $\text{LiAlH}_4$  and distilled under nitrogen. Bis(2-methoxyethyl)ether (diglyme) was refluxed with sodium under nitrogen and distilled. All of the chromium catalysts were prepared under dry oxygen-free conditions. The diglyme was deoxygenated by bubbling nitrogen for 20 min. Neutron activation analysis was used to analyze for chromium.

*Preparation of homogeneous chromium catalysts.*  $\text{Cr}(\text{CO})_5\text{PPh}_3$ , *trans*- $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$  and *cis*- $\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  were prepared by reacting chromium hexacarbonyl with a stoichiometric amount of the phosphine in diglyme. The mixtures were heated under nitrogen at ca.  $150^\circ\text{C}$  for 24 hr. After reaction, the diglyme was distilled off at  $80^\circ\text{C}$  under vacuum.  $\text{Cr}(\text{CO})_5\text{PPh}_3$  was purified by recrystallizing three times from hexane. *trans*- $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$  and *cis*- $\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  were washed four times with hot hexane. The yields were

40%, 44% and 80% for the pentacarbonyl, *trans*-tetracarbonyl and *cis*-tetracarbonyl compounds, respectively. Infrared spectra of these homogeneous catalysts agreed well with reported values in the literature (7,8) and showed that these compounds did not contain unreacted chromium hexacarbonyl or free phosphine, and did not contain other chromium carbonyl species.

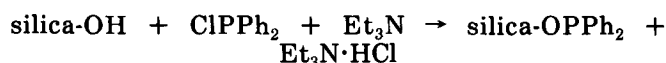
*Preparation of supported chromium catalysts.* Method 1. The phosphinated silica (silica- $\text{OSi}(\text{OCH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{PPh}_2$ ) was prepared as reported in the literature (9,10). Phosphinated silica heated at  $110^\circ\text{C}$  under vacuum was more stable with respect to the anchorage of the phosphine group than untreated phosphinated silica. Apparently, additional molecules of ethanol are driven off, yielding (silica- $\text{O})_2\text{Si}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{PPh}_2$  by the same mechanism by which water is removed from silica.



This results in the phosphine chain doubly bonded or chelated to the surface of the silica.

The phosphinated silica (0.4255 g) was heated with chromium hexacarbonyl (0.4672 g) in 40 ml of diglyme at  $120^\circ\text{C}$  for 22 hr under nitrogen. The next day, the product was filtered off, washed well with dichloromethane and air dried. Yield 0.4054 g,  $0.71 \pm 0.09\%$  chromium by weight or  $0.44 \pm 0.08$  atoms of  $\text{Cr}/100\text{\AA}^2$  of silica surface. A total of 40 g of silica- $\text{OSi}(\text{OCH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Cr}(\text{CO})_5$  was prepared which contained  $0.21 \pm 0.03\%$  chromium by weight.

Method 2. A mixture of silica (39.9 g, dried at  $155^\circ\text{C}$  under vacuum for 2 hr), triethylamine (8.0 ml, 58 mmol) and 700 ml of diglyme was treated with chlorodiphenylphosphine (8.2 ml, 45 mmol) under nitrogen and stirred for three hr at room temperature.



Chromium hexacarbonyl (11.47 g, 50 mmol) was then added and the mixture heated under nitrogen at  $120^\circ\text{C}$  for six hr. The product, silica- $\text{OPPh}_2\text{Cr}(\text{CO})_5$ , was filtered, washed three times with dichloromethane, rinsed with hexane and air dried. Yield 44.0 g,  $0.56 \pm 0.07\%$  chromium by weight or  $0.33 \pm 0.06$  atoms of  $\text{Cr}/100\text{\AA}^2$  of silica surface.

