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Thermodynamic and kinetic studies of stable low valent transition metal radical complexes

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Contents

Abstract

The majority of stable low valent transition metal organometallic complexes obey the familiar eighteen-electron rule. Oxidative addition reactions of these complexes normally proceed by initial generation of sixteen electron coordinatively unsaturated species. Low valent 17 electron transition metal radical complexes $^{\bullet}ML_n$ can be generated thermally or photochemically. Since radical recombination to form metal-metal bonded dimers $L_nM–ML_n$

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is a rapid process, the absolute concentration of metal radicals that can be achieved in solution is normally quite low. In cases where either there is no stable metal–metal bonded dimer or the metal–metal bond is so weak that the complex is completely dissociated in solution, relatively high concentrations (ca. 1 mM) are readily achieved. Illustrative mechanisms for oxidative addition reactions of $^{\bullet}ML_n$ are discussed with a focus on reaction mechanisms that are second order in total metal concentration.

Keywords: Thermodynamic; Kinetic; Transition metal radical

1. Introduction

This article discusses selected aspects of oxidative addition reactions of stable low valent metal radical complexes. Understanding of the reaction mechanisms of organometallic radical species has developed largely in the last 20 years and can be expected to continue well into the next century. In particular the pioneering studies of Brown [1] and Poe [2] in mechanistic organometallic radical chemistry set the stage for following investigators. The literature of low valent transition metal radicals is vast, and no attempt is made to cover this area or its many contributors comprehensively [3]. The presentation is meant to be illustrative of the general concepts and principles of reactivity of low valent metal radicals that have been developed in recent years. Reactions involving chromium, molybdenum, and tungsten complexes are highlighted since these are the metals most familiar to the author.

This article will focus on reaction mechanisms under conditions of relatively high radical concentrations, on the order of 1 mM or higher. Oxidative addition reactions are normally first order in substrate and either first order or second order in metal radical leading to overall second order or third order rate laws, respectively. The third order reactivity is normally only observed under conditions of high radical concentrations and it is in these reactions that even strong bonds can be attacked by two moles of 'weak' metal radicals.

For most metal complexes, it is not possible to attain 1 mM concentration of radicals. Radical combination to form metal–metal dimers normally is thermodynamically favored [4] and as discussed later often occurs at close to the diffusion controlled rate:

$$L_nM^{\bullet} + {}^{\bullet}ML_n \rightarrow L_nM\text{–}ML_n \tag{1}$$

A metal radical generated photochemically or electrochemically can attain only a limited steady state concentration due to the rapid nature of reaction (1). The rate of oxidative addition of a substrate A to a metal radical by parallel pathways that are first order and second order in metal radical concentration will be of the general form:

$$-\,d[P]/dt = k^{\text{second order}}\,[A][{}^{\bullet}ML_n] + k^{\text{third order}}\,[A][{}^{\bullet}ML_n]^2 \tag{2}$$

For a fixed [A] the branching ratio for the two reaction channels is clearly equal to: $k^{\text{third order}}\,[{}^{\bullet}ML_n]/k^{\text{second order}}$. The linear dependence on $[{}^{\bullet}ML_n]$ can have the consequence that different reaction pathways will be followed for 'transient' versus 'persistent' radicals simply due to the fact that the reactions are studied in different concentration domains.

It is important to understand the mechanisms of reactions under relatively high metal radical concentrations even though a catalyst system based on such a high metal load might not be practical. Locally high concentrations of metal radicals may also be achieved by linking together one or more radicals by a bridging ligand system. There is considerable evidence that several metalloenzyme catalyzed reactions involve radical/radical pair intermediates [5,6]. Catalyst design, incorporating a vacant coordination site for binding of substrate, and proximate radical or other activating agents will be a challenge for inorganic/organometallic chemists in the new millennium.

2. Generation of transition metal radicals

There are several examples of low valent radicals which are stable and retain their radical character even in the solid state. The metal carbonyl radical ${}^{\bullet}V(CO)_6$, and a number of metallocene radicals being the best and earliest examples [7]. The majority of other radical species are derived by thermal, photochemical, or electrtochemical cleavage of the metal–metal bond of dimeric materials. Observations made earlier on by insightful investigators, coupled with changes in ancillary ligands, have yielded complexes which either have no metal–metal bond in the solid state or have a bond that is so weak that dissociation to radicals is essentially quantitative at room temperature (r.t.). This is illustrated by three examples. Several key developments in the past are presented for the first example, $[{}^{\bullet}M(CO)_2(L)(C_5R_5)$ $M = Cr, Mo, W]$, not from any attempt to give a complete historical account, but to show how a progression of ideas has evolved (and is continuing to evolve) in this area. The other two examples $[{}^{\bullet}Rh(Porphyrin)$ and ${}^{\bullet\bullet\bullet}Mo(N(Ar)R)_3]$ are from quite different areas of chemistry. These three systems are highlighted since they have entirely different 'roots' — organometallic metal carbonyl chemistry, bioinorganic chemistry of metalloporphyrins, and 'classical' higher valent coordination chemistry, respectively. The common link to all three is that in each case the careful choice of ancillary ligands was called for to allow direct observation of the free radical.

