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Factors affecting the equilibrium constant of homolysis of complexes with metal–carbon σ bonds in aqueous solutions. Pulse radiolysis studies

Dan Meyerstein

R. Bloch Coal Research Center and Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva, Israel.

Abstract. Pulse-Radiolysis is a powerful technique for the determination of the equilibrium constants of the homolytic cleavage of metal-carbon σ bonds in aqueous solutions. In most systems studied the observed reaction is: $L_{m-1}M^{(n+1)}\text{-}R + L \rightleftharpoons ML_m^{(n)} + \cdot R$. Therefore the results do not enable a direct determination of the metal-carbon bond dissociation energies. The results obtained indicate that these equilibrium constants are not directly related to the redox potential of either $L_mM^{(n)}$ or of ·R, or to the activation energies for the homolytic cleavage of a family of similarly substituted ethanes.

The measurement of the dissociation energies of metal-carbon σ bonds and the study of the factors affecting these energies is of importance in the framework of the research of many organometallic, biochemical and catalytic systems (ref. 1). The most common method used to measure these dissociation energies is the kinetic technique. In this technique the activation energy, ΔH^*, of reaction (1) is determined and it is assumed that

$$L_mM^{(n+1)}\text{–}R \longrightarrow L_mM^{(n)} + \cdot R \qquad (1)$$

the bond dissociation energy equals ΔH^* (ref. 1,2). This assumption is based on the observation that the reverse reaction:

$$L_mM^{(n)} + \cdot R \longrightarrow L_mM^{(n+1)}\text{–}R \qquad (2)$$

is very fast, often approaching the diffusion controlled limit, and therefore it is assumed that the activation energy for it is negligible (ref. 1,2). This assumption introduces an error of several kjoule/mole into the bond dissociation energy. The specific rates of reaction (1) are determined by following the rate of disappearance of $L_nM\text{–}R$ in the presence of a good scavenger for the free radicals ·R.

It should be pointed out that this technique is applicable only for complexes with relatively stable metal-carbon σ bonds, *i.e.* usually only to systems where the metal-carbon bond is not formed in situ. This limitation has several important implications:

a. Regarding the models for coenzyme B_{12} the bond dissociation energies can be determined only for systems where R is an alkyl or a benzyl with no substituents on the ∝ carbon (ref.1) which transform the radical ·R into a reducing agent. Thus for radicals of the type $\cdot C(OH)R_1R_2$, $\cdot C(NH_2)R_1R_2$, $\cdot C(OR)R_2R_3$ *etc.*, no stable complexes are obtained as they reduce the central cobalt ion in B_{12}, and in model compounds, to $Co^{(I)}$. However in nature these radicals are of importance in enzymatic processes *e.g.* in dioldehydrase and in ethanolamine deaminase. (ref. 3)

b. The active transients in catalytic processes are by nature unstable *i.e.* their metal-carbon σ bonds are weak. Therefore the common technique does not enable the determination of the dissociation energies of the metal-carbon bonds in these systems.

c. It is impossible to determine the dissociation energies of the metal-carbon bonds in other systems of biological importance *e.g.* in complexes with iron-carbon (ref. 4), nickel-carbon (ref. 5) and copper-carbon (ref. 6) bonds as these complexes are not stable enough.

d. It is impossible to change systematically the ligands L and the central cation M in order to study their effect on the bond strength. This limitation stems from the lack of relatively stable series of analogous complexes.

Recent pulse radiolytic studies have pointed out that reaction (2) can be followed in aqueous solutions for complexes of a variety of transition metals, *e.g.* for $L_mM^{(n)}$=Cr(II) (ref. 7), Mn(II) (ref. 8), Fe(II) (ref. 8,9), Co(II) (ref. 10), Ni(I) (ref.11), Ni(II) (ref. 12), Cu(I) (ref. 13) and Cu(II) (ref. 6,14). The product complexes $L_mM^{(n+1)}$–R are usually short lived and in several systems the results point out that decomposition *via* homolysis indeed occurs.

