Contribution from the Department of Chemistry, Technion, Israel Institute of Technology, Haifa, Israel

Organometallic Studies. XXXV.[1] Selective Hydrogenation of Dienes Catalyzed by Arenechromium Tricarbonyl Complexes[2]

M. Cais and A. Rejoan

Received July 30, 1970

The effect of arene Cr(CO)$_3$ complexes as hydrogenation catalysts in homogeneous solution has been studied. Rates of hydrogenation of methyl sorbate (methyl 2,4-hexadienoate) have been measured. Nearly all the various catalysts studied have been found to be highly selective in the hydrogenation of a diene to a monoene. The concept of coordinative unsaturation has been used in proposing a mechaism for the catalytic role of arene Cr(CO)$_3$ complexes in the hydrogenation of dienes.

Introduction

Recently we have presented results from a study of the catalytic role played by iron carbonyl complexes in the hydrogenation of polyolefins in homogeneous media.[1b] The mechanism suggested for the catalytic behaviour of the iron complexes was based on the concept of coordinative unsaturation and provided an explanation for the ligand exchange and double bond isomerization reactions which were observed to accompany hydrogenation.

In this communication we wish to report additional data to the preliminary results[3] obtained from a similar study on the effect of arene-cromium tricarbonyl complexes in the homogeneous catalytic hydrogenation of conjugated dienes. It will be shown that the mechanistic concepts applied to the reactions with iron carbonyl complexes[1b] can be extended to cover those of the arenechromium tricarbonyl catalysts.

Results

(a) *Products from Hydrogenation of Methyl Sorbate.* Methyl sorbate (methyl 2,4-hexadienoate) was chosen as model substrate for testing the catalytic properties of arenechromium tricarbonyl complexes in the hydrogenation of conjugated dienes. The same substrate had been previously chosen by us in our studies with iron carbonyl complexes[1b] because it represented a suitable simple model for diene fatty acid glycerides and because it allowed for relatively facile analysis of all possible hydrogenation products. In order to facilitate comparison of results from the arenechromium tricarbonyl studies with those of the iron carbonyl complexes, we employed, in the initial stages of this investigation, comparable conditions of temperature (150-160°) and pressure (~700 psi) for the hydrogenation reaction.

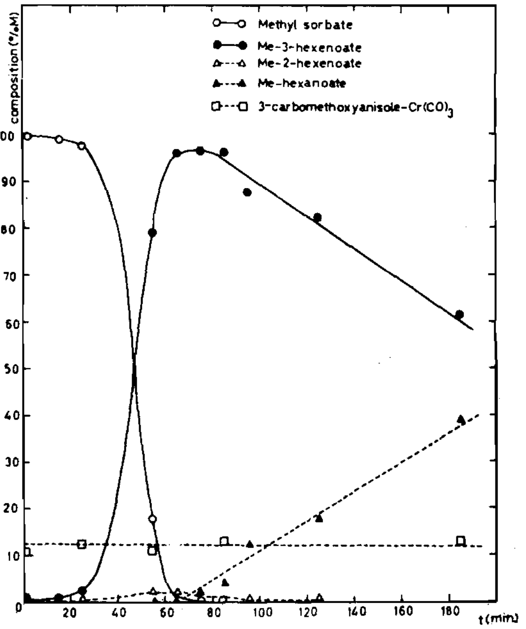


Figure 1. Product distribution in hydrogenation of methyl sorbate (0.211 mole ℓ^{-1}) with (3-carbomethoxy)anisole Cr(CO)$_3$ (0.011 mole ℓ^{-1}) (cyclohexane, 150°, 700 psi H$_2$).

A typical distribution of hydrogenation products in the reaction mixture is shown in Fig. 1. Several important features emerge from this graph: (i) an induction period was required before the onset of hydrogenation; (ii) the major hydrogenation product was methyl 3-hexenoate; (iii) the disappearance of substrate (methyl sorbate) and the appearance of methyl 3-hexenoate approached a reciprocal relationship; (iv) the isomeric monoene, methyl 2-hexenoate, and the fully saturated product methyl hexanoate were formed only in very small amounts (0-4%) for as long as the diene substrate was still present

---

(1) (a) Part XXXIV, M. Cais and D. Fraenkel, *Israel J. Chem.*, in press, (1970); (b) Part XXXIII, M. Cais and N. Maoz, *J. Chem. Soc.*, (A), in press.

(2) For preliminary communications see, (a) M. Cais, N. Maoz, and A. Rejoan, *Inorg. Chim. Acta* Second Intern. Symposium, Venice, Italy, August 1969, Proceedings p. 25; (b) M. Cais and A. Rejoan in « Progress in Coordination Chemistry », M. Cais, ed., Elsevier, Amsterdam, 1968, p. 32.

(3) M. Cais, E. N. Frankel, and A. Rejoan, *Tetrahedron Letters, 16,* 1919 (1968).