*Preparation of precipitated chromium catalysts.* Chromium metal was precipitated onto silica by thermally decomposing chromium hexacarbonyl in the presence of silica. Chromium contents of 5 to 6% were obtained by heating a mixture of 6 g of silica and 2 g of chromium hexacarbonyl in 250 ml of diglyme at an oil bath temperature of  $185^\circ\text{C}$  for 24 hr. This reaction was carried out under two different types of conditions, exposed to air

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(oxygen and water) and under inert conditions (nitrogen atmosphere, dry and deoxygenated diglyme, dry glassware and silica) where attempts were made to remove all oxygen and water from the system. The products were filtered, washed three times with dichloromethane, air dried and then heated under vacuum at 185°C to ensure complete decarbonylation.

Different colored chromium on silica catalysts were obtained depending upon the amount of oxygen and water present in the system. Under inert conditions the product was black. This compound shall be referred to as Cr/silica #1 and most likely contains chromium in the zero oxidation state deposited onto silica. A blue chromium/silica compound (Cr/silica #2) was also obtained under inert conditions. The blue coloration indicates the presence of chromium in the 2+ oxidation state. Some oxygen or water must have been present in the system and oxidized the chromium which was initially present in the zero oxidation state. When chromium hexacarbonyl was precipitated onto the silica in air a green product (Cr/silica #3) was obtained. The green color indicates the presence of chromium in the 3+ oxidation state. The infrared spectra of these chromium on silica compounds showed no carbonyl absorption bands. Hence, all of the carbonyl groups had been driven off the metal. These compounds contained highly divided chromium in different oxidation states on silica.

**Hydrogenations.** The hydrogenation reactions were carried out in a stainless steel 300-ml Parr hydrogenation apparatus agitated at 900 rpm. For comparison purposes, all chromium compounds were tested under the same conditions: 200°C, 250 psi partial pressure of hydrogen, 20 g of canola oil, 80 ml of hexane (dried over LiAlH<sub>4</sub> and distilled under nitrogen), 4 hr. After the hydrogenation reaction the catalyst was filtered from the oil and washed with hexane. The oil was heated to 60°C under vacuum to remove the hexane and stored in a refrigerator. Iodine values (Wijs' method) and percent *trans*-isomers as percent elaidic acid (IR spectrophotometric method) of the oil were determined by the official methods of the American Oil Chemists' Society (11,12).

## RESULTS AND DISCUSSION

**Homogeneous chromium catalysts.** Three homogeneous chromium catalysts were prepared from chromium hexacarbonyl (Fig. 1). The series Cr(CO)<sub>5</sub>PPh<sub>3</sub>, *trans*-Cr(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> and *cis*-Cr(CO)<sub>4</sub>(Ph<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) made an interesting study because of the different stereochemistry and number of accessible coordination sites (assuming that only the carbonyl groups can come off) for hydrogenation to take place. *cis*-Cr(CO)<sub>4</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) was substituted for *cis*-Cr(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> because under the conditions of hydrogenation (200°C), *cis*-Cr(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> would isomerize to the thermodynamically more stable *trans*-Cr(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> species (13). *cis*-Cr(CO)<sub>4</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) cannot form the *trans*-isomer because the carbon-carbon backbone holds the two phosphorus atoms too close together.

The hydrogenation results are listed in Table 1. Chromium hexacarbonyl hydrogenation has been well studied and documented in the literature (14). Unlike nickel metal, the industrially used catalyst, chromium hexacarbonyl and tricarbonyl complex catalysts are very

