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The rate and mechanism of oxidative addition of H_2 to the $^{\bullet}Cr(CO)_3C_5Me_5$ radical—generation of a model for reaction of H_2 with the $^{\bullet}Co(CO)_4$ radical[☆]

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

Abstract

The rate of reaction of hydrogen with the 17 e^- metal centered radical $^{\bullet}Cr(CO)_3C_5Me_5$ obeys the third-order rate law $d[P]/dt = k_{obs}[^{\bullet}Cr]^2[H_2]$ in toluene solution. In the temperature range 20–60°C, $k_{obs} = 330 \pm 30$ M^{-2} s^{-1}, $\Delta H^{\neq} = 0 \pm 1$ kcal mol^{-1}, $\Delta S^{\neq} = -47 \pm 3$ cal mol^{-1} deg^{-1}. The rate of oxidative addition is not inhibited by added pressure of CO. The rate of binding of D_2 is slower than that of H_2: $k(H_2)/k(D_2) = 1.18$. These results are combined with earlier work to generate a complete reaction profile for hydrogenation of the metal–metal bonded dimer $[Cr(CO)_3C_5Me_5]_2 + H_2 \rightarrow 2H–Cr(CO)_3C_5Me_5$. A similar reaction profile for $Co_2(CO)_8 + H_2 \rightarrow 2H–Co(CO)_4$ under high pressures of CO is constructed based on literature data and estimated activation parameters for reaction of the $^{\bullet}Co(CO)_4$ radical with hydrogen. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chromium; Cobalt; Free radicals; Hydrogen; Oxidative addition

1. Introduction

The pathway to formation of metal dihydrides is now accepted to proceed through initial formation of molecular hydrogen complexes (which may be of a transient nature) as shown generally in Eq. (1).

$$L_nM–S + H_2 \rightleftharpoons S + L_nM(H_2) \rightleftharpoons L_nM(H)_2 \qquad (1)$$

This process involves generation of a vacant site at the metal center by dissociation of a weakly held ligand, agostic bond, or solvent molecule (S) to form a molecular hydrogen complex which undergoes subsequent oxidative addition to form a metal dihydride. The detailed kinetic and thermodynamic factors that govern Eq. (1) vary greatly as a function of the metal and its substituents. The synthesis and structural determination of $W(PCy_3)_2(CO)_3(H_2)$ by Kubas [1] presented the first clear example of the role of molecular hydrogen complexes in oxidative addition reactions of formal 16 e^- complexes. A complete reaction profile for Eq. (2) was later determined including the rate of binding and dissociation of molecular hydrogen compared to its rate of oxidative addition.

$$\begin{aligned} W(PCy_3)_2(CO)_3(py) &\rightleftharpoons W(PCy_3)_2(CO)_3 + H_2 \\ &\rightleftharpoons W(PCy_3)_2(CO)_3(H_2) \\ &\rightleftharpoons W(PCy_3)_2(CO)_3(H)_2 \end{aligned} \qquad (2)$$

[☆] This article is dedicated to Professor László Markó. Two of the articles authors (G.K. and C.D.H.) were fortunate enough to work in the Szerves Kémia Tanszék, Veszprémi Vegyipari Egyetem, while he led the team efforts in mechanistic organometallic research there. The experimental skill, mechanistic insight, and spirit of the entire group remain a guide to us and all who have worked there.

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The most interesting result from that study was that the rate of binding and dissociation of molecular hydrogen was much faster than its rate of oxidative addition [2].

This type of 'even' addition of molecular hydrogen to a 16 e^- complex is probably also involved in the mononuclear reductive elimination of alkanes [3] shown in Eq. (3).

$$R{-}Co(CO)_4 + H_2 \rightleftharpoons R{-}Co(CO)_3(H_2) + CO \rightarrow R{-}H + H{-}Co(CO)_4 \quad (3)$$

The net rate of reductive elimination in Eq. (3) was shown to be much slower than the rate of substitution by ^{13}CO or phosphines, or even reductive elimination by reaction with $HCo(CO)_4$. The significance of that result was first pointed out [4] to one of the authors (C.D.H.) by Professor László Markó.

In contrast to the fairly well understood activation of hydrogen by familiar 16/18 e^- 'even' processes are reactions which may follow 17/19 e^- 'odd' pathways. A mass of indirect but convincing evidence supports that ligand substitution [5] occurs through associative 19 e^- intermediates which contain bond strengths roughly half those of their 18 e^- counterparts. There are few structures reported which clearly prove the role of these species, and their role in oxidative addition reactions is still evolving.

The authors are not aware of any stable 19 e^- molecular hydrogen complexes. In spite of their discovery, 18 e^- molecular hydrogen complexes remain rare and difficult species to isolate and characterize. Taking the Kubas complex as an example, binding of molecular hydrogen is a 'close call' and it readily loses hydrogen. The favorable enthalpy of binding (-10 kcal mol^{-1}) of molecular hydrogen is nearly offset by the unfavorable entropy of binding [6] (about -25 cal mol^{-1} deg^{-1}) leading to a net free energy of formation at 300 K of -2.5 kcal mol^{-1}. Cutting the enthalpy of binding in half, as might be expected for a 19 versus 18 e^- complex, to -5 kcal mol^{-1} would lead to a positive free energy of formation at this temperature of $+2.5$ kcal mol^{-1}.