Table I. The Effect of Substituents on the Catalytic Activity of $(CO)_3Cr . C_6H_5$—R in Hydrogenation of Me Sorbate[a]

Compound No.	Substituent-R (or arene)	Total Reaction time (min)	Approximate Induction time (min)	10^5k_{obs} (sec^{-1})	Reaction Products (weight %) Me Sorbate	Me 3—	x-hexenoates 2—	Me hexanoate
1	—H	480[b]	(285)[b]	(39.6)[b]	0.4	93.9	3.6	2.1
2	$—CH_3$	420	240	24.2	0.0	93.6	5.3	1.1
3	$—CH_2—CH_3$	420	120	15.3	4.8	90.1	5.1	0.0
4	$—CH_2C_6H_5$	450	285	1.41	84.8	13.7	1.5	0.0
5	$—CH_2CH_2C_6H_5$	480	330	0.44	95.3	4.7	0.0	0.0
6	$—OCH_3$	360	180	1.00	88.4	11.6	0.0	0.0
7	$—C_6H_5$	450	275	4.93	52.6	44.5	2.9	0.0
8	$—CH=CH—C_6H_5$	130	45	72.8	2.2	93.0	3.5	1.3
9	$—(CH=CH)_2C_6H_5$	120	15	64.0	0.0	95.3	1.8	2.9
10	$—CO . C_6H_5$	90	25	111	0.0	97.3	1.8	0.9
11	$—CO_2CH_3$	120	45	56.0	0.0	98.9	0.1	1.1
12	—Cl	120	15	61.5	0.0	95.7	0.1	4.3
13	$1—CO_2CH_3$, $3—OCH_3$	60	25	143	0.9	96.0	2.2	0.9
14	Phenanthrene	20[c]	—	—	0.0	97.4	2.4	0.0

[a] Reaction conditions: Me sorbate (0.211 mole ℓ^{-1}); catalyst (0.011 mole ℓ^{-1}); solvent, cyclohexane; temp., 150°; pressure, 700 psi H_2. [b] Reaction temp., 165°. [c] Time required to reach reaction conditions given in *a* above.

Table II. The Effect of Solvents on Hydrogenation of Me Sorbate

Solvent	Catalyst	Reaction temp. (°C)	Total Reaction time (min)	Approx. Induction time (min)	10^5k_{obs} (sec^{-1})	Reaction Products (weight %) Me Sorbate	Me 3—	x-hexenoates 2—	Me hexanoate
Cyclohexane[a, b]	Benzene $Cr(CO)_3$	165	480	285	39.6	0.4	93.9	3.6	2.1
Acetone[a, b]	Benzene $Cr(CO)_3$	165	30	[f]	246	0.0	91.8	3.1	5.1
Benzene[a, b]	Benzene $Cr(CO)_3$	175	420	150	0.63	92.6	6.9	0.5	0.0
Cyclohexane[a, b]	Anisole $Cr(CO)_3$	150	420	180	1.0	88.4	11.6	0.0	0.0
Methylene Chloride[a, b]	Anisole $Cr(CO)_3$	150	420	135	16.8	11.6	85.0	3.4	0.0
Cyclohexane[a, c]	(1,4-Diphenylbutadiene) $Cr(CO)_3$	160	240	30	35.5	1.0	96.3	2.1	0.6
Acetone[a, c]		160	45	[f]	169	0.5	94.4	5.1	0.0
Cyclohexane[a, b]	phenanthrene $Cr(CO)_3$	150	20	[f]	—	0.0	97.4	2.6	0.0
Cyclohexane[d, e]	phenanthrene $Cr(CO)_3$	150	60	[f]	—	0.0	96.3	3.7	0.0

[a] Hydrogen pressure, 700 p.s.i. [b] 5% mole catalyst concentration. [c] 1.3% mole catalyst concentration. [d] Reaction carried out under N_2 (pressure 700 psi) in the absence of molecular hydrogen. [e] 2.5% mole catalyst concentration. [f] Analysis of first aliquot taken upon reaching the reaction temperature (~20 min) showed significant amounts of hydrogenated products.

in the reaction mixture. Once most of the diene had been converted to products and following what appeared to be a second induction period, the mono-olefins were further hydrogenated to the fully saturated product. (In most experiments the reaction was stopped when maximum monoene formation had occurred). (V) the concentration of arenechromium tricarbonyl catalyst seemed to have remained virtually unchanged.

(b) *Effect of Arene Substituents on Catalytic Activity.* The ratio of substrate (19 mmole, 0.211 mole ℓ^{-1}) to catalyst (1 mmole, 0.011 mole ℓ^{-1}) and large hydrogen excess used in most of the experiments enabled us to assume conditions of pseudo-first order reaction. Rate constants, k_{obs}, were calculated from the expression $-d[S]/dt = k_{obs}[S]$. A typical curve for the calculation of k_{obs} is given in Fig. 2. As can be seen from the data collected in Table I the values of k_{obs} appear to be significantly affected by the electronic nature of the substituent. In addition, and not less significant the induction period is also markedly altered by the type of arene moiety present in the arenechromium tricarbonyl complex. The data in Table I present the distribution of products from the hydrogenation reaction carried out to completion (*i.e.* maximum monoene formation) or stopped after 7-8 hrs.