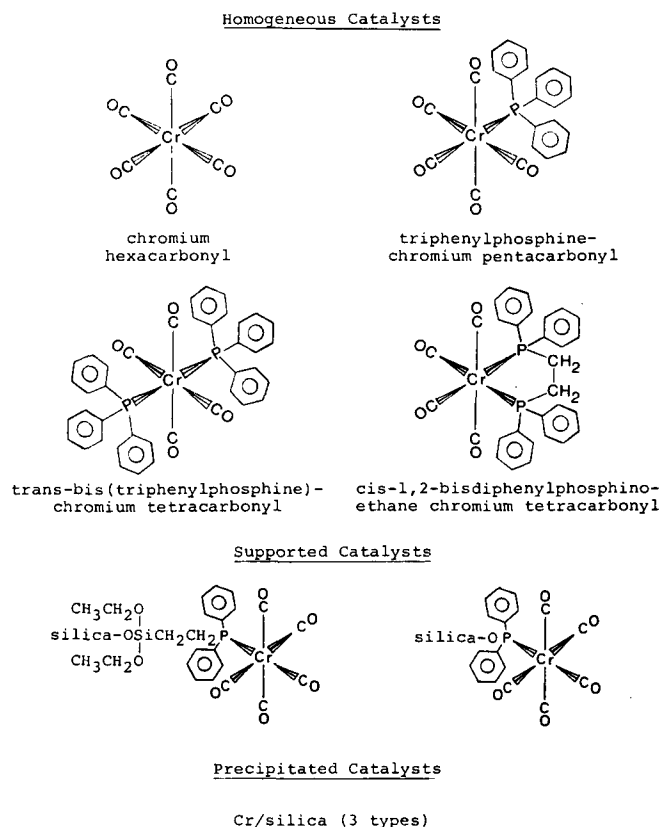
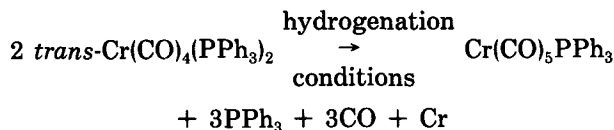


FIG. 1. Chromium catalysts.

selective. They will hydrogenate polyunsaturated fats to monoenes with very little increase in saturates and less than 10% *trans*-isomers (1,14). Chromium hexacarbonyl has been shown to be most active and selective at 500 psi hydrogen, in hexane and at a concentration of 1% chromium by weight (14). Using this catalyst a relatively high temperature of 200° is needed to conjugate double bonds before hydrogenation can occur (15,16).

The Cr(CO)<sub>5</sub>PPh<sub>3</sub> catalyst (run 2) hydrogenated canola oil down to an iodine value of 110 with very little increase in the amount of *trans*-isomers. Infrared spectroscopy revealed that the phosphine group remained on the chromium carbonyl complex. No free triphenylphosphine was identified in the hydrogenated oil or in the catalyst that precipitated from the oil. The oil, however, was green, reflecting the large amount of chromium present. The hydrogenation behavior of the Cr(CO)<sub>5</sub>PPh<sub>3</sub> catalyst at 200°C (run 2, IV 110, 0.7% *trans*-isomers) was similar to that of Cr(CO)<sub>6</sub> at 175°C (same conditions as run 1 except at 175°C, IV 106, 0.9% *trans*-isomers). Cr(CO)<sub>5</sub>PPh<sub>3</sub> has been reported in the literature (17) to hydrogenate 1,3,7-octatriene to 1,5-octadiene (14%) and the 1,4-addition product 1,6-octadiene (52%) at 210°C. This product distribution was almost identical to that using chromium hexacarbonyl at 200°C. Hence, these two hydrogenation catalysts behave in the same manner.

Almost all of the *trans*-Cr(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> catalyst transformed into Cr(CO)<sub>5</sub>PPh<sub>3</sub> during the hydrogenation reaction at 200°C. The balanced equation is



The nature of the other chromium product was not identified. If the *trans*-chromium catalyst is converted to  $\text{Cr(CO)}_5\text{PPh}_3$  in 50% yield there should be less hydrogenation compared to  $\text{Cr(CO)}_5\text{PPh}_3$ , but this was not observed (Table 1). No doubt some hydrogenation occurred via  $\text{Cr(CO)}_5\text{PPh}_3$ , but there must have been a significant contribution from the other chromium species.