The role of such 19 e^- molecular hydrogen intermediates may be important in generation of $HCo(CO)_4$ for oxo catalysts. The thermodynamic parameters for Eq. (4) reported by Ungváry and Markó [7] are in agreement with more recent determinations [8], but the exact mechanism of this reaction remains a matter of debate.

$$Co_2(CO)_8 + H_2 \rightarrow 2H{-}Co(CO)_4 \quad (4)$$

$\Delta H° = 3.2$ kcal mol^{-1}, $\Delta S° = 4.4$ kcal mol^{-1} deg^{-1}.

The debate [9] over the mechanism of Eq. (4) and its reverse usually invoke either loss of CO, as shown in Eq. (5), or Co–Co bond cleavage as shown in Eq. (6), as the first step towards activation of hydrogen.

$$Co_2(CO)_8 \rightleftharpoons CO + Co_2(CO)_7 \quad (5)$$

$$Co_2(CO)_8 \rightleftharpoons 2{}^{\bullet}Co(CO)_4 \quad (6)$$

Starting from those two relatively simple looking steps, very complex mechanisms can be built. Under high pressures of CO, the rate of the reverse step in Eq. (5) is increased and so pathways based on generation of $Co_2(CO)_7$, $HCo(CO)_3$, and other coordinatively unsaturated species can be expected slow down or stop as [CO] increases. However, radical processes such as that shown in Eq. (6) will continue at essentially the same rate and so increase in significance by the process of elimination.

In the same way that the plausibility of molecular hydrogen complexes was known long before the isolation of the Kubas complex, the role of ${}^{\bullet}Co(CO)_4$ in hydroformylation has a long history [9]. It was not until 1994, however, that Klingler and Rathke [10] reported the first reliable estimates for the equilibrium constants and thermodynamic parameters for Eq. (6). Using high pressure NMR and magnetic susceptibility measurements in supercritical CO_2, they have determined $\Delta H° = 19 \pm 2$ kcal mol^{-1} and $\Delta S° = -29 \pm 4$ cal mol^{-1} deg^{-1}.

The equilibrium constant for the generation of ${}^{\bullet}Co(CO)_4$ is small. The fact that equilibrium concentrations of ${}^{\bullet}Co(CO)_4$ are low has two consequences. First, since its concentration can not be directly monitored, conclusions regarding its role are often tentative. Second, where branch points occur in a mechanism the relative importance of pathways that are first- and second-order in radical will depend critically on absolute radical concentrations.

Can the reactivity of the ${}^{\bullet}Co(CO)_4$ radical be modeled by comparison to other transition metal radicals? The initial answer to that question by most chemists (and the authors as well) would be: "No—the character of any other transition metal radical would be expected to differ greatly from that of ${}^{\bullet}Co(CO)_4$ and so would the rate of reaction with hydrogen". Nevertheless, this article will test that hypothesis. The choice of using the ${}^{\bullet}Co(CO)_4$ radical for comparison is made due to its importance in hydroformylation and the history of contributions of the Veszprém group [1] in this area.

The 17 e^- chromium centered radical shown in Eq. (7) provides a good system for the study of low valent metal carbonyl radical reactions.

$$[Cr(CO)_3C_5Me_5]_2 \rightleftharpoons 2{}^{\bullet}Cr(CO)_3C_5Me_5 \quad (7)$$

$\Delta H° = +15$ kcal mol^{-1}, $\Delta S° = +45$ cal mol^{-1} deg^{-1}.

The metal–metal bonded dimer dissociates quantitatively in dilute solution at room temperature [11]. The absolute concentration of radical is readily monitored by FTIR and the equilibrium is rapidly established [12]. These factors allow mechanistic studies not readily accessible to the cobalt analog.

The heats of hydrogenation of the complexes $[Cp(CO)_3M]_2$ (M = Cr, Mo, W), as well as direct calorimetric measurement of the enthalpy of hydrogenation of the radical shown in Eq. (8), have been reported [13].

$$2^{\bullet}Cr(CO)_3C_5Me_5 + H_2 \rightarrow 2H{-}Cr(CO)_3C_5Me_5 \quad (8)$$

$\Delta H^{\circ} = -20$ kcal mol^{-1}

In this paper, a kinetic and mechanistic study of this reaction is reported. When combined with earlier work, it presents a complete reaction profile for the hydrogenation of the chromium dimer. The data reported here is combined with other literature data on reaction of metal radicals with hydrogen to generate a 'composite' sketch of the expected kinetic parameters for reaction of other 17/19 e$^-$ species with molecular hydrogen. This composite picture is then combined with the data of Ungváry and Markó [7], as well as Klingler and Rathke [10], to construct a reaction profile for $Co_2(CO)_8$ under high pressure of CO.