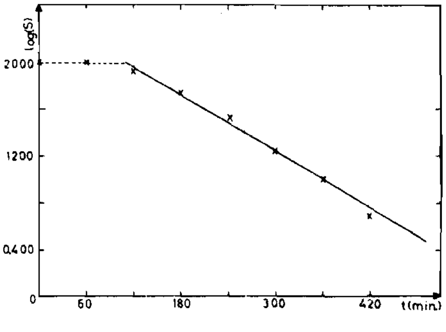


Figure 2. Rate of hydrogenation of methyl sorbate (0.211 mole ℓ^{-1}) with ethylbenzene $Cr(CO)_3$ (0.011 mole ℓ^{-1}) (cyclohexane, 150°, 700 psi H_2) $k_{obs} = 15.3 \times 10^{-5}$ sec^{-1}.

(c) *Effect of Solvents.* The data collected in Table II show that the rate of hydrogenation of diene to monoene is significantly enhanced in acetone or methylene chloride, as reaction solvents, relative to cyclohexane. The latter can serve as a source of hydrogen for the reduction of the diene, an observation similar to that made in the study of iron carbonyl complexes.[1b] Benzene as solvent highly inhibits the hydrogenation reaction. (See also Table VII).

(d) *Catalysts with Two $Cr(CO)_3$ Groups per Molecule of Arene.* Experiments have been carried out

Table III. Catalytic Activity of bis—$Cr(CO)_3$ Complexes in Hydrogenation of Me Sorbate[a]

Catalyst	Concentration mmoles ℓ^{-1}	Reaction time (min)	Approx. Induction time (min)	10^5k_{obs} (sec^{-1})	Reaction Products (weight %) Me Sorbate	Me 3—	x-hexenoate 2—	Me hexanoate
1,2-Diphenylethane—M_2[b]	5.55	120	65	157	0.0	98.5	1.5	0.0
1,2-Diphenylethane—M	11.1	250	180	102	0.8	95.5	3.8	0.0
Diphenylmethane—M_2	5.55	190	105	197	0.0	96.1	3.9	0.0
Diphenylmethane—M	11.1	210	145	145	0.0	96.9	3.1	0.0
Biphenyl—M_2	5.55	150	45	203	0.0	97.6	2.4	0.0
1,4-Diphenylbutadiene—M_2	5.55	60	35	447	0.0	98.1	1.9	0.0

[a] Reaction conditions: Me Sorbate (211 mmole ℓ^{-1}); temp. 125°; pressure, 700 p.s.i. (H_2); solvent, acetone. [b] M = $Cr(CO)_3$.

Table IV. Catalytic Activity of Arene—bis—$Cr(CO)_3$ Complexes in Hydrogenation of Me Sorbate at 65 psi H_2 and 100°

Arene (in bis—$Cr(CO)_3$ Complex)	Reaction[a] time (min)	Approx. Induction time (min)	10^5k_{obs} (sec^{-1})	Reaction Products (weight %) Me Sorbate	Me 3—	x-hexenoate 2—	Me hexanoate
Diphenylmethane	450	270	0.85	90.6	8.9	0.5	0.0
Stilbene	250	150	71.5	0.0	98.3	1.7	0.0
1,4-Diphenylbutadiene	300	190	74.3	1.6	96.6	1.8	0.0

[a] Reaction conditions: Me Sorbate (0.211 mole ℓ^{-1}); catalyst (0.005 mole ℓ^{-1}); solvent, acetone.

to study the efficacy of catalysts containing two $Cr(CO)_3$ moieties per molecule. Two types of complexes were investigated: (i) The two Cr-bearing phenyl rings were in conjugation either directly or through an unsaturated group. (ii) A saturated group, $(CH_2)_n$, (n=1, 2), intervened between the two phenyl rings. The latter type of bis—$Cr(CO)_3$ derivatives at half the molar concentration of the analogous mono—$Cr(CO)_3$ complexes (*i.e.* equal $Cr(CO)_3$ equivalents), appear to have a higher catalytic activity per unit equivalent of $Cr(CO)_3$ groups. (Table III).

The higher activity of the bis—$Cr(CO)_3$ complexes enabled us to perform hydrogenations of methyl sorbate under milder conditions of temperature and pressure, as shown in Table IV.

(e) *Effect of Hydrogen Pressure on Induction Time.* Lowering the hydrogen pressure from 700 psi to 75 psi in the reduction of methyl sorbate catalyzed by 1-phenyl-4-(phenylchromium tricarbonyl) buta-1,3-diene caused some increase in the induction time required for the start of hydrogenation as shown in Fig. 3.