The compound *cis*- $\text{Cr(CO)}_4(\text{diphos})$  did not hydrogenate canola oil at all (run 4). The iodine value of the oil remained the same, and there was no increase in the concentration of *trans*-isomers. The IR of the oil was unchanged and did not show any dissolved *cis*- $\text{Cr(CO)}_4(\text{diphos})$  or free diphos even though the resulting oil contained a small amount of chromium. The fact that absolutely no hydrogenation occurred is important. The chelating phosphorus ligand must have stayed on chromium preventing hydrogenation from occurring by tying up two adjacent coordination sites.

**Supported chromium catalysts.** Two heterogeneous supported catalysts were prepared, silica- $\text{OPPh}_2\text{Cr(CO)}_5$  and silica- $\text{OSi(OCH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Cr(CO)}_5$ , which are illustrated in Figure 1. In both cases, the chromium-carbonyl phosphine complex is covalently bonded to the silica. The IR spectra of both these compounds showed peaks at 2061(m), 1984(w) and 1936(s,broad)  $\text{cm}^{-1}$  confirming the presence of  $\text{Cr(CO)}_5\text{P}$  on the surface of the silica. Another peak at 1893(s,broad) revealed the presence of disubstituted  $\text{Cr(CO)}_4\text{P}_2$  on the silica. The absence of an absorption band around 2013  $\text{cm}^{-1}$  ruled out the possibility of *cis*- $\text{Cr(CO)}_4\text{P}_2$ . Agreement with the IR spectrum of *trans*- $\text{Cr(CO)}_4(\text{PPh}_3)_2$  was very good. Hence, both of the chromium-carbonyl-silica compounds prepared contained supported  $\text{Cr(CO)}_5\text{P}$  and *trans*- $\text{Cr(CO)}_4\text{P}_2$  species.

There were several indications that a  $\text{Cr(CO)}_5\text{P}$  complex anchored to a support via the phosphorus ligand would selectively hydrogenate vegetable oils without contaminating the product with chromium.

1.  $\text{Cr(CO)}_5\text{PPh}_3$  hydrogenates 1,3,7-octatriene with the same selectivity as chromium hexacarbonyl (17). In this work, both  $\text{Cr(CO)}_5\text{PPh}_3$  and  $\text{Cr(CO)}_6$  hydrogenated canola oil to the same iodine value and percent *trans*-isomers albeit at different temperatures.

2. The phosphorus group in  $\text{Cr(CO)}_5\text{PPh}_3$  remained on chromium under the hydrogenation conditions used in Table 1.

3. Chromium carbonyls could be multibonded to silica. Some chromium was chelated to phosphinated silica via  $\text{Cr(CO)}_4\text{P}_2$  which, in turn, was chelated to the silica via  $(\text{silica-O})_2\text{Si(OCH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{PPh}_2$ .

There were, however, many problems associated with these silica-supported  $\text{Cr(CO)}_5\text{P}$  catalysts.

1. They were difficult to make, requiring dry and inert conditions.

2. The amount of  $\text{Cr(CO)}_5\text{P}$  on the silica was small. This meant that very large amounts of the catalysts were needed to make a run; 36.08 g of silica- $\text{OPPh}_2\text{Cr(CO)}_5$  (0.56% Cr by weight) was needed in order to have 0.20 g of chromium in the reactor. Unfortunately, the silica- $\text{OSi(OCH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Cr(CO)}_5$  compound could not be tested because the amount of  $\text{Cr(CO)}_5\text{P}$  on the surface of the silica was too low.