2.1. ${}^{\bullet}M(CO)_2(L)(C_5R_5)$ $M = Cr, Mo, W$

Preparation of the dimeric complexes $C_5\ R_5(CO)_3M–M(CO)_3C_5R_5$ was made during the rush of activity in organometallic chemistry in the late 1950s and throughout the 1960s. Numerous contributions, many of them hinting at radical processes, were made by these original investigators and can be found in the original articles [7]. In 1974, Hackett, O'Neil, and Manning [8] observed the facile substitution that occurs for the chromium dimer:

$$[C_5H_5(CO)_3Cr]_2 + 2PPh_3 \rightarrow [Cr(PPh_3)(CO)_2C_5H_5]_2 + 2CO \tag{3}$$

The yellow crystalline product was formulated as a dimer, and it was noted that reaction (2) was much different than that observed for the molybdenum analog $[C_5H_5(CO)_3Mo]_2$. The phosphine substituted product would later be shown by Baird and coworkers [9] to be in fact the stable free radical $^{\bullet}Cr(CO)_2(PPh_3)C_5H_5$. Also in 1974, the crystal structure of $[C_5H_5(CO)_3Cr]_2$ was determined by Adams, Collins, and Cotton [10] and shown to have an unusually long M–M bond — longer in fact than for the molybdenum dimer and attributed to steric repulsion between adjacent ligands. Variable temperature NMR investigations [11] by this group showed a low energy of activation for interconversion of *gauche–anti* conformers ca. 13 kcal mol^{-1}. One possible mechanism for this fluxional process would be dissociation and radical recombination as shown in Eq. (4):

$$[C_5H_5(CO)_3Cr]_2 \Leftrightarrow 2^{\bullet}Cr(CO)_3C_5H_5 \tag{4}$$

The value of the Cr–Cr bond strength, measured much later as discussed below, is only ca. 15 kcal mol^{-1}.

Early structural reports highlighted the strain energy that can be apparent in metal–metal bonded dimers, particulary for the smaller first row metals. The role of steric repulsion in weakening a bond is not new. The structure of $(C_6H_5)_3C–C(C_6H_5)_3$ shows an elongated weak C–C bond. Dissociation of hexaaryl ethanes to yield stable free radicals dates back to the work of Moses Gomberg [12] in 1900:

$$(Ar)_3C–C(Ar)_3 \rightarrow 2^{\bullet}CAr_3 \tag{5}$$

The stability of aryl substituted carbon radicals has two additional consequences for inorganic chemists. Olefin insertion reactions for aryl substituted alkenes can lead to generation of radical pairs as shown in Eq. (6):

$$H–ML_n + Ar_2C{=}CH_2 \rightarrow LnM–C(Ar)_2(CH_3) \rightarrow [LnM^{\bullet}][^{\bullet}CAr_2CH_3] \tag{6}$$

The detection of these radical pairs by CIDNP techniques has played an important role in understanding catalytic mechanisms [13]. In addition, stable substituted trityl radicals have been used to study the rate and mechanisms of H atom transfer [14]:

$$H–ML_n + {}^{\bullet}C(Ar)_3 \rightarrow {}^{\bullet}ML_n + H–C(Ar)_3 \tag{7}$$

The crystal structure of $[C_5H_5(CO)_2(P(OMe)_3)Cr]_2$ was determined by Muetterties and coworkers [15] in 1979. It was shown to exist largely as radicals in solution, and to rapidly add hydrogen:

$$\begin{tikzcd}[Cr(CO)_2(P(OMe)_3)Cp]_2 \arrow[r, Leftrightarrow] & 2\,{}^{\bullet}Cr(CO)_2(P(OMe)_3)Cp \arrow[d, "H_2"] \\ & 2\,H\text{-}Cr(CO)_2(P(OMe)_3)Cp\end{tikzcd} \tag{8}$$

Many significant advances in the chemistry of $^{\bullet}Cr(CO)_2(L)C_5R_5$ in recent years have been made by Baird and coworkers [9]. In addition to determination of the crystal structure of $^{\bullet}Cr(CO)_2(PPh_3)C_5H_5$, the fact that the pentamethyl cyclopentadienyl complex shown in Eq. (9) largely dissociates into radicals was made by this group:

$$[C_5Me_5(CO)_3Cr]_2 \Leftrightarrow 2^{\bullet}Cr(CO)_3C_5Me_5 \tag{9}$$

For Eq. (9), $\Delta H = 14.7$ kcal mol^{-1}, $\Delta S = 45$ cal mol^{-1} deg [16]. The enthalpy of dissociation for the Cp* dimer is ca. 1 kcal mol^{-1} less endothermic than that for $[C_5H_5(CO)_3Cr]_2$ $\Delta H = 15.8$ kcal mol^{-1}, $\Delta S = 37.1$ cal mol^{-1} deg as determined by McClain [17]. The more favorable entropy of dissociation of the Cp* substituted dimer provides the principal driving force for its dissociation. This is attributed to restricted rotation in the Cp* dimer which is sterically 'locked in' place. Geiger and coworkers [18] have obtained data for the rate of radical recombination for the rate of the reverse of reaction (8), $k_{(\mathrm{dimerization})} = 7.0 \times 10^6$ M^{-1} S^{-1}. Wayland and coworkers [19,20] have developed detailed NMR techniques for measuring the rate and activation parameters for metal–metal bonded systems and applied them successfully to this system.

The only evidence, to the author's knowledge, for persistent radicals analogous to those described above but using the heavier metals molybdenum and tungsten is from the work of Tyler [21]:

$$[C_5Ph_5(CO)_3Mo]_2 \Leftrightarrow 2^{\bullet}Mo(CO)_2C_5Ph_5 \tag{10}$$

Reaction of a chelating diphosphines with $[Mo(CO)_3(C_5Ph_5)]_2$ was shown to yield a phosphine substituted radical. Spectroscopic evidence indicated that the diphosphine substituted molybdenum radical existed in equilibrium between 17 e^- {only on P atom of the diphosphine donates to metal} and 19 e^- {both P atoms of the diphosphine donate to the metal} forms.