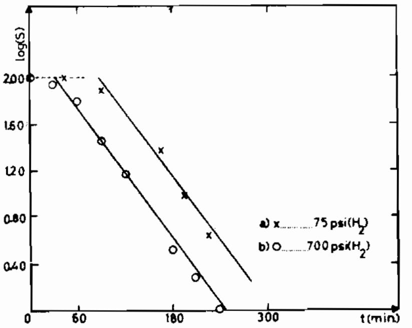


Figure 3. Effect of hydrogen pressure on induction time in hydrogenation of methyl sorbate (211 mmole ℓ^{-1}) with 1,4-diphenylbutadiene $Cr(CO)_3$ (2.7 mmole ℓ^{-1}) in cyclohexane at 160°, at: (a) 75 psi H_2, induction time ~90 min.; k_{obs} = 35.2×10^{-5} sec^{-1} and (b) 700 psi H_2, induction time ~30 min., k_{obs} = 35.2×10^{-5} sec^{-1}.

A more significant effect on induction time is described in the following section (f).

(f) *Effect of Preheating the Reactants on Observed Induction Time.* In order to secure additional information about the long induction times observed with the less active catalysts in the hydrogenation reaction, a solution of substrate and catalyst, in a molar ratio of 19:1, in cyclohexane was heated under nitrogen for the approximate duration of the observed induction time. No reduction was detected at this stage. The subsequent introduction of H_2 into the reaction vessel was followed by much shorter, or no, induction times for the onset of hydrogenation. Results from some of these experiments are collected in Table V.

As a consequence of these, and similar results, we carried out the following set of experiments aimed at obtaining further information about the effect of preheating the reactants:

(i) The substrate, methyl sorbate, and the catalyst, phenanthrenechromium tricarbonyl, in cyclohexane solution, were heated to 120° under N_2 pressure for 5 minutes. This was followed by the introduction of H_2 into the reaction system and monitoring the course of hydrogenation.

(ii) The catalyst, as in (i), in cyclohexane solution was heated to 120° under H_2 pressure for 75 minutes. This was followed by the introduction of substrate, methyl sorbate, into the reaction system and the rate of disappearance of the substrate was measured as in (i).

(iii) The same catalyst, as used in (i) and (ii) in cyclohexane solution was heated to 120° under nitrogen for 5 minutes. Subsequently methyl sorbate and H_2 were introduced in the reaction and the hydrogenation continued as before.

(iv) A control experiment was carried out in which all the reactants, methyl sorbate, catalyst and hydro-

Table V. Effect of Phe-heating Reactants on Hydrogenation Induction Time

Catalyst	Reaction temp. °C	Reaction pressure, psi	Solvent	Preheating period (min) [a]	Induction Time (min)	10^5k_{obs} (sec^{-1})
1,2-Diphenylethane—M [b]	125	700	Acetone	0	180	102
				120	100	109
Stilbene—M	150	700	Cyclohexane	0	45	72.8
				60	0 [c]	77.8
Phenanthrene—M	120	65	Cyclohexane	0	50	10.3
				75	0	11.5

[a] See text for conditions and explanation of procedure. [b] M = $Cr(CO)_3$. [c] Zero induction time here means that analysis of first aliquot immediately following the pre-heating period showed hydrogenated products.

Table VI. Effect of Preheating (75 min) Reactants on Initial Rate of Hydrogenation [a]

Experiment No. [b]	Reactants in preheating stage	Reactants added	Initial Rate [c] mmoles ℓ^{-1} hr^{-1}	Relative Initial rates
(i)	M+S	H_2	166.0	39.5
(ii)	M+H_2	S	7.3	1.7
(iii)	M	S+H_2	4.2	1.0
(iv)	—	M+S+H_2	72.0	17.1

[a] Reaction conditions: S = methyl sorbate (211 mmole ℓ^{-1}); M = phenanthrene $Cr(CO)_3$ (5.5 mmole ℓ^{-1}); solvent, cyclohexane; temp. 120°; pressure, 65 p.s.i. [b] See Text. [c] Rate of disappearance of methyl sorbate.

Table VII. Change in Catalyst Concentration during Hydrogenation Reaction [a]

Reaction Time (hrs)	Catalyst Conc. (weight %) [b]	Reaction Products (weight %)		
		Me Sorbate	Me 3—	x-hexenoates 2—
0.0	6.7	100	0	0
1.0	7.4	100	0	0
2.0	6.2	100	0	0
3.0	6.1	99.0	1.0	0
6.0	6.6	92.6	6.9	0.5

[a] Reaction Conditions: Substrate, Me sorbate (0.211 mole ℓ^{-1}); catalyst, $C_6H_5Cr(CO)_3$ (0.011 mole ℓ^{-1}); solvent, C_6H_6; temp., 175°; hydrogen pressure, 700 p.s.i. [b] Determined by i.r. analysis (see Experimental).

gen were introduced in the reaction system from the start and the hydrogenation was carried out at 120° and 65 psi as in the previous three experiments.

In each case the initial rate (V_0) was obtained from the slopes of tangents to the curves, at the point of intersection with the concentration coordinate. The results, summarized in Table VI, show that preheating the catalyst and substrate, as described in (i), provide conditions for fastest initial rate of hydrogenation.