2. Experimental

2.1. General procedures

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or in a Vacuum Atmospheres glove box. Toluene was distilled from sodium/benzophenone under argon into flame dried glassware. Carbon monoxide (99.99%), hydrogen (99.9999%), and deuterium (99.5% isotopic purity) from Matheson Gas or Liquid Carbonic were used as obtained. $[C_5Me_5(CO)_3Cr]_2$ was prepared and purified by literature procedures [14]. Kinetic studies were performed on a Perkin–Elmer Spectrum 2000 FTIR equipped with an i-series microscope described in detail elsewhere [15]. A typical kinetic procedure is described below.

2.2. Kinetics of oxidative addition of H_2 to $^{\bullet}Cr(CO)_3C_5Me_5$

Under 1.5 atm CO, 25 ml freshly distilled toluene was added to $[Cr(CO)_3C_5Me_5]_2$ (100 mg, 0.185 mmol) and allowed to stir for 30 min until all of the black dimer dissolved to give a solution of the radical. Toluene (20 ml) was added to a thermostatted glass reactor under a controlled atmosphere of H_2/CO and allowed to equilibrate to the given temperature with saturation of the gas. The pressures of the gases and gas mixtures were determined from a pressure transducer obtained from Omega Instruments. The reaction was initiated by injection of 5 ml of the radical solution in toluene via a stainless steel cannula. Following initiation of the reaction, the reaction was monitored about every 15 s by removing a fresh aliquot from the reactor system for FTIR analysis. Rate data is the average of two to five measurements at each temperature and pressure. Conversion of H_2 gas pressure to values based on the concentration of H_2 in solution is readily accomplished using published solubilities of solution of hydrogen in toluene [16]. **CAUTION**: care must be taken when venting gases (carbon monoxide, hydrogen) to the hood to avoid build-up of explosive mixtures.

3. Results

3.1. Reaction of H_2 and D_2 with $^{\bullet}Cr(CO)_3C_5Me_5$

Representative spectroscopic data for the rate of reaction of H_2 and D_2 with toluene solutions of $^{\bullet}Cr(CO)_3C_5Me_5$ (Eq. (8)) are shown in Fig. 1. Absorbances of $^{\bullet}Cr(CO)_3C_5Me_5$ at 1994 and 1886 cm^{-1} convert to the $HCr(CO)_3C_5Me_5$ product with absorbances at 1995 and 1929 cm^{-1}. Owing to the close proximity of the A bands of both starting radical and hydride, there is little change in this region of the spectrum, however, the E bands are sufficiently resolved to allow convenient monitoring of the reaction. There is a clear isosbestic point at ca. 1900 cm^{-1}, indicative of a clean reaction. No side products or intermediates are observed during the course of reaction.

The rate of reaction for Eq. (8) was found to obey overall third-order kinetics (Eq. (9)).

$$d[P]/dt = k_{obs}[^{\bullet}Cr(CO)_3C_5Me_5]^2[H_2] \quad (9)$$

Under pseudo second-order conditions of constant $[H_2]$, plots of $1/[^{\bullet}Cr(CO)_3C_5Me_5]$ versus time were linear through four half-lives as shown in Fig. 2. The rate of reaction as a function of H_2 pressure was linear in the range of 1–3 atm. The rate of reaction was also shown to be the same when done under pure hydrogen or hydrogen with added carbon monoxide with partial pressures of CO ranging from 0 to 5 atm.

The rate constant for reaction with hydrogen at 20°C: $k_{obs}(H_2) = 330$ M^{-2} s^{-1} is 1.18 times faster than that determined for deuterium at the same temperature: $k_{obs}(D_2) = 280$ M^{-2} s^{-1}. The rate of reaction with hydrogen was studied at both 40 and 60°C. Identical values of the rate constant were found at those temperatures. Experimental error is on the order of 5% for this well behaved system. Derived activation parameters calculated for Eq. (8) were $\Delta H^{\neq} = 0 \pm 1$ kcal mol^{-1} and $\Delta S^{\neq} = -47 \pm 3$ cal mol^{-1} deg^{-1} for H_2.

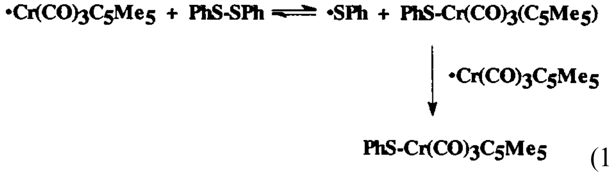
4. Discussion

The goal of this work was to determine the mechanism of hydrogenation of $^{\bullet}Cr(CO)_3C_5Me_5$. The enthalpy of hydrogenation of this radical was reported by us earlier [13] and led to a value for the $H{-}Cr(CO)_3C_5Me_5$ bond strength of 62 kcal mol^{-1}. The weak nature of this bond immediately rules out a mechanism involving first-order H atom transfer as shown in Eq. (10).

$$^{\bullet}Cr(CO)_3C_5Me_5 + H_2 \rightleftharpoons H{-}Cr(CO)_3C_5Me_5 + {}^{\bullet}H \quad (10)$$

The minimum enthalpy of activation for Eq. (10) would correspond to the difference between the H–H (104 kcal mol^{-1}) [17] and Cr–H (62 kcal mol^{-1}) bond strengths. The difference is too large to allow single radical attack.