2.2. $^{\bullet}$*Rh(Porphyrin)*

In a manner analogous to changing the ancillary ligands described above for metal carbonyl complexes, substituents on the porphyrin ring can be manipulated to weaken the metal–metal bond:

$$[(\mathrm{porphyrin})M\text{–}M(\mathrm{porphyrin})] \Leftrightarrow 2^{\bullet}M(\mathrm{porphyrin}) \tag{11}$$

The long standing work of Collman [22] in this area has demonstrated the strong influence of substituents on not only the equilibrium in reaction (11) but other reactions as well. Wayland and coworkers [23] reported an estimate of the Rh–Rh bond of 18.5 kcal mol^{-1} based on detailed NMR analysis of the octaethyl porphyrin dimer in solution. The tetramesityl porphyrin complex dissociates essentially completely to radicals in solution [24]. A number of important mechanistic aspects of these reactions have been discovered including activation of hydrogen, carbon monoxide, methane, and olefins [25]. In addition, these synthetic complexes bear a strong resemblance to and may provide models for insight reactions of metalloporphyrin complexes present in biological systems [5].

2.3. $^{\bullet\bullet\bullet}$Mo(N(Ar)R)$_3$

The steric arguments presented above for metal carbonyl derivatives and porphyrin complexes carry over to higher valent complexes as well. The high stability of the metal–metal triple bonded complexes [26] such as the dimethyl amino complex shown in Eq. (12) prevent formation of significant amounts of paramagnetic monomer in solution.

$$(Me_2N)_3Mo{\equiv}Mo(NMe_2)_3 \rightarrow X \rightarrow 2Mo(NMe_2)_3 \tag{12}$$

Replacement of this group by the N(Ar)R moiety yields stable monomeric complexes which have been shown by Cummins and coworkers [27] to undergo a number of interesting reactions including oxidative addition of dinitrogen:

$$2Mo(N(Ar)R)_3 + N_2 \rightarrow (R(Ar)N)_3MoN{\equiv}NMo(N(Ar)R)_3 \rightarrow 2N{\equiv}Mo(N(Ar)R)_3 \tag{13}$$

While these complexes are not ‘simple’ radicals in the sense that they contain three and not one unpaired electron, the basic principles and evolution of ligand design to achieve metal reactivity are well illustrated by these complexes as well. As with the other systems, earlier work by a number of researchers, as pointed out by Cummins [28], have paved the way for these discoveries.

2.4. Kinetic barriers to radical combination and atom transfer for $^{\bullet}ML_n$

Radical reactions of low valent transition metals are often observed to have very low activation barriers. Three relatively recent investigations from molybdenum and tungsten chemistry are listed here to illustrate this. Photochemical studies by Zauarine and Kubiak [29] have shown that the second order rate constant for reaction (14) $\cong 4 \times 10^9$ M^{-1} s^{-1}:

$$2^{\bullet}W(CO)_5^- \rightarrow W_2(CO)_{10}^{-2} \tag{14}$$

Franz and coworkers [30] have recently reported the rate of H atom abstraction by organic radicals from molybdenum hydrides as shown in Eq. (15) have rate constants ca. 10^8 M^{-1} s^{-1} and activation energies in the range of 1.2–3.2 kcal mol^{-1}:

$$^{\bullet}R + H{-}Mo(CO)_3(C_5R_5) \rightarrow R{-}H + {}^{\bullet}Mo(CO)_3(C_5R_5) \tag{15}$$

Creutz, Bullock and coworkers [31] have investigated heteroatom transfers to photochemical generated radicals such as that shown in Eq. (16):

$$^{\bullet}Mo(CO)_3C_5H_5 + X{-}Mo(CO)_3C_5D_5 \rightarrow X{-}Mo(CO)_3C_5H_5 + {}^{\bullet}Mo(CO)_3(C_5D_5) \tag{16}$$

The second order rate constants determined in CD_3CN at 25°C for reaction (16) for X = I, Br, and Cl were 2.6×10^8, 1.0×10^7, and 0.8×10^6 M^{-1} s^{-1}, respectively. These observations all serve to indicate that thermodynamic favorability, and not kinetic barriers tend to dominate the reactivity of low valent metal radicals for radical recombination and heteroatom transfer. Alkyl group transfer is a much more complex process and appeared to be generally several orders of magnitude slower than H and X atom transfer rates.

3. Ligand substitution of transition metal radicals

A key step in many catalytic cycles is ligand exchange [32]. Radical complexes are generally much more labile with respect to ligand substitution reactions. The photochemically generated 17 e^- complexes $^{\bullet}M(CO)_5$ ($M = Mn$ [33], Re [34]) were shown early on to undergo rapid associative substitution reactions in contrast to the typical dissociative reactions of 18 e^- analogs. The rate enhancements for the paramagnetic species can be on the order of 10^6 or more. The stable carbonyl metal radical $^{\bullet}V(CO)_6$ was also shown to undergo rapid associative ligand substitution by Basolo and coworkers [35]. These effects are often interpreted in terms of the 'half-bond' that is formed when a 17-electron complex binds a ligand L to form a 19-electron complex [36]:

$$\begin{array}{llllllll} ^{\bullet}ML_n & +\acute{L} & \rightarrow & \acute{L}\cdots{}^{\bullet}ML_n & \rightarrow & ^{\bullet}M\acute{L}L_{n-1} & +L \\ 17\,e^- & & & 19\,e^- & & 17\,e^- & \end{array} \tag{17}$$