(g) *Fate of Catalysts during Hydrogenation.* A number of experiments were carried out in order to observe whether the concentration of the arene $Cr(CO)_3$ catalysts remains constant or not during and after the hydrogenation reaction. It appears that in such cases where hydrogenation is slow, no apparent change is observed in the concentration of the catalyst. For example, the concentration of benzene $Cr(CO)_3$ remains the same aftr a reaction time of six hours, as shown in Table VII. In this case less than 8% of substrate was hydrogenated at the end of that period. However, in the reactions where hydrogenation does take place we have observed that the beginning of hydrogenation, i.e. formation of monoene, is usually accompanied by the appearance of a new carbonyl band at 2000 cm^{-1} in the i.r. spectrum of the reaction mixture. It seems likely that these bands are due to the formation of $Cr(CO)_6$ in a side, disproportionation reaction of one of the active intermediates (see Discussion). Product analysis of one of the hydrogenation reaction mixtures, following 100% conversion of methyl sorbate to monoenes with stilbene $Cr(CO)_3$ as catalyst, showed that 76% of the catalyst was recovered unchanged, 18% was recovered in the form of metal-free arene and the rest appeared in the form of a Cr-containing green, insoluble powder. In several instances, small amounts of $Cr(CO)_6$ could be isolated.

When a solution of the catalyst, stilbene $Cr(CO)_3$ in cyclohexane was heated for 5.5 hours at 150°, under 700 psi hydrogen pressure, in the absence of diene substrate, no change was observed in the concentration of the catalyst and no new band appeared at 2000 cm^{-1}.

Discussion

In discussing the results of our studies with iron carbonyl complexes[1b] we proposed that the active intermediate in the hydrogenation of dienes must incorporate the catalyst (M), the substrate (S) and hydrogen (H_2). In other words, we assumed that reaction must take place between species suitably situated on the coordination sphere of the central metal atom, thereby enabling the latter to exercise the observed catalytic ffect. Formation of the active intermediate [SMH$_2$] can be represented schematically to occur by one or both of the following two pathways:

(i)

$$(M)+(H_2) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (MH_2)$$

$$(MH_2)+(S) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (SMH_2)$$

$$(SMH_2 \xrightarrow{k_3} (M)+SH_2$$

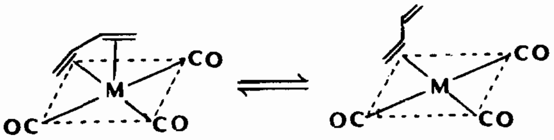
(ii)

$$(M)+(S) \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} (SM)$$

$$(SM)+(H_2) \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} (SMH_2)$$

$$(SMH_2) \xrightarrow[k_3]{} (M)+SH_2$$

We used the concept of coordinative unsaturation by proposing that pentacoordinate saturated d^8 complexes, such as dieneiron tricarbonyls, can achieve coordinative unsaturation if the bidentate four-π-electron diene ligand vacates a coordination site and thus becomes a monodentate two-π-electron ligand. This is shown schematically in the equilibrium I⇄II.



I II

A similar approach is suitable for dealing with the hexacoordinate saturated d^6 complexes arenechromium tricarbonyls. In this case the arene moiety is considered to act as a tridentate six-π-electron ligand which upon attack by suitable reagents can vacate one or two coordination sites around the chromium atom thereby acting as a four- or two-π-electron ligand respectively. We have been led to this hypothesis by analogy to concepts found in a number of pertinent literature reports. Thus, the mechanism proposed for reactions of (AA)M(CO)$_4$ complexes, (M = Cr, Mo, W) with Lewis bases is thought by Angelici,[4-6] Dobson,[7-10] and their coworkers to involve reversible dissociation of one end of the bidentate ligand, followed by attack of the nucleophile on the intermediate pentacoordinate species and other subsequent fast steps leading to th observed products.

Second order kinetics were found[11,12] for displacement of the arene moiety in arene Mo(CO)$_3$ complexes by three molecules of triphenylphosphine. Basolo and coworkers explain[11] this result by proposing that the rate determining step involves formation of the hexacoordinate active intermediate areneMo(CO)$_3$[P(C$_6$H$_5$)$_3$] in which the arene group, having vacated one coordination position for the entering P(C$_6$H$_5$)$_3$ molecule, acts as a bidentate ligand. In subsequent fast steps the remaining two arene-molybdenum bonds are broken to be replaced by new bonds to two additional P(C$_6$H$_5$)$_3$ molecules, leading to the observed product *cis*–(CO)$_3$Mo[P(C$_6$H$_5$)$_3$]$_3$.

Formation of the complexes [arene V(CO)$_4$][V(CO)$_6$] from the reaction between V(CO)$_6$ and arenes such as benzene, toluene, p-xylene and mesitylene has been explained by Calderazzo[13] to proceed through a stepwise displacement of CO groups leading first to (arene)V(CO)$_5$ and then to (arene)V(CO)$_4$ in which the arene moiety acts as a two- and four-π-electron ligand respectively. Either or both of the latter intermediates could be oxidized by excess V(CO)$_6$ to produce the observed products.