The fact that first-order reactivity as shown in Eq. (10) does not occur with hydrogen is due entirely to thermodynamic factors. There is no evidence that steric crowding or factors other than bond strength considerations limit first-order reactivity of the chromium radical. The rate of metal–metal bonded dimer formation is rapid [12]. Attack on the sulfur–sulfur bond of phenyl disulfide is first-order (in $^{\bullet}Cr$) with a low overbarrier to the thermodynamic estimate [18] as shown in Eq. (11).



$$\begin{array}{l} {}^{\bullet}Cr(CO)_3C_5Me_5 + PhS{-}SPh \rightleftharpoons {}^{\bullet}SPh + PhS{-}Cr(CO)_3(C_5Me_5) \\ \qquad\qquad\qquad\qquad\qquad \downarrow {}^{\bullet}Cr(CO)_3C_5Me_5 \\ \qquad\qquad\qquad\qquad\qquad PhS{-}Cr(CO)_3C_5Me_5 \end{array} \quad (11)$$

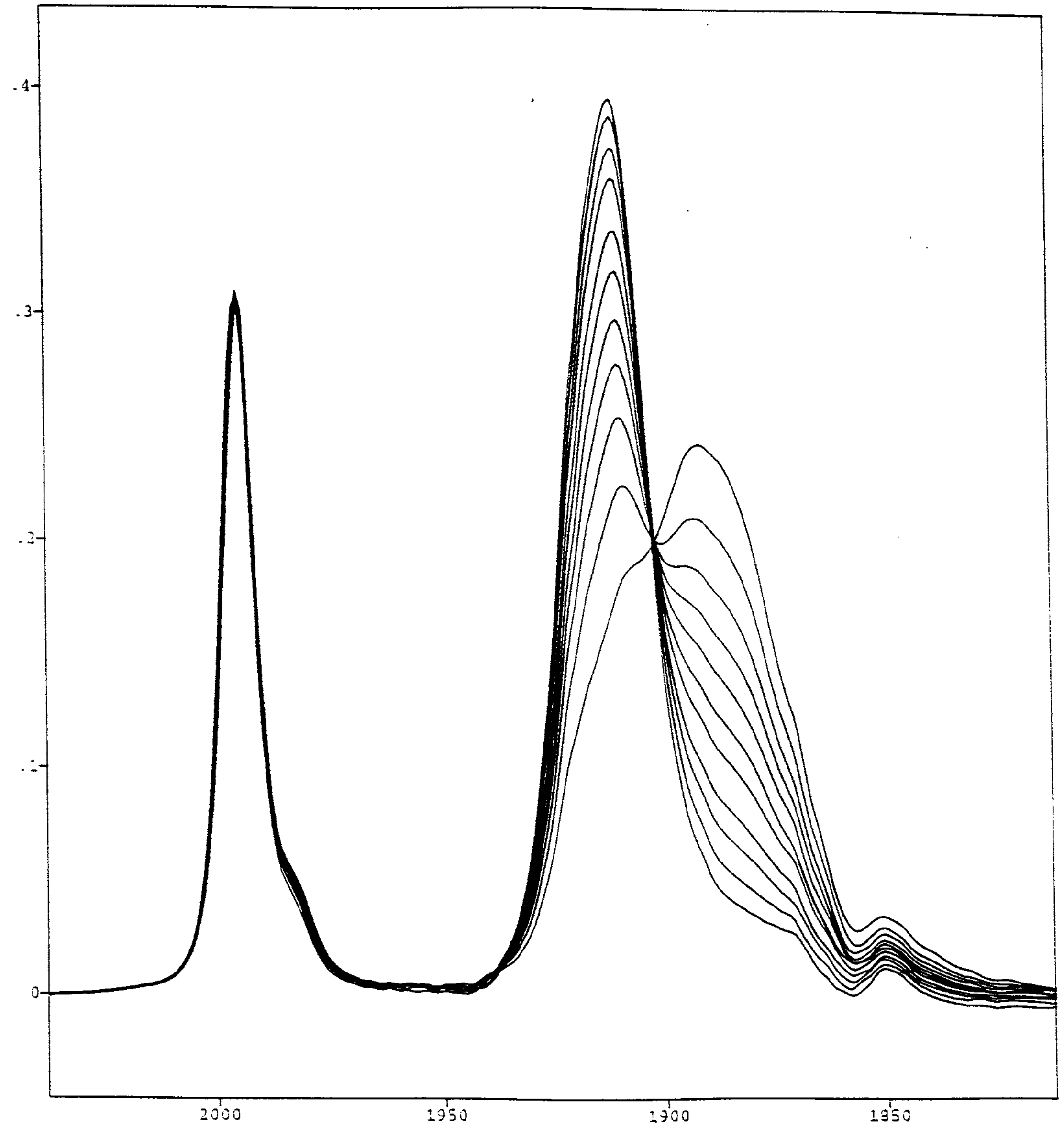


Fig. 1. FTIR (absorbance vs. wavenumber) plots for kinetic study of D_2 (1.6 atm) and $^{\bullet}Cr(CO)_3C_5Me_5$ (3 mM), in toluene solution at 20°C. The bands at 1994 and 1896 cm^{-1} are due to the radical decrease while the bands at 1995 and 1929 cm^{-1} are due to the $DCr(CO)_3C_5Me_5$ increase.