The facile associative substitutions of 17 e^-/19 e^- radicals can have two consequences regarding oxidative addition reactions. The same type of 19 e^- adduct that is formed in ligand substitutions can be formed in coordinative activation of substrates for oxidative addition. Moreover, substrates for oxidative addition which contain relatively strong donors can undergo ligand substitution and enter the primary coordination sphere of the metal, generating a new 17 e^- radical species:

$$\begin{array}{lllllll} ^{\bullet}ML_n & +A\text{–}B & \rightarrow & A\text{–}B\cdots{}^{\bullet}ML_n & \rightarrow & ^{\bullet}M(A\text{–}B)L_{n-1} & +L \\ 17\,e^- & & & 19\,e^- & & 17\,e^- & \end{array} \tag{18}$$

The substituted radical complex $^{\bullet}M(A\text{–}B)L_{n-1}$ may then be attacked by a second mole of radical. An example of this type of reactivity is discussed later in reactions of hydrogen sulfide.

4. Second order oxidative addition reactions of transition metal radicals

For weak A–B bonds, direct radical attack may occur as shown in Eq. (19):

$$\begin{tikzcd} \bullet ML_n + A\text{-}B \arrow[r] & A\text{-}B\cdots\bullet ML_n \arrow[r] & \bullet A \arrow[d, "\bullet ML_n"] + B\text{-}ML_n \\ & & A\text{-}ML_n \end{tikzcd} \tag{19}$$

However, thermochemical factors severely limit the substrates for direct attack by a transition metal based radical as depicted in Eq. (19). For example, for H-atom transfer, since the H–ML$_n$ bond strength is typically 60–70 kcal mol^{-1} [37], only for substrates with H–A bonds <75 kcal mol^{-1} will this reaction be facile. In fact, transition metal radicals are rather low on the ‘pecking order’ and most radicals will abstract an H atom from them as shown in Eqs. (7) and (15). Photochemically generated thiyl radicals, for example, react according to Eq. (15) at near diffusion controlled rates [38]

$$^{\bullet}\mathrm{SPh} + \mathrm{H{-}Mo(CO)_3C_5H_5} \rightarrow \mathrm{PhS{-}H} + {}^{\bullet}\mathrm{Mo(CO)_3C_5H_5} \tag{20}$$

The reverse of Eq. (20), attack of a single metal radical on a sulfur–hydrogen bond, will be endothermic for almost all combinations of metal complexes and free thiols.

In terms of second order H atom transfer, the most likely source of an H atom is a second metal hydride. The rates of H atom transfer between metal complexes, are generally rapid if thermodynamically allowed as shown by the data in reaction (21) [39]:

$$\begin{aligned} &^{\bullet}\mathrm{Cr(CO)_3Cp^*} + \mathrm{H{-}Cr(CO)_2(PPh_3)C_5H_5} \\ &\qquad \rightarrow \mathrm{HCr(CO)_3Cp^*} + {}^{\bullet}\mathrm{Cr(CO)_2(PPh_3)C_5H_5} \end{aligned} \tag{21}$$

$$\Delta H^{\circ} = -3\ \text{kcal mol}^{-1};\ \Delta H^{\ddagger} = 2\ \text{kcal mol}^{-1};\ \Delta S^{\ddagger} = -38\ \text{cal mol}^{-1}\ \text{deg}$$

Transfer of halogen atoms from a metal halo-carbonyl complex to a metal radical has been shown by Song, Bullock, and Creutz [31] to be a rapid second order process when thermochemically allowed as discussed above. Baird and coworkers [40] have reported generation of alkyl radicals by first order attack of chromium based radicals on alkyl halides. Reaction of phenyl disulfide and the chromium radical in Eq. (22) was shown [41] to proceed by the process first order in metal radical:

$$^{\bullet}\mathrm{Cr(CO)_3C_5Me_5} + \mathrm{PhSSPh} \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} \mathrm{PhS{-}Cr(CO)_3C_5Me_5} + \mathrm{PhS}^{\bullet} \tag{22}$$

$$\mathrm{PhS}^{\bullet} + {}^{\bullet}\mathrm{Cr(CO)_3C_5Me_5} \xrightarrow{k_2} \mathrm{PhS{-}Cr(CO)_3C_5Me_5}$$

The PhS–SPh bond (43 kcal mol^{-1}) is stronger than the Cr–SPh bond (35 kcal mol^{-1}) and so the first step in Eq. (22) is endothermic by ca. 8 kcal mol^{-1}. The enthalpy of activation for this reaction was found to be ca. 10 kcal mol^{-1}. This implies a low barrier to the reverse reaction ca. 2 kcal mol^{-1}, which was observed since addition of PhS–Cr(CO)$_3$C$_5$Me$_5$ was shown to slow down the rate of reaction. The chemically generated $^{\bullet}$SPh radicals formed in the first step of reaction (22) were found to react with metal hydrides in a manner analogous to that observed by Franz and coworkers [38] for photochemically generated $^{\bullet}$SPh radicals as shown in Eq. (20). As discussed later the stronger sulfur-sulfur bond in MeSSMe (63 kcal mol^{-1}) was shown to react by a third order rather than a second order mechanism since the enthalpy of activation for single radical attack is too high to be competitive.