Sheline and collaborators[14] have reported the photochemical formation of complexes W(CO)$_5$L (L = benzene, toluene, *p*-xylene, naphthalene, anthracene, phenantrene, pyrene). These complexes, though not isolated, showed infrared patterns in the terminal CO stretching region characteristic of a square pyramidal arrangement of the CO groups. This is interpreted to mean that the arene molecules act as monodentate ligands in these complexes and that bonding is directed from the metal to the ring center and not to a fixed double bond.

In 1966, King reported[15] the first benzyl complex of a transition metal, (C$_6$H$_5$CH$_2$)Mo(C$_5$H$_5$)(CO)$_2$ in which three carbon atoms of the benzyl moiety were presumed to act as an allyl group attached to the metal atom. Subsequently, Cotton and Laprade[16] carried out an X-ray analysis of π–(*p*–CH$_3$C$_6$H$_4$CH$_2$)–π–(C$_5$H$_5$)Mo(CO)$_2$ and confirmed the structure proposed by King.[15]

We shall now proceed to discuss a possible mechanism for the arenechromium tricarbonyl-catalyzed hydrogenation of dienes, using the concept that a benzene molecule is able to employ fewer than its three pairs of π-electrons in forming an arene-metal bond. The main features of the proposed mechanism are shown schematically in Fig. 4. The first essential step, which we believe occurs during the (observed) induction period, involves the reversible dissociation of one bond of the tridentate arene ligand in III, followd by attack of the diene substrate on the pentacoordinate intermediate IV, leading to the hexacoordinate complex V and therefrom to VI. This part of the mechanism is in effect a ligand exchange process in which the diene substrate eventually occupies two of the chromium atom coordination sites vacated by the arene ligand. The nature of substituent R in III would be expected to have a marked effect on

---

[4] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, *87*, 5586 (1965).

[5] J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, *87*, 5590 (1965).

[6] J. R. Graham and R. J Angelici, *Inorg. Chem.*, *6*, 2082 (1967).

[7] G. C. Faber and G. R. Dobson, *Inorg. Chem.*, *7*, 584 (1968).

[8] G. C. Faber, T. D. Walsh, and G. R. Dobson, *J. Am. Chem. Soc.*, *90*, 4178 (1968).

[9] G. R. Dobson, *Inorg. Chem.*, *8*, 90 (1969).

[10] G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, *4*, 87 (1970).

[11] F. Zingales, A. Chresa, and F. Basolo, *J. Am. Chem. Soc.*, *88*, 2707 (1966)

[12] A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc.* (A), 872 (1967).

[13] F. Calderazzo, *Inorg. Chem.*, *3*, 1207 (1964); *4*, 223 (1965).

[14] I. W. Stolz, H. Haas, and R. K. Sheline, *J. Am. Chem. Soc.*, *87*, 716 (1965).

[15] R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, *88*, 709 (1966).

[16] F. A. Cotton and M. D. Laprade, *J. Am. Chem. Soc.*, *90*, 5418 (1968).

the process III→VI, and therefore on the observed induction period. Electronwithdrawing groups, by removing electron density from the π-electron system of the arene, should facilitate the dissociation process III→IV and thus shorten the induction period. Electron-releasing groups should have the opposite effect. These expectations are borne out by the experimentally found induction times as shown in Table I.

The process III→IV would also be expected to proceed better in a medium of suitable nucleophilic solvents, whose molecules could act as coordinating ligands and thus help stabilize the pentacoordinate intermediate IV. The overall effect of such solvent assistance should lead to shorter induction times. Data in Table II show that this is indeed what has been observed: the use of cyclohexane as solvent results in significantly longer induction times than in the case of acetone. Furthermore, a solvent such as benzene, which can enter into a ligand exchange reaction with the catalyst leading to stable products, would be expected to compete with the diene substrate and thus inhibit the reaction IV→VI. The overall effect of such a solvent should be a slow down in the hydrogenation rate and this indeed was the experimental observation (Tables II and VII). In addition, since our experiments (see sections) (e) and (f)), have shown that the presence of hydrogen has a significantly smaller effect on the induction time relative to the presence of the diene substrate we believe that scheme (ii) represents the preferred, though not exclusive, pathway leading to the reactive intermediate (SMH_2).