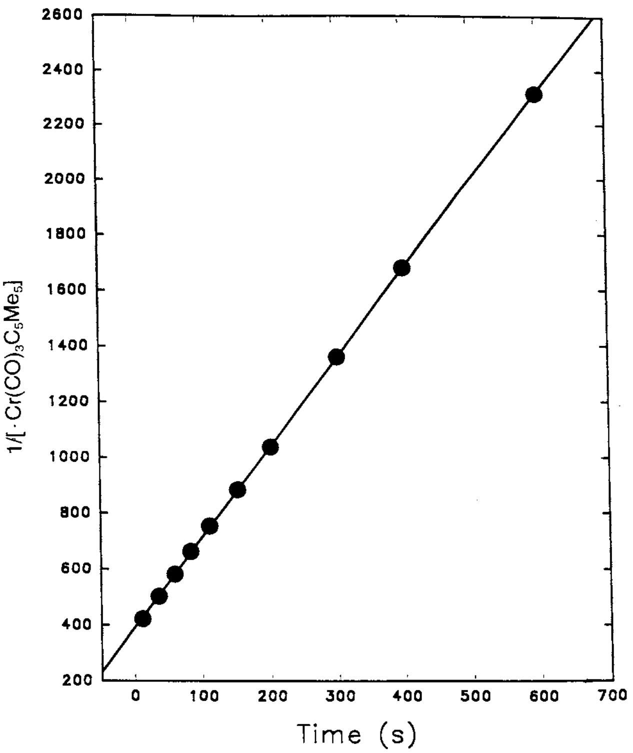
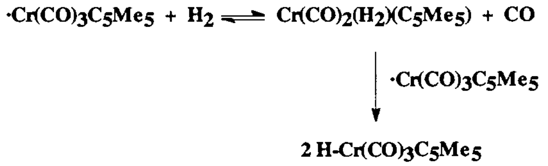


Fig. 2. Second-order plot of 1/[$^{\bullet}Cr(CO)_3C_5Me_5$] versus time for spectroscopic data in Fig. 1.

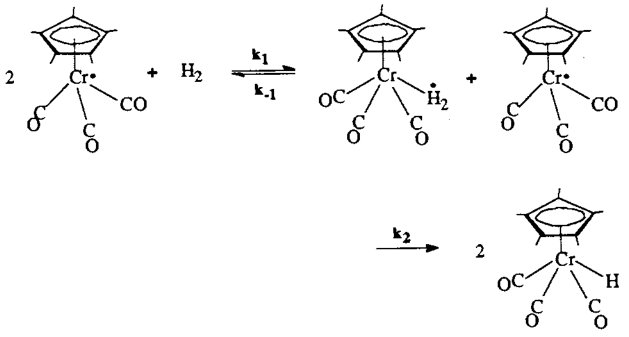
'Weak' 17 e^- radicals such as $^{\bullet}Cr(CO)_3C_5Me_5$ can undergo rapid associative ligand substitution, radical recombination, or attack of weak bonds such as PhS–SPh. They cannot directly attack a strong bond such as H–H by the first-order process shown in Eq. (10). However, ligand substitution processes such as that shown in Eq. (12) can lead to first-order kinetics in metal radical provided the first step is rate determining.



$$\cdot Cr(CO)_3C_5Me_5 + H_2 \rightleftharpoons Cr(CO)_2(H_2)(C_5Me_5) + CO \xrightarrow{\cdot Cr(CO)_3C_5Me_5} 2\,H\text{-}Cr(CO)_3C_5Me_5 \quad (12)$$

The first step involves the associative substitution and is expected to be endothermic owing to the fact that molecular hydrogen is a much weaker ligand than carbon monoxide. Radical attack on a formal 17 e^- molecular hydrogen complex leads to products. No evidence for the mechanism in Eq. (12) was found for the chromium radical. Through four half-lives the reaction remained pure second-order in metal radical concentration. Reactions done in the absence of CO occurred at the same rate as those with 5 atm added CO pressure. That is not the case for cobalt, where it is well known that the rate of hydrogenation depends strongly on CO pressure. In cobalt chemistry the [$^{\bullet}Co(CO)_3(H_2)$] radical or its dihydride tautomer may be the most important intermediate at low pressures of CO. No sign of this type of behavior was found for reaction of the chromium radical and hydrogen.