The reactions following the general path shown in Eq. (19) can be expected to be qualitatively similar for both concentrated and dilute solutions of metal radicals. Thus there will be a strong similarity in observed reactivity between photochemically or thermally generated radicals and stable metal radicals. Weak A–B bonds including halogens, metal complexes, or special organic systems may be attacked by a single metal radical. However such bonds are readily activated by other techniques as well, and it is the concerted attack on strong bonds that shows most promise for future development.

5. Third order oxidative addition reactions of H_2 and transition metal radicals

Halpern [42] provided the first detailed kinetic study of oxidative addition of hydrogen to transition metal radicals and has highlighted much earlier than this review the importance of third order reaction mechanisms for oxidative addition:

$$2{}^{\bullet}\mathrm{Co(CN)}_5^{-3} + \mathrm{H}_2 \rightarrow 2\mathrm{H{-}Co(CN)}_5^{-3} \tag{23}$$

In aqueous solution, the Co(II) cyanide complex was shown to obey a simple third order rate law $d[P]/dt = k[{}^{\bullet}\mathrm{Co(CN)}_5^{-3}]^2\,[\mathrm{H}_2]$. The possibility that oxidative addition of hydrogen occurred via initial formation of a dimeric metal complex was considered but discounted. To date, kinetic study of the rate of oxidative addition of hydrogen to three low valent transition metal radical systems have been reported. Wayland and coworkers [23,24] have reported data on the ${}^{\bullet}$Rh(II)(TMP) complex (TMP = tetramesitylporphyrin), and recently the rate of reaction of the ${}^{\bullet}\mathrm{Cr(CO)_3C_5Me_5}$ radical with H_2 and D_2 has been reported [43]. All three of these systems were found to obey third order rate laws. Derived rate constants and activation parameters are shown in Table 1.

In view of the different nature of the radicals shown in Table 1 — an ionic complex in aqueous solution, a porphyrin complex of a late transition metal, and a metal carbonyl complex of an early transition metal — the rate and activation parameters for oxidative addition of hydrogen are remarkably similar. All have high negative entropies of activation and enthalpies of activation near zero.

The large negative entropies of activation [average value ca. -47 cal mol^{-1} deg] are expected for a transition state in which three particles are brought together [44]. The low enthalpies of activation for oxidative addition [average value ca. 2 kcal

Table 1
Experimental and average activation parameters third order activation of hydrogen: $2{}^{\bullet}\mathrm{ML}_n + \mathrm{H}_2 \rightarrow 2\mathrm{HML}_n$

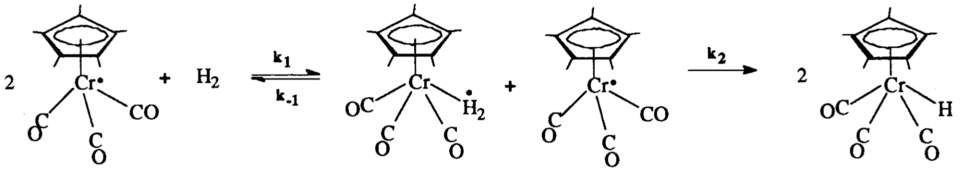
Radical	${}^{\bullet}\mathrm{Co(CN)}_5^{-3}$	${}^{\bullet}$Rh(TMP)	${}^{\bullet}\mathrm{Cr(CO)_3C_5Me_5}$	${}^{\bullet}\mathrm{ML}_{n(\mathrm{avg})}$
$\Delta H^{\ddagger}$ (kcal mol^{-1})	-1	$+5$	0	2
$\Delta S^{\ddagger}$ (cal mol^{-1} deg)	-55	-40	-47	-47
Reference	[42]	[24]	[43]	Avg.

mol^{-1}] are remarkable. It should be recalled that the H–H bond (ca. 104 kcal mol^{-1}) is one of the strongest single bonds [45] between any two elements. Furthermore, oxidative addition of H_2 in molecular hydrogen complexes, where the H–H bond is split at a single metal center often have significant enthalpies of activation [46]. For example $\Delta H_o \approx 1$ kcal mol^{-1} and $\Delta H^{\ddagger} \approx 10$ kcal mol^{-1} for oxidative addition of bound dihydrogen in the Kubas complex [47,48] shown in Eq. (19):

$$W(PCy_3)_2(CO)_3(H_2) \rightarrow W(PCy_3)_2(CO)_3(H)_2 \tag{24}$$

How is it possible that radical cleavage occurs with a lower enthalpy of activation than does cleavage at a single metal site? The barriers to oxidative addition in transition metal molecular hydrogen complexes have been investigated theoretically and are reasonably well understood, much more so in the author's opinion than are the radical pathways. For oxidative addition at a single metal center, there is clearly a 'no-man's land' to be crossed in the trajectory from H–H going from a sigma donor ligand to a *cis* dihydride. Why is this barrier apparently absent for attack of two radicals?

The simplest explanation for the near zero enthalpies of activation for oxidative addition to 2 moles of radical is that this too proceeds through initial formation of a molecular hydrogen complex as shown in the general scheme in Eq. (25):



(25)

The first step in Eq. (25) involves reversible formation of a thermodynamically unstable 19 e^- molecular hydrogen complex. The second step involves attack of a second mole of transition metal radical on this adduct and leads to the termolecular transition state. The near zero enthalpies of activation are rationalized by the fact that the first step can be viewed as exothermic preequilibrium, and the endothermic barrier to the second step is roughly cancelled by this.