The next essential step in the hydrogenation reaction involves activation of the hydrogen molecule. We propose that the (diene)(arene)$Cr(CO)_3$ intermediate, VI, *i.e.* (SM) in (ii) interacts with H_2 to form (SMH_2) as either the dihydride complex (diene)(arene)-$CrH_2(CO)_3$, VII (path a), or the complex (diene)-$CrH_2(CO)_3$, VIII, (path b). The transfer of hydrogen to the complexed diene could take place on either of these two intermediates. We suggest that this addition must be a stepwise and not a concerted process. Concommitantly with transfer of the first hydrogen atom to the diene, formation of a π-allyl bond would occur leading to complex IX (path a) or X (path b). This would be followed very rapidly by transfer of the second hydrogen atom, to either end of the π-complexed allyl group, leaving the resulting monoene π-complexed to the metal atom, such as depicted in the hexacoordinate complex XI (path a) or the tetracoordinate complex XII (path b). The diene substrate could displace the monoene in XI leading back to the active intermediate VI (path a) or it could attack XII to form XIII (path b). The latter would react with hydrogen to release the monoene and reform the active intermediate VIII. Whilst the evidence available so far does not enable us to choose conclusively between path (a) and (b), we do venture to express preference for the former. At any rate, our results compel us to discard the S_N1 mechanism proposed by Frankel, Selke and Glass,[17] which envisages the rate limiting dissociation of the catalyst (arene)$Cr(CO)_3$ to form as active intermediate the tricoordinated species [$Cr(CO)_3$] followed by the fast addition of H_2 thereby leading to the reactive intermediate [$H_2Cr(CO)_3$]. The latter is then held responsible for the *concerted* 1,4-addition of two hydrogen atoms to the substrate diene. The above authors[17] proposed their mechanism by analogy to that suggested by Wilkinson for the Rh^I-catalyzed hydrogenation of olefins,[18,19] but they seem to have ignored the fact that Wilkinson himself had stated that his data could

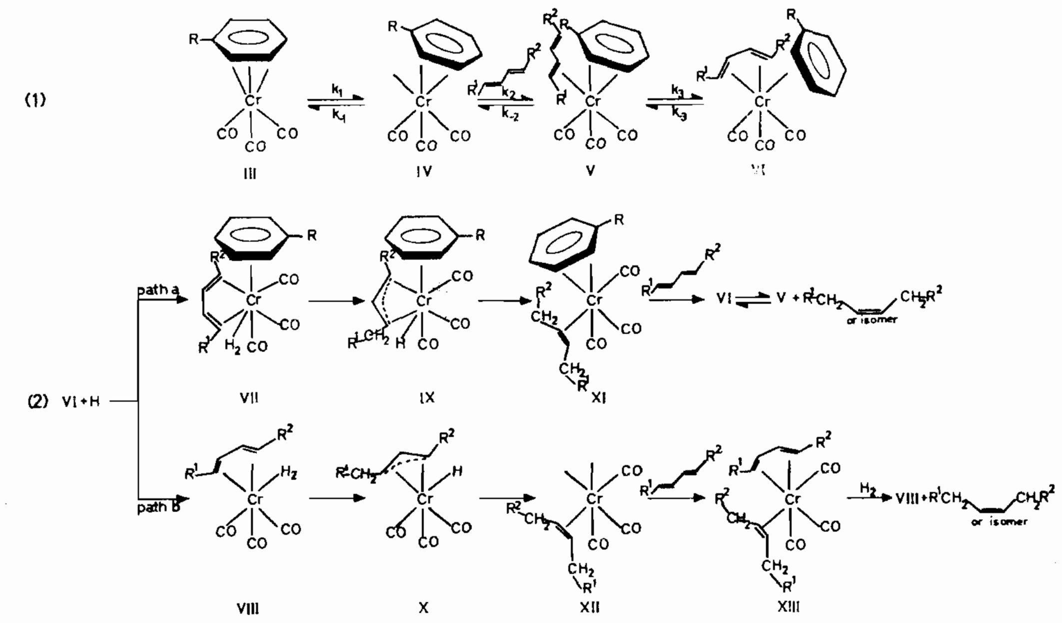


Figure 4. Proposed Mechanistic Scheme for Arene $Cr(CO)_3$-Catalyzed Hydrogenation of Dienes.

---

(17) E. N. Frankel, E. Selke, and C. A. Glass, *J. Am. Chem. Soc.*, *90*, 2446 (1968).

(18) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, (*A*), 1711 (1966).

(19) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1574 (1967) and leading references thereof.

not distinguish between concerted and stepwise addition of H_2 to olefins. Indeed, Hussey and Takeuchi have since shown that whilst transfer of the two hydrogens from the metal atom to the olefin substrate can be regarded to occur simultaneously in a practical sense, the reaction is nevertheless a stepwise process.[20] Moreover, since we have shown that the reaction occurs in two distinctive stages, the proposed[17] dissociation should take place during the induction period. If so, only the length of the induction time should have been affected by the nature of the substituent on the arene moiety, and the subsequent rate of hydrognation should have been the same in all cases, irrespective of the arene substituent in the original catalyst. That this is not so is shown by our data in Table I-IV, where the values of both the induction times and k_{obs} (measured as shown in Fig. 3) are seen to change greatly with variation of the arene moiety. Our mecharnstic scheme, (Fig. 4) especially path (a), is not inconsistent with the experimental evidence available so far.