The results in most systems studied suggest that reaction (1), in aqueous solutions at least, is better described by the equation:

$$L_{m-1}M^{(n+1)}\text{-}R + L \rightleftharpoons ML_m^{(n)} + \cdot R \qquad (3)$$

i.e. the coordination number is not changed during the reaction, (Note a). Thus for example the coordination number of the cobalt in the reactions:

$$[N(CH_2CO_2)_3(H_2O)Co^{(III)}\text{-}R]^- \rightleftharpoons [N(CH_2CO_2)_3Co^{(II)}(H_2O)_2]^- + \cdot R \qquad (4)$$

is six for both the di- and tervalent complexes as can be concluded from their visible absorption spectra (ref.15). A detailed analysis of reaction (-4) suggests that it occurs *via* the "SN_2" mechanism, (Note b). This conclusion is based on the observation that $k_{-4}=1.6\times10^8$ $dm^3mol^{-1}s^{-1}$ for $\cdot R= \cdot CH_3$ *i.e.* only about an order of magnitude slower than the diffusion controlled limit. It is difficult to envisage that about 10% of $[N(CH_2CO_2)_3Co^{(II)}(H_2O)_2]^-$ are present in the solution in the pentacoordinated form, $[N(CH_2CO_2)_3Co^{(II)}(H_2O)]^-$ which would be required if reaction (-4) would occur *via* the "SN_1" mechanism. According to the principle of microscopic reversibility this is also the nechanism of reaction (4). Thus the measurement of $\Delta H°$ of reaction (4) does not yield the metal-carbon bond dissociation energy, but the difference between this energy and the metal-water bond dissociation energy. However when $\Delta H°$ of reaction (4) is measured for a series of aliphatic free radicals the effect of substituents on the metal-carbon bond dissociation energy is determined.

Two general approaches are available for the detrmination of the homolysis equilibrium constant K_3:

a. For systems with a large equilibrium constant the dependence of the rate of formation of $L_{m-1}M^{(n+1)}$-R on $[ML_m^{(n)}]$ is determined. The slope of the straight line obtained equals k_{-3} and the intercept yields k_3. Alternatively the dependence of the yield of $L_{m-1}M^{(n+1)}$-R on $[ML_m^{(n)}]$ is measured by following the absorption due to $L_{m-1}M^{(n+1)}$-R, from the results K_3 is calculated. These techniques were used for the measurement of K_3 in a variety of systems, *e.g.* for the determination of K_4, see below.

Note a: As the free L on the right side of equation (3) is usually a solvent molecule it does not appear in the kinetic equations,*i.e.* the forward reaction (3) obeys a first order rate law.

Note b: The ligand exchange reaction in which H_2O, or another two electron donating ligand, is exchanged by a free radical $\cdot R$ is formally a redox process. Thus the mechanism is not accurately described by either the SN or the SH notations, therefore the "SN" notation is used here.

b. For systems with a small equilibrium constant the previous techniques are inapplicable as the intercept is too small to be accurately determined, and nearly a full yield of $L_{m-1}M^{(n+1)}$-R is obtained even in solutions containing the lowest useful concentration of $ML_m^{(n)}$. In such systems the addition of a scavanger, S, for the free radicals ·R is required. The kinetics of decomposition of $L_{m-1}M^{(n+1)}$-R in the presence of S are:

$$\cdot R + S \longrightarrow \text{products} \tag{5}$$

$$-\frac{d[L_{m-1}M^{(n+1)}\text{-}R]}{dt} = \frac{k_5k_3[L_{m-1}M^{(n+1)}\text{-}R][S]}{k_{-3}[L_mM^{(n)}] + k_5[S]} \tag{6}$$

$$i.e.: \quad \frac{1}{k_{obs}} = \frac{[L_mM^{(n)}]}{K_3k_5[S]} + \frac{1}{k_3} \tag{7}$$

Therefore by plotting $1/k_{obs}$ *vs.* $[L_mM^{(n)}]$ or *vs.* 1/[S] K_3 and k_3 can be determined. This technique was used for a variety of systems.

The equilibrium constants for reaction (3), for $L_mM^{(n)}=[N(CH_2CO_2)_3Co^{(II)}(H_2O)_2]^-$ thus determined (ref. 15), for several aliphatic residues are summed up in table 1. For comparison purposes are included also the equilibrium constants for the analogous reaction for $L_mM^{(n)}= Cr(H_2O)_6^{2+}$ (ref. 2). (It is of interest to note that k_{-3} in the latter system were also determined by the pulse radiolytic technique, (ref. 7)

Table 1 Equilibrium constants for reaction (3), mol·dm^{-3}.