Estimates of the equilibrium properties for binding of molecular hydrogen to $^{\bullet}Cr(CO)_3C_5Me_5$, the first step in Eq. (25) can be made and used to estimate the activation parameters for the key second step-attack of a second mole of radical on the 19 e^- molecular hydrogen complex. The enthalpy and entropy of binding of molecular hydrogen to the chromium analog of the Kubas complex has been determined [49]. Moderate to high pressures of hydrogen is required to observe the reaction shown in Eq. (26):

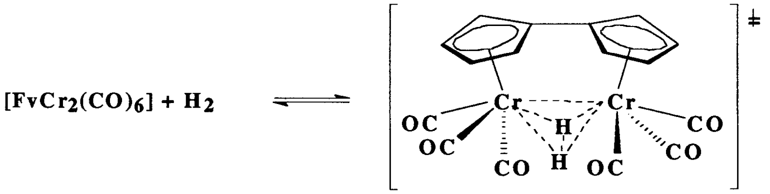
$$(P(Cy)_3)_2Cr(CO)_3 + H_2 \rightarrow (P(Cy_3))_2Cr(CO)_3(H_2) \tag{26}$$

$\Delta H^\circ = -7$ kcal mol^{-1}, $\Delta S^\circ = -25$ cal mol^{-1} deg

The fact that the 17 e^- radical is not observed to bind H_2 in the same range of pressures implies that its enthalpy of binding is < -7 kcal mol^{-1}. The entropy of binding of H_2 can be taken to be the similar for both complexes, and the enthalpy of binding to be approximately one half that of the 18 electron analog [36]. Using estimated thermodynamic parameters for binding of H_2 to $^{\bullet}Cr(CO)_3C_5Me_5$ in the first step in Eq. (25) [$\Delta H° = -4 \pm 3$ kcal mol^{-1}, $\Delta S° = -25 \pm 5$ cal mol^{-1} deg] leads to estimation of $\Delta H^{\ddagger} = 4 \pm 4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22 \pm 5$ cal mol^{-1} deg for the second step in Eq. (20). Thus the key step — attack of a second mole of radical on the 19 e^- molecular hydrogen adduct — has an enthalpy of activation on the order of 4 ± 4 kcal mol^{-1}. The enthalpy of activation, while not zero, is still lower that what is normally observed for oxidative addition to a single metal site and implies that more favorable electronic factors may exist for concerted diradical attack on H–H. This is an important conclusion since it is only the large negative entropy of activation that serves to slow down these third order reactions. Proper design of a complex with two radicals held in the optimal geometric configuration could significantly reduce the entropy of activation.

The advantages of two-site activation are no doubt a significant factor in heterogeneous catalysis. The detailed structures and true nature of the actual sites of heterogeneous catalysis are much more difficult to characterize compared to isolated complexes. Enzymatic systems may also incorporate stable radicals or radical pairs in which the structure of the enzyme restricts radical recombination.

There are a number of ligand systems that can be used to link two metals together. The fulvalene ligand has been extensively studied by Vollhardt and coworkers [50]. For the chromium complex shown in Eq. (22) the kinetics and thermodynamics of oxidative addition of H_2 have recently been reported [51]:



(27)

Under H_2 pressure, reaction (27) was observed to proceed and was uninhibited by added CO pressure. This and other observations were in keeping with a diradical mechanism for oxidative addition in the tethered system. Unlike the $^{\bullet}Cr(CO)_3C_5Me_5$ system in which the two radicals operate independently and the H–H bond can be attacked from any direction, oxidative addition/reductive elimination in the fulvalene complexes is restricted in its trajectory by constraints placed by the ligand. An enthalpy of activation ca. 10 kcal mol^{-1} above that needed to break the Cr–Cr bond was observed in reaction (27) and implies that with regard to oxidative addition of H_2, the system may have a non-optimal geometry [51].

A motivating factor for studying the rate of oxidative addition to metal-metal bonded dimers is one of the key steps in cobalt catalyzed hydroformylation–generation of $HCo(CO)_4$:

$$Co_2(CO)_8 + H_2 \rightarrow 2H\text{–}Co(CO)_4 \tag{28}$$

The two most likely first steps for reaction (28), like those for many metal-meal bonded dimers can involve either CO dissociation or metal-metal bond cleavage [52] as shown in Eqs. (29) and (30):

$$Co_2(CO)_8 + H_2 \Leftrightarrow Co_2(CO)_7(H_2) + CO \tag{29}$$

$$Co_2(CO)_8 \Leftrightarrow 2^{\bullet}Co(CO)_4 \tag{30}$$

Under high concentrations of CO, however, the reaction channel shown in Eq. (29) will be inhibited, whereas that in Eq. (30) will be relatively uninfluenced and hence gain in relative significance. Radical reaction pathways under high CO pressure will ultimately become dominant. Ungvary and Marko [53] originally studied the high pressure rate of hydrogenation of cobalt carbonyl. More recently, Klingler and Rathke [54] have developed high pressure NMR techniques and studied the equilibrium of Eq. (30). A composite profile for the rate of hydrogenation of transition metal radicals from data in Table 1, when combined with the equilibrium concentration of $^{\bullet}Co(CO)_4$ calculated based on the work of Klingler and Rathke [54] was recently shown [43] to lead to calculated rates of hydrogenation of $Co_2(CO)_8$ under limiting high pressure conditions in agreement with the original data of Ungvary and Marko [53]. These observations imply that the rate of hydrogenation of the $^{\bullet}Co(CO)_4$ radical is in keeping with the other three radical systems shown in Table 1.