We further wish to emphasize[21] that for the sake of clarity, formation of a product such as methyl 3-hexenoate in the metal complex catalyzed reduction of methyl 2,4-hexadienoate should be referred to as *pseudo-* 1,4-addition and thus avoid the implication of a concerted mechaisnm. It must be recalled that 1,2-addition products, *e.g.* methyl 2-hexenoate, are also formed in these reactions. The stepwise addition mechanism and the proposed π-allyl intermediates, IX or X, could account for the production of isomeric monoenes. We are unable at present to explain convincingly as to why formation of one isomer is highly favoured over the other. Recent observations in our laboratory have shown that steric factors may be involved. In the hydrogenation of norbornadiene, catalyzed by arenechromium tricarbonyls, the 1,2-addition product, norbornene, was formed in relatively higher yields (18%) at the expense of the pseudo-1,4-addition product, nortricyclene (82%). The two hydrogen atoms, in the 1,2-addition product, were shown conclusively to have been added *cis-* and endo-.[21]

Finally, we wish to draw attention to the kinetic measurement limitations inherent in the experimental techniques used for the hydrogenations described in this report. W are currently engaged in the construction of specially designed hydrogenation equipment which hopefully will enable us to expand our studies on the homogeneous catalytic properties of arenechromium tricarbonyls and other similar complexes. The special activity of the phenanthrene complex will form the subject of a separate communication.

Experimental Section

Apparatus. Infrared spectra were taken on a Perkin-Elmer grating « Infracord 237 ». Instrument calibration for quantitative measurements allowed an accuracy of ±5%. G.l.c. analyses wre carried out with a Packard model 81 chromatograph with flame ionization detector, and disc integrator; calibration with standard samples indicated an accuracy of ±1%. High pressure hydrogenation experiments were performed in an ABP-300 Mc « Magne Drive » 300 ml autoclave, equipped with stirrer, inlet and outlet valves for gases, sampling tube for removing aliquot samples under pressure during the course of the reaction, a cooling system and a glass insert. Heating to required reaction temperatures (160°) took about 20 min. Reaction temperatures were constant within ±1°. The lower pressure hydrogenations (65 psi) were carried out in a Parr Hydrogenator fitted with a 3-way valve to allow for removing aliquot samples and introduction of reagents.

Materials. The syntheses of the arene $Cr(CO)_3$ complexes were carired out by refluxing the arene and $Cr(CO)_6$ in di-*n*-butyl ether under nitrogen and purification by chromatography on basic alumina. Hydrogen (Air Products, U.S.A.) and nitrogen (Oxygen Stored Ltd., Israel) were used without further treatment.

Samples of methyl 2-, 3-, 4- and 5-hexenoate were received as a gift from Northern Regional Research Laboratories, U.S.D.A., Peoria, Ill. Distilled methyl sorbate was usually freed from peroxides prior to a reaction by passage through a basic aluminium oxide column.

All other substrates as well as all solvents were of reagent-grade quality and were used without further treatment unless otherwise specified.

All experiments were routinely performed under nitrogen or hydrogen.

Procedures. Two typical hydrogenation experiments will be described:

(i) The « Magne Drive » autoclave was charged with the diene substrate (19 mmole), arene $Cr(CO)_3$ complex (1 mmole) and solvent (generally cyclohexane) (90 ml). The system was flushed with nitrogen (3 times) and then with hydrogen (3 times) under stirring. Hydrogen was then introduced until a pressure of 500 psi was reached when heating was begun. Within 20 min the temperature rose to 150° and the pressure built to 700 psi. Samples were collected at 10-30 min intervals as required. Each sample (1 ml) was evaporated to remove solvent, diluted with CS_2 and subjected to g.l.c. on a glass column (6'×1/4") filled with 15% diethylene glycol succinate (DEGS) on Chromosorb W (acid washed, 60-80 mesh) at 90°. The separated reaction components were identified by comparison with known standards and the relative amounts (weight %) determined from the disc integrator curves. The amounts of catalyst arene $Cr(CO)_3$ complex in the reaction samples were determined by quantitative i.r. spectroscopy as follows: a 1 ml sample was evaporated to dryness and the weighed residue dissolved in CCl_4 (10 ml). The i.r. spectrum of this solution was measured (*vs.* air as reference) in the CO region (1900-2100 cm^{-1}). The arene $Cr(CO)_3$ complex concentration was calculated by comparing the absorbance of the sharpest peak to a calibrated curve obtained with samples of known concentration of the pure complex. The results obtained in weight

---

(20) A. S Hussey and Y. Takeuchi, *J. Am. Chem. Soc.*, *91*, 672 (1969).

(21) M. Cais and D. Fraenkel, *Israel J. Chem.*, in press (1970).

% were then normalized to mole % for use in the kinetic treatment.

(ii) The Parr hydrogenator was charged with the diene substrate, arene $Cr(CO)_3$ catalyst and solvent in amounts as described in (i). The system was evacuated to 20 mm Hg and then flushed with hydrogen. This operation was repeated three times. Hydrogen was then introduced until a pressure of 18 psi was reached when heating was begun. Within 30-40 minutes the temperature rose to 120° and the pressure built to 65 psi. The procedure was then as described in (i).

Acnowledgment. We thank the U.S. Department of Agriculture, Southern Regional Research Laboratories, New Orleans, La., for partial support of this work under a P.L. 480 grant, Project UR-A10-(40)-34, and the Northern Regional Research Laboratories, Peoria, Ill., for a gift of authentic methyl 2-, 3-, 4- and 5-hexenoates.