3. The chromium carbonyl entity could come off the support and contaminate the oil.

The amount of hydrogenation using the silica- $\text{OPPh}_2\text{Cr(CO)}_5$  compound (run 5) was small, smaller than that obtained using its homogeneous analogue  $\text{Cr(CO)}_5\text{PPh}_3$ . The silica supported catalyst, however, was not adequately suspended in the oil. A lot more than 80 ml of hexane was required to allow proper mixing of the catalyst and the oil. The amount of chromium in the oil product was very low even though a  $\text{Cr(CO)}_5\text{P}$  species could be seen in the infrared spectrum of the oil. This was to be expected because the chromium carbonyl compound was water sensitive. Water probably added across the O-P bond releasing  $\text{Cr(CO)}_5\text{P}$  from the surface of the silica. Previously, Awl et al. (3,5) attached  $\text{Cr(CO)}_6$  to the phenyl groups of polymers yielding arene-anchored  $\text{Cr(CO)}_3$  moieties. These catalysts were as selective as their corresponding homogeneous arene- $\text{Cr(CO)}_3$  catalysts. The chromium entities, however, also came off

TABLE 1

Hydrogenation of Canola Oil<sup>a</sup>

Run no.	Catalyst	Catalyst (g)	Chromium (g)	Hydrogenated oil		
				IV ±1	% <i>trans</i> ±0.5	% Cr by weight
	Starting oil			119	0.0	0.000 ± .005
1	$\text{Cr(CO)}_6$	0.87	0.21	90	7.9	0.37 ± .03
2	$\text{Cr(CO)}_5\text{PPh}_3$	1.68	0.19	110	0.7	0.28 ± .03
3	<i>trans</i> - $\text{Cr(CO)}_4(\text{PPh}_3)_2$	2.70	0.20	107	0.8	0.42 ± .03
4	<i>cis</i> - $\text{Cr(CO)}_4(\text{diphos})^b$	2.13	0.20	118	0.0	0.047 ± .005
5	silica- $\text{OPPh}_2\text{Cr(CO)}_5$	36.08	0.20	115	0.7	0.008 ± .001
6	Cr/silica #1	3.30	0.20	112	9.3	0.005 ± .005
7	Cr/silica #2	3.13	0.20	112	0.8	0.015 ± .005
8	Cr/silica #3	3.56	0.20	114	1.5	0.010 ± .005

<sup>a</sup> Conditions: 200°C, 4 hr, 250 psi partial pressure  $\text{H}_2$ , 20 g canola oil, 80 ml hexane.

<sup>b</sup> Diphos is  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ .

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the support during hydrogenation. In this case the arene-Cr bond was broken, releasing  $\text{Cr}(\text{CO})_3$  into solution. A supported catalyst is only as strongly bound as the weakest bond present. The supported catalysts examined in this work were found to be impractical for industrial use due to their low activity and because of the difficulty in preparing them, the low concentration of chromium on the surface of the support, and the ease with which the chromium could come off the surface.

**Precipitated chromium catalysts.** This novel approach to the preparation of heterogeneous catalysts had many desirable properties:

- The catalysts were easy to make and were chemically and thermally very stable.
- The chromium metal did not contain carbonyl ligands and was, therefore, much less toxic than chromium carbonyl complexes.
- A lot of chromium could be deposited on the silica. Five to six percent chromium by weight was arbitrarily chosen for this work.
- The oxidation state of the metal could be varied. These catalysts could also be easily pretreated with various gases at different temperatures.
- Mixed metal catalysts could, in principle, be prepared by decomposing two different metal carbonyls in the presence of the support.

The Cr/silica catalysts reduced canola oil to an iodine value around 112 with the least amount of chromium in the hydrogenated oil (runs 6, 7 and 8). The lack of color in the hydrogenated oils reflected the small amount of chromium present. These heterogeneous catalysts were as active as the homogeneous catalyst  $\text{Cr}(\text{CO})_5\text{PPh}_3$ . The Cr/silica #1 (see Experimental section for details) stands out from all of the catalysts in Table 1 by isomerizing the oil to 9.3% *trans*-isomers. The other two chromium on silica compounds produced very low levels of *trans*-isomers. These two heterogeneous chromium catalysts were the most successful in terms of ease of preparation, low chromium content in the oil and low concentration of *trans*-isomers. It must be clearly stated, however, that none of the catalysts tested were active enough for application.