The use of two disparate radicals to activate H_2 was recently attempted by the Argonne group [55]. Addition of relatively large amounts of the stable paramagnetic complex $^{\bullet}V(CO)_6$ which itself does not form a stable hydride was shown to accelerate hydrogenation of $Co_2(CO)_8$ under conditions of high CO pressure. This may involve as a key step a $(CO)_4Co^{\bullet}\cdots H_2\cdots {}^{\bullet}V(CO)_6$ transition state. It can be anticipated that the use of two disparate radicals, either two transition metal radicals or possibly those involving main group and transition metal groups, may be designed for activation of H_2 and other related species of relevance to catalytic processes in the future.

6. Third order oxidative addition reactions of the $^{\bullet}Cr(CO)_3C_5Me_5$ radical with thiols, disulfides, and hydrogen sulfide

In addition to third order reactivity with molecular hydrogen, the chromium radical has been shown to also react by third order mechanism with butanethiol, thiophenol [56], and methyl disulfide [41]:

$$2^{\bullet}Cr(CO)_3C_5Me_5 + RSH \rightarrow H\text{–}Cr(CO)_3C_5Me_5 + RS\text{–}Cr(CO)_3C_5Me_5 \tag{31}$$

$$2^{\bullet}Cr(CO)_3C_5Me_5 + MeSSMe \rightarrow 2MeS\text{–}Cr(CO)_3C_5Me_5 \tag{32}$$

Rate and activation parameters for selected reactions of the $^{\bullet}Cr(CO)_3C_5Me_5$ radical are summarized in Table 2.

As was found for dihydrogen, the third order reactions have near zero enthalpies of activation and large negative entropies of reaction. Examination of the data in Table 2 shows that the strength of the A–B bond broken by attack of 2 moles of the chromium radical plays no clear role in the kinetics. The rates of reaction only span about 2 orders of magnitude and it is in the entropies of activation that the principal kinetic differences appear.

Table 2
Reactivity patterns of $^{\bullet}Cr(CO)_3C_5Me_5$

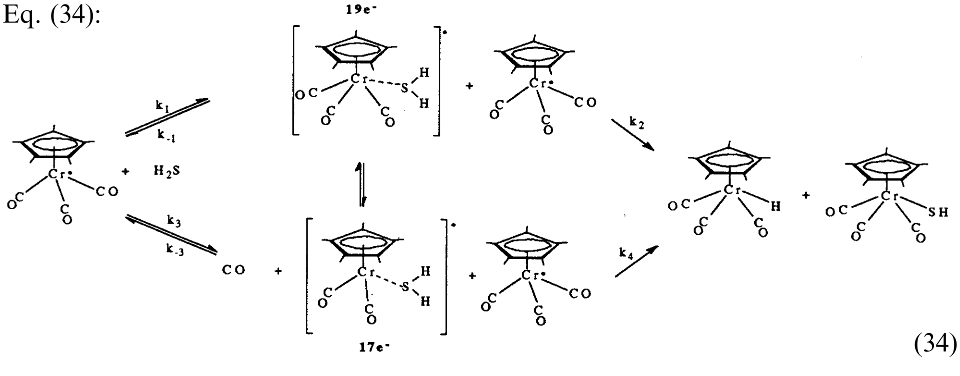
Substrate	Reaction mechanism	K_{obs}	$\Delta H^{\neq}$ [c]	$\Delta S^{\neq}$ [d]	Reference
MeSSMe	3rd order	400 [a]	0	−47	[41]
H_2	3rd order	330 [a]	0	−47	[43]
D_2	3rd order	280 [a]	0	−49	[43]
H_2S (15 atm CO)	3rd order	75 [a]	0	−51	[57]
PhSH	3rd order	25 [a]	0	−52	[56]
BuSH	3rd order	5 [a]	0	−55	[56]
PhSSPh	2nd order (produces ($^{\bullet}$SPh)	1.3 [b]	+10	−24	[41]
H_2S	2nd order (inhibited by CO)	1.0 [b]	+10	−27	[57]
PMe_2Ph	2nd order	1.0 [b]	+10	−25	[57]
^{13}CO	2nd order	Very fast			[58]
NO	2nd order?	Very fast			[58]
$W(phen)(CO)_3BuSH$	2nd order	5×10^{4} [b]			[56]
$^{\bullet}Cr(CO)_3C_5Me_5$	2nd order (dimerization)	5×10^{7} [b]			[18]

[a] Third-order rate constants in M^{-2} s^{-1}.
[b] Second-order rate constants in M^{-1} s^{-1}.
[c] Enthalpy of activation in kcal mol^{-1}.
[d] Entropy of activation in cal mol^{-1} deg.