A mechanism consistent with the rate data, and also with earlier studies of thiols [19], methyl disulfide [18], or hydrogen sulfide under pressure of CO [20] is shown in Eq. (13).



(13)

This involves formation of a 19 e^- adduct which is then attacked by a second mole of radical in the rate determining step. Applying steady state in the 19 e^- $(H_2)Cr(CO)_3C_5Me_5$ intermediate leads to the predicted rate law (Eq. (14)).

$$\begin{aligned} d[P]/dt &= 1/2\, d[^{\bullet}Cr]/dt = k_1k_2[^{\bullet}Cr]^2[H_2]/k_{-1} + k_2[^{\bullet}Cr] \\ &= [k_1k_2/k_{-1}][^{\bullet}Cr]^2[H_2] \quad \text{when } k_{-1} \gg k_2[^{\bullet}Cr] \end{aligned} \quad (14)$$

Third-order rate constants [18–20] for the reaction of the chromium radical with other substrates span ca. two orders of magnitude [k_{obs} in M^{-2} s^{-1}]: MeSSMe(400) > H_2(330) > D_2(280) > H_2S(75) > PhSH-(25) > BuSH(5). To date, only MeSSMe has been found to react faster with the chromium radical than H_2. In all cases studied so far, the enthalpies of activation for the third-order reactions of the chromium radical are near zero, and the differing rates are due primarily to different entropies of activation. There is no apparent relation to the strength of the bond broken and rate of reaction (the one exception is PhSSPh, which due to its very weak sulfur–sulfur bond undergoes direct radical attack as mentioned above). It should be pointed out that the ca. two orders of magnitude difference in third-order rate constants observed so far corresponds to differences in free energies of activation energies < 3 kcal mol^{-1} at 300 K.

The complete reaction profile for hydrogenation of the chromium dimer is shown in Fig. 3. The data of Geiger [12] are in keeping with a free energy of activation for radical combination on the order of 5 kcal mol^{-1}. All other data in Fig. 3 are the result of direct measurement. To the author's knowledge, this is the first complete experimentally determined reaction profile for hydrogenation of any metal–metal bonded complex.

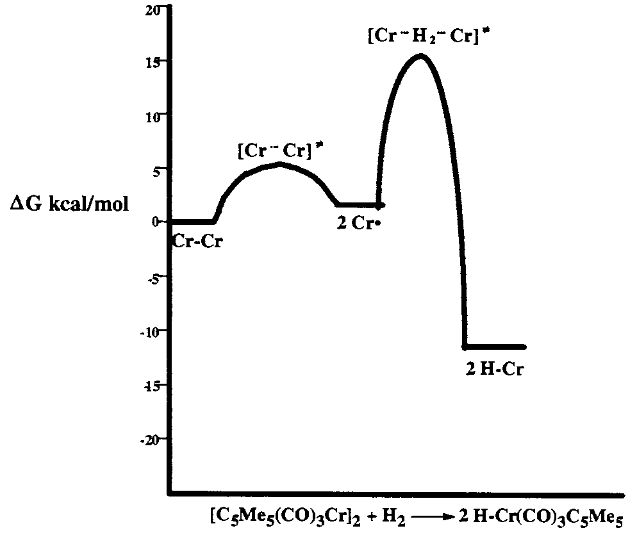


Fig. 3. Reaction profile ΔG (kcal mol^{-1} in toluene solution at 300 K) for: $[Cr(CO)_3C_5Me_5]_2 + H_2 \rightarrow 2H{-}Cr(CO)_3C_5Me_5$ (see text for full discussion). The overall thermochemistry of the reaction [13] [$\Delta H° = +5$ kcal mol^{-1}, $\Delta S° = +20$ cal mol^{-1} deg^{-1}, $\Delta G° = -11$ kcal mol^{-1}] is combined with data for the thermochemical and activation energy data or estimates of the following separate steps: (i) dissociation to radicals [11]: [$\Delta H° = +15$ kcal mol^{-1}, $\Delta S° = +45$ cal mol^{-1} deg^{-1}, $\Delta G° = 1.5$ kcal mol^{-1}, $\Delta G^{\neq} = 5$ kcal mol^{-1} for radical recombination]; (ii) reaction of 2 mol of radical with hydrogen: [$\Delta H° = -20$ kcal mol^{-1}, $\Delta S° = -25$ cal mol^{-1} deg^{-1}, $\Delta G° = -12.5$ kcal mol^{-1}, $\Delta H^{\neq} = 0$ kcal mol^{-1}, $\Delta S^{\neq} = -47$ cal mol^{-1} deg^{-1}, $\Delta G^{\neq} = +14$ kcal mol^{-1}].

Detailed mechanistic studies of the oxidative addition of hydrogen to two other transition metal radicals have been reported. The first is the aqueous cobalt(II) cyanide complex shown in Eq. (15).