## REACTION MECHANISM

Chromium carbonyl catalysts have been shown to selectively hydrogenate unsaturated fats to *cis*-monoene (1). The selectivity of these chromium catalysts can be understood by considering two possible mechanisms of hydrogenation of a conjugated diene, 1,2-addition and 1,4-addition as shown in Figure 2. 1,4-addition of hydrogen results in a *cis*-monoene. 1,2-addition, on the other hand, results in a *cis*- or *trans*-monoene product which could be further hydrogenated to a saturate.

Deuterium studies (18) have provided direct evidence that chromium carbonyl complexes hydrogenate dienes by a 1,4-addition mechanism. A 1,4-addition mechanism explains why nonconjugated double bonds are conjugated before hydrogenation occurs and illustrates why *cis*-monoene products are highly favored. It also explains why isolated double bonds are not hydrogenated and, hence, why hydrogenation products contain very low levels of saturates.

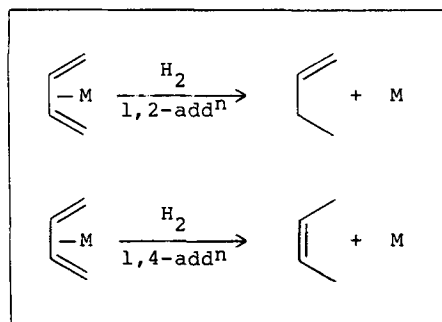


FIG. 2. 1,2- and 1,4-addition of hydrogen to a conjugated diene metal complex.

A 1,4-addition mechanism, however, results in slow hydrogenation because the dienes must be conjugated before hydrogenation can occur. This will also result in low levels of hydrogenation, because only conjugatable dienes will be hydrogenated to monoenes. Monoenes and difficult-to-conjugate dienes (double bonds very far apart from each other) will not be hydrogenated.

The presently accepted mechanism of hydrogenation using chromium tricarbonyl catalysts was proposed by Frankel (18). According to Frankel the induction period is the time necessary to generate the active intermediate  $[\text{Cr}(\text{CO})_3]$  by dissociation. He regarded this first step as rate determining. The actual process of *cis*-addition of hydrogen to the diene was assumed to occur by a concerted 1,4-addition mechanism. Note, however, that if the diene actually coordinates to a  $[\text{H}_2\text{Cr}(\text{CO})_3]$  intermediate this would result in seven groups about chromium, but would still obey the 18-electron rule and allow the transfer of hydrogen to the diene to take place on the metal.

Three distinctive carbonyl peaks were discovered at 1979(s), 1913(s) and 1906(s)  $\text{cm}^{-1}$  in the hydrogenated oil using the  $\text{Cr}(\text{CO})_5\text{PPh}_3$  and *trans*- $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$  catalysts. The three carbonyl bands were characteristic of a metal complex containing three CO ligands (19). The position of these peaks suggested that the carbonyl stretches were due to a  $\text{Cr}(\text{CO})_3(\text{diene})\text{P}$  species (20). The diene is probably a conjugated diene of canola oil, and the phosphine is most likely triphenylphosphine. This finding is not unusual. Using iron pentacarbonyl, Frankel and coworkers (21) have also characterized a stable iron-tricarbonyl complex of methyl octadecadienoate. As a result, metal-diene complexes are probably important catalytic intermediates in the hydrogenation of unsaturated fats.

Three types of chromium catalysts were examined in this work, chromium carbonyls, supported chromium carbonyls and precipitated chromium catalysts, representing the three general types of catalysts, homogeneous, supported and heterogeneous. All of these chromium compounds showed low activity. Chromium may show very desirable selectivity, but by itself was too slow a hydrogenation catalyst. The authors believe that if chromium is to have a future as an edible oil hydrogenation catalyst it will lie in the development of a mixed metal catalyst. In this manner, the hydrogenation selectivity of chromium could be combined with another catalyst whose sole purpose is to conjugate isolated double bonds. This may open up new areas of research in the future.

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