Extension of these studies to oxidative addition of H_2S led to several surprising observations [57]. In spite of having a stronger H–S bond than either BuSH or PhSH, hydrogen sulfide was found to react much faster. Initial observations appeared to show that the reaction obeyed a second order rate law — first order in hydrogen sulfide and first order in metal complex. In addition there was a marked temperature dependence of the rate of reaction implying a significant enthalpy of activation. Direct attack of a chromium radical on H_2S as shown in Eq. (29) is readily calculated to be endothermic by 28 kcal mol^{-1}:

$$^{\bullet}Cr(CO)_3C_5Me_5 + H\text{–}SH \rightarrow H\text{–}Cr(CO)_3C_5Me_5 + {}^{\bullet}SH \tag{33}$$

The observed temperature dependence, however, yielded an enthalpy of activation much lower than this. In contrast to the other third order oxidative addition reactions for this radical which were shown to be independent of CO pressure, however, there was a strong retarding influence of added carbon monoxide on the rate of oxidative addition. Full kinetic studies yielded the two channel reaction mechanism shown in Eq. (34):

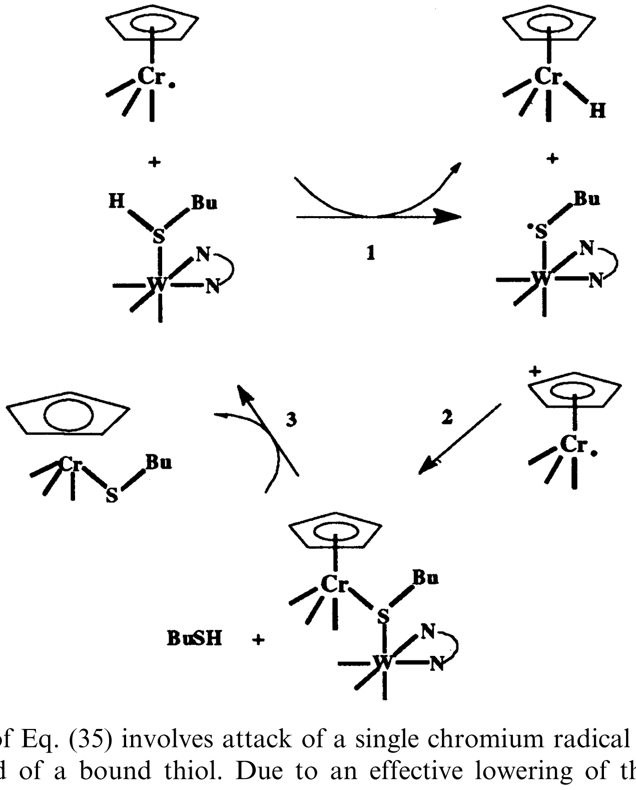


(34)

The top mechanism shown in Eq. (34) is a third order mechanism similar to what was observed for thiols and hydrogen. This reaction pathway is independent of added CO. The lower reaction mechanism involves initial ligand substitution to form the substituted radical complex $^\bullet Cr(H_2S)(CO)_2C_5Me_5$. Attack of a second mole of metal radical on the bound H_2S is rapid (see next section) and under appropriate conditions the rate of oxidative addition of hydrogen sulfide approaches that of the rate of ligand substitution by $PPhMe_2$ (see Table 2). This mode of reactivity utilizes the facile ligand substitution characteristics of 17 e^- complexes to activate substrate towards attack by a second mole of metal radical.

7. Reaction mechanisms of transition metal radicals and bound substrates

The reactions discussed above have all involved attack of two metal radicals on a substrate. It is well known that coordination serves to activate the bonds of substrates towards external attack. The third order reactivity of thiols and the chromium radical discussed above (see Eq. (31)) was shown to be catalyzed by addition of a metal complex capable of binding and activating thiol as shown in Eq. (35):



(35)

The first step of Eq. (35) involves attack of a single chromium radical on the sulfur hydrogen bond of a bound thiol. Due to an effective lowering of the S–H bond strength by prior coordination, this reaction may proceed by a first order process.

In step 2, rapid radical combination is proposed to occur to yield the coordination complex between the chromium thiolate and tungsten. Thiol–thiolate exchange in step 3 completes the catalytic cycle. This reaction was found to be rate determining and buildup of the chromium thiolate–tungsten complex could be detected spectroscopically. This combination of 16/18 e^- binding and activation combined with 17/19 e^- atom transfer reactions represents an additional tool available for small molecule activation. Attempts to achieve the same type of effect with molecular hydrogen complexes, however, have so far been unsuccessful [58]. For example, the rate of hydrogenation of the $^\bullet Cr(CO)_2(PPh_3)C_5H_5$ (which is much slower than the rate of hydrogenation of $^\bullet Cr(CO)_3C_5Me_5$) by addition of the Kubas molecular hydrogen complex failed to achieve any notable difference in rate [59]. This was taken to imply that reaction (36) did not occur:

$$\begin{aligned}&^\bullet Cr(CO)_2(PPh_3)C_5H_5 + (H_2)W(PCy_3)_2(CO)_3\text{–}X\\&\rightarrow H\text{–}Cr(CO)_2(PPh_3)C_5H_5 + {}^\bullet(H)W(PCy_3)_2(CO)_3\end{aligned} \tag{36}$$

Failure to achieve reaction (36) however, may simply be a result of the severe steric factors involved. The challenge in designing dinuclear activating systems is that steric restrictions are required to limit the rate of deactivating side reactions, but that these same steric factors must allow binding and reaction when the substrate is inserted.

8. Conclusions

The goal of this paper has been to illustrate selected aspects of metal radical reactivity. Much more is known about homogeneous catalysis based on ‘even’ (14/16/18 e^-) than ‘odd’ (15/17/19 e^-) complexes. Little is known about the true nature of multi-site activation processes of any type. Distinct advantages exists for the use of either two radicals or one radical and a second ‘even’ metal in the activation of strong bonds. For most metal complexes, the relatively weak nature of the radicals involved will dictate that they must work in concert with either a second radical or an activating receptor if strong bonds are to be broken. Catalyst design based on mechanistic principal is a realistic goal for the future of inorganic/organometallic chemists.

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