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2HCo(CN)_5^{3-} \quad (15)$$

The work of the Halpern group [21] on this reaction yielded a third-order rate law and highlighted the plausibility of third-order reactivity of metal complexes. More recent work by Wayland and Sherry [22] showed that the Rh(II) metalloporphyrin radical in Eq. (16) also reacted by a third-order mechanism with hydrogen.

$$2^{\bullet}Rh(TMP) + H_2 \rightleftharpoons 2Rh(TMP)(H) \quad (16)$$

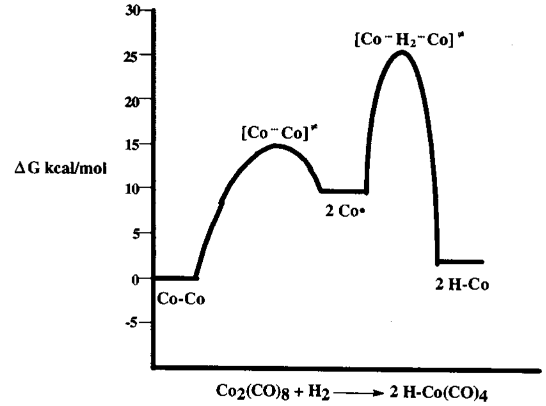


Fig. 4. Reaction profile ΔG (kcal mol^{-1} estimated as described in text at 300 K) for: $[Co_2(CO)_8]_2 + H_2 \rightarrow 2H{-}Co(CO)_4$. The overall thermochemistry [7]of the reaction [$\Delta H° = +3.4$ kcal mol^{-1}, $\Delta S° = +4.4$ cal mol^{-1} deg^{-1}, $\Delta G° = +2.0$ kcal mol^{-1}] is combined with data for the thermochemical and activation energy data or estimates of the following separate steps: (i) dissociation to radicals [10]: [$\Delta H° = +19$ kcal mol^{-1}, $\Delta S° = +29$ cal mol^{-1} deg^{-1}, $\Delta G° = +10$ kcal mol^{-1}, $\Delta G^{\neq} = 15$ kcal mol^{-1} for radical recombination]; (ii) reaction of 2 mol of radical with hydrogen activation parameters used on 'composite' picture from Table 1 as described in the text: [$\Delta H^{\neq} = 2$ kcal mol^{-1}, $\Delta S^{\neq} = -47$ cal mol^{-1} deg^{-1}, $\Delta G^{\neq} = +16$ kcal mol^{-1}].

The data in Table 1 summarize rate and activation parameters for the three systems. The variation is surprisingly small considering the large differences between the complexes, with a composite enthalpy of activation of 2 ± 3 kcal mol^{-1}, entropy of activation of -47 ± 8 cal mol^{-1} deg^{-1}, and a third-order rate constant of 50 M^{-2} s^{-1} with an error of about one order of magnitude. This 'average' behavior for metal radicals will be used to model $^{\bullet}Co(CO)_4$.

The pieces needed to construct a hypothetical reaction profile for hydrogenation of the cobalt dimer are in place in the literature if the composite sketch of $^{\bullet}Co(CO)_4$ discussed above is used. The combined picture is shown in Fig. 4. The data of Klingler and Rathke are used with an overbarrier of about 5 kcal mol^{-1} for radical combination to yield the position of 2 mol of $^{\bullet}Co(CO)_4$. From that point, composite activation parameters are used to model reaction with molecular hydrogen. The thermochemical parameters determined by Ungváry [7] are used to calculate the position $2HCo(CO)_4$.

Table 1
Rates and activation parameters[a] for reaction of metal radicals and hydrogen

Metal radical	T (°C)	k (M^{-2} s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} deg^{-1})	Ref.
$^{\bullet}Co(CN)_5^{-3}$	15–35	40	−1(0.5)	−55(5)	[22]
$^{\bullet}$Rh(II)(TMP)	23–80	3–11	5(1)	−40(5)	[23]
$^{\bullet}Cr(CO)_3C_5Me_5$	20–60	330	0(1)	−47(3)	This work

[a] $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are presented with one, and entropies of activation with two significant figures. The variation is surprisingly small considering the large differences between the complexes. A composite enthalpy of activation of 2 ± 3 kcal mol^{-1} and entropy of activation of -47 ± 8 cal mol^{-1} deg^{-1} with a third-order rate constant of 50 M^{-2} s^{-1} with an error of about one order of magnitude. This 'average' behavior for metal radicals will be used to model $^{\bullet}Co(CO)_4$.

The mechanism proposed for hydrogenation under high CO and H_2 pressure [23] is that shown in Eq. (17).