·R \ $L_mM^{(n)}$	$Cr(H_2O)_6^{2+}$	$[N(CH_2CO_2)_3Co^{(II)}(H_2O)_2]^-$
·CH_3	-	3.7×10^{-7}
·CH_2OH	2.3×10^{-13}	2.0×10^{-4}
·$CH(CH_3)OH$	1.1×10^{-11}	9.1×10^{-4}
·$C(CH_3)_2OH$	2.5×10^{-9}	2.0×10^{-3}
·$CH(CH_3)OC_2H_5$	5.9×10^{-11}	9.1×10^{-3}

These results indicate that the dependence of K_3 on the nature of the substituents on the free radical is different for the two complexes. Thus K_3 is not directly related to the redox potential of ·R, or to the activation energies for the homolytic cleavage of a family of similarly substituted ethanes, as has earlier been suggested (ref. 2). Furtheremore K_3 is too small to be measured for R = CH_2O^- for $L_mM^{(n)}$ = $[N(CH_2CO_2)_3Co^{(II)}(H_2O)_2]^-$,though ·$CH_2O^-$ is a considerably stronger reducing agent than ·CH_2OH, (ref.15) In analogy it was found (ref. 16) that K_3 for $L_mM^{(n)}$ = $[N(CH_2CO_2)_3Fe^{(II)}(H_2O)_2]^-$ is smaller by about a factor of 40 for ·R = ·CO_2^- than for ·R = ·CH_3 though the former is a a considerably stronger reducing agent.

The activation energies of reaction (4) for R = CH_2OH were measured, the results are: ΔH^*_4= 67.7, ΔH^*_{-4}= 20.3 and $\Delta H°_4$= 45.3 kjoule·mol.(ref. 15) This result clearly points out that though the specific rate of reaction (-4) approaches the diffusion controlled limit, $k_{-4}=1.6\times10^8$ mol^{-1}dm^{3}s^{-1}, ΔH^*_{-4} is not negligible, at least in this system.

The mechanism of decomposition of the complexes $[N(CH_2CO_2)_3(H_2O)M^{(III)}\text{-}R]^-$, in the absence of scavengers for the free radicals ·R, studied so far involves the reaction:

$$L_{m-1}M^{(n+1)}\text{-}R + \cdot R \longrightarrow L_mM^{(n)} + R\text{-}R \quad (\text{or } RH + ROH) \tag{8}$$

For R = CH_3 or CH_2OH the products are the dimers in all systems studied, (ref. 8,15) whereas for R = CO_2^- and $L_mM^{(n)}$ = $[N(CH_2CO_2)_3Fe^{(II)}(H_2O)_2]^-$ the products are CO and CO_2, *i.e.* the latter complex catalyses the disproportionation of CO_2^-.(ref. 16)

It is of interest to note that the alcoholic group in the complexes $[N(CH_2CO_2)_3(H_2O)Co^{(III)}\text{-}CR^1R^2OH]^-$, where R^1,R^2 = H, CH_3, behaves as a relatively strong acid. (ref. 15) The results (ref. 15) indicate that the acidity increases with the tendency towards homolytic decomposition of the cobalt-carbon bond.

In order to study the effect of the central cation on the equilibrium constant of homolytic cleavage of metal-carbon σ bonds, reaction (9) was studied for M =Co, Fe and Mn.

$$[N(CH_2CO_2)_3(H_2O)M^{(III)}\text{-}CH_3]^- \rightleftharpoons [N(CH_2CO_2)_3M^{(II)}(H_2O)_2]^- + \cdot CH_3 \quad (9)$$

The results yield K_8 = 3.7×10^{-7}, $4.\times10^{-4}$ and 8.3×10^{-4} mol·dm^{-3} respectively. (ref. 8) These results seem to suggest that the effect of the nature of the central cation on K_8 is smaller than expected, *i.e.* the difference between the cobalt complex and the other two is relatively small. However one should remember that reaction (-9) involves a loss of a water ligand and therefore $\Delta G°$ for the metal carbon bond dissociation is considerably larger than $\Delta G°_9$. The free energy of reaction (10)

$$[(nta)(H_2O)_2M(II)]^- \rightleftharpoons [(nta)(H_2O)M(II)] + H_2O \quad (10)$$

is not known. However it is reasonable that the effect of the nature of the central cation on $\Delta G°_{10}$ is analogous to that observed for $\Delta G°_{11}$.

$$M(H_2O)_6^{2+} \rightleftharpoons M(H_2O)_5^{2+} + H_2O \quad (11)$$

i.e. that $\Delta G°_{10}(Co(II)) > \Delta G°_{10}(Fe(II)) > \Delta G°_{10}(Mn(II))$. Thus it is reasonable to assume that the metal-carbon bond dissociation energy indeed decreases considerably from $Co^{(III)}\text{-}CH_3$ to $Fe^{(III)}\text{-}CH_3$ and $Mn^{(III)}\text{-}CH_3$ as expected.

The reaction of methyl free radicals with NiL^{2+} was studied, (ref. 12) (where L = 1,4,8,11-tetraazacyclotetradecane). It was found that the mechanism of this process also consists of reaction (3) followed by reaction (8). (ref. 12) As the complex $LNi^{III}\text{-}CH_3$ is relatively stable the addition of a scavenger of methyl free radicals is required for a detailed kinetic analysis. The results indicate that the detailed mechanism of reaction under these conditions involves the following reactions: (ref. 12)

$$L(H_2O)Ni^{(III)}\text{-}CH_3^{2+} \rightleftharpoons LNi^{2+} + \cdot CH_3 \quad K_{12}=9.1\times10^{-8}\ mol\cdot dm^{-3} \quad (12)$$

$$L(H_2O)Ni^{(III)}\text{-}CH_3^{2+} + \cdot CH_3 \longrightarrow LNi^{2+} + C_2H_6 \quad 2k_{13}= 8\times10^{7}\ mol^{-1}dm^3s^{-1} \quad (13)$$

$$O_2 + \cdot CH_3 \longrightarrow \cdot O_2CH_3 \quad k_{14}= 3.7\times10^{9}\ mol^{-1}dm^3s^{-1} \quad (14)$$

$$\cdot O_2CH_3 + LNi^{2+} \longrightarrow L(H_2O)Ni^{(III)}\text{-}O_2CH_3^{2+} \quad (15)$$

In reaction (12), in contrast to reaction (3), the coordination number of the central cation changes from four for the divalent complex to six for the tervalent complex. Thus $\Delta H°$ of reaction (12) is the sum of the nickel- carbon bond dissociation energy and the binding energy of water to the tervalent complex, whereas $\Delta H°$ of reaction (3) is the difference between the metal-carbon bond dissociation energy and the binding energy of water to the divalent complex. This difference might explain the relatively high stability of $L(H_2O)Ni^{(III)}\text{-}CH_3^{2+}$ though the redox potential of the $LNi(H_2O)_2^{3+}/LNi^{2+}$ couple is considerably higher than that of all the other complexes discussed above.

The reactions of $\cdot CH_3$ and $\cdot CH_2C(CH_3)_2OH$ free radicals with $Cu^{(II)}(tspc)^{4-}$ were studied, (where tspc=tetrasulfophthalocyanine).The formation of $(tspc)Cu^{(III)}\text{-}CH_3^{4-}$ and $(tspc)Cu^{(III)}\text{-}CH_2C(CH_3)_2OH^{4-}$ respectively is observed. (ref.17) However the results indicate that the mechanism of decomposition of these two transient complexes is different, only the latter one decomposes *via* homolysis:

$$(tspc)Cu^{(III)}\text{-}CH_2C(CH_3)_2OH^{4-} \rightleftharpoons Cu^{(II)}(tspc)^{4-} + \cdot CH_2C(CH_3)_2OH \quad (16)$$

$$K_{16}= 4\times10^{-5}\ mol\cdot dm^{-3}$$

This result suggests that steric hindrance facilitates homolysis, as has earlier been pointed out for cobalamins and their model compounds. (ref. 18)

The role of the nature of the ligands L in enabling the observation of these transient complexes, and their effect on the homolysis equilibrium constants is not fully understood. Several factors have to be considered:

a. The ligands affect the rate of the ligand exchange reactions; in particular the specific rate of the aquo ligand exchange. A relatively high rate of ligand exchange is required in order that reaction (-3) will compete effectively with other modes of free radical reactions.

b. The ligands change the redox potential of the M(III)/M(II) couple. As reaction (-3) is at least formally an oxidation process, it is expected that the stability of the transient will be enhanced by lowering the redox potential of the central cation.

c. The ligands affect the water-metal bond dissociation energy and thus ΔG° of reaction (3).

d. The ligands cause in some systems steric hindrance which enhances the homolysis equilibrium constants.

The data obtained thus far clearly indicate that pulse-radiolysis is a powerful technique for the determination of metal-carbon homolysis equilibrium constants, mainly for relatively unstable complexes. However the data is far from sufficient for a detailed analysis of the factors affecting the magnitude of these equilibrium constants.

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