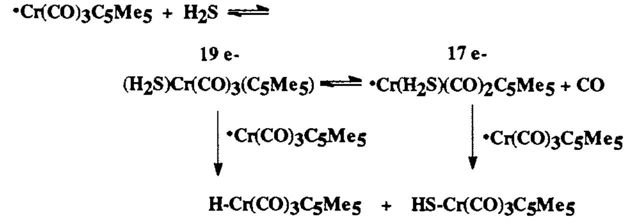
$$Co_2(CO)_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2^{\bullet}Co(CO)_4 + H_2 \xrightarrow{k_2} 2H-Co(CO)_4 \qquad (17)$$

Assuming under these conditions a rapid prequilibrium in $^{\bullet}Co(CO)_4$ yields the rate law in Eq. (18).

$$\begin{aligned} d[P]/dt &= k_1k_2/k_{-1}[Co_2(CO)_8][H_2] \\ &= K_{eq}k_2[Co_2(CO)_8][H_2] \end{aligned} \qquad (18)$$

The value of k_{obs} corresponds to the product of the equilibrium constant for dissociation of the cobalt dimer and the rate constant for net third-order activation of molecular hydrogen. Using the estimated value of K_{eq} at 64°C of 10^{-6} M and composite value for k_2 of 50 M^{-2} s^{-1} leads to a predicted value of $k_{obs} = 5 \times 10^{-5}$ M^{-1} s^{-1} for the rate of reaction at 64°C with $\Delta H^{\neq} = 21 \pm 5$ kcal mol^{-1} and $\Delta S^{\neq} = -18 \pm 11$ cal mol^{-1} deg^{-1}. This estimate can be compared to original experimental data performed under CO/H_2 pressures of 160 atm reported by Ungváry in heptane solution at 64°C in 1972: $k_{obs} = 2.6 \times 10^{-5}$ M^{-1} s^{-1}; $\Delta H^{\neq} = 25$ kcal mol^{-1} and $\Delta S^{\neq} = -6$ cal mol^{-1} deg^{-1}. The agreement between experiment and model is convincing.

It should be pointed out that this model is only valid under high pressure of CO where dissociative pathways are inhibited. It is well known that hydrogenation of $Co_2(CO)_8$ is inhibited by CO. Why is this not the case for the chromium radical, and why was no influence of CO found on the rate of reaction? The answers may be due to the much higher radical concentrations present in the chromium system. Consider the reaction of H_2S, which was recently shown [20] to proceed by the branched mechanism in Eq. (19).



(19)

Oxidative addition of hydrogen sulfide can follow either of the two pathways. At pressures of CO above 10–15 atm however, the 17 e^- pathway is no longer competitive. Since molecular hydrogen is a weaker ligand donor than hydrogen sulfide, even the presence of traces of CO are probably enough to prevent reaction via the mechanism in Eq. (12). The relatively high concentration of chromium radicals present in solution will generally tend to favor interception of the 19 e^- complex by a second mole of radical in preference to the ligand substitution/activation pathway. That situation will be different for cobalt where radical concentrations are much lower. Klingler and Rathke have recently reported that addition of relatively large amounts of $^{\bullet}V(CO)_6$ to solutions of $Co_2(CO)_8$ accelerates hydrogenation under CO pressure, in keeping with these observations [23].

5. Conclusions

This paper presents quantitative data and a complete reaction profile for reaction of hydrogen and $[Cr(CO)_3C_5Me_5]_2$. Dissociation of the metal–metal bonded complex yields 2 mol of the metal radical which then react by an overall third-order reaction with hydrogen to yield 2 mol of metal hydride. Thermodynamic and kinetic data for all major aspects of this reaction have been determined. The transition state in this reaction involves formation of a ternary complex $L_nM^{\bullet}\cdots H_2\cdots {}^{\bullet}ML_n$, similar to what has been found in the two other well-studied systems reported to date. A composite picture of the activation parameters from the data in Table 1 was applied to estimate the rate of reaction of the $^{\bullet}Co(CO)_4$ radical with hydrogen. This data, when combined with literature values for dissociation of $Co_2(CO)_8$ to 2 mol of $^{\bullet}Co(CO)_4$, yield predicted rate and activation parameters for hydrogenation of $Co_2(CO)_8$ under high pressure of CO.

The agreement between predicted rates and those observed is as good as can be expected for data collected by different groups using different solvents and techniques. This implies that while the exact position of the $^{\bullet}Co(CO)_4$ radical in Table 1 is not known with certainty, its estimated rate of reaction with H_2 is in keeping with that displayed by other transition metal based radical systems studied to date. That is in contrast to the results of Mirbach [24] who concluded based on photochemical experiments that $^{\bullet}Co(CO)_4$ radicals do not react with H_2..

The rates of reaction and activation parameters describing third-order reactivity of transition metal radicals and hydrogen does not appear to vary much for the complexes in Table 1. The high negative entropy of activation will always be an integral part of third-order reactions of this type and not much can be done to change it for mononuclear complexes. That will be different for clusters, or tethered diradicals, but the loss of translation entropy in bringing the three particles together will always be in the range outlined in Table 1. The enthalpy of activation is already near zero. It remains to be seen how general that conclusion remains [25].

It should be pointed out that this type of reaction is the slowest rate of reaction that will be observed and represents a 'fall-back' or limiting rate of reaction. Especially for $Co_2(CO)_8$, reduction of CO pressure will open additional, more rapid mechanisms for hydrogenation. Even under active oxo conditions (where high pressures of CO exist, but where additional pathways and possibly even other radical species may be present) the situation is far from clear. A myriad set of intricate pathways exist for $Co_2(CO)_8$ reactivity. Many of them start in Veszprém Hungary.

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