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SOLUTION THERMODYNAMIC STUDIES OF TRANSITION METAL ORGANOMETALLIC ANION RADICALS

I. THE ANION RADICALS OF 2,2′-BIPYRIDYLTETRACARBONYL COMPLEXES OF GROUP VIB METALS vs. THE 2,2′-BIPYRIDINE ANION RADICAL

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Summary

The thermodynamic parameters controlling the equilibria of the type bipy$^{\bar{\cdot}}$ + bipyM(CO)$_4$ $\rightleftharpoons$ bipy + bipyM(CO)$_4^{\bar{\cdot}}$, where M equals Cr, Mo or W and bipy stands for 2,2′-bipyridyl, in hexamethylphosphoramide (HMPA) have been determined. The equilibrium constants fluctuates from 400 (M = Cr) to 1200 (M = Mo and W). The large thermodynamic stability of bipyM(CO)$_4^{\bar{\cdot}}$ relative to bipy$^{\bar{\cdot}}$ is favored by the enthalpy and the entropy changes. The enthalpy changes become more negative in the order $Cr < Mo \approx W$ while the entropy changes are more positive in the opposite order, $Cr > Mo \approx W$. These observations are explained in terms of differences in gas phase electron affinities of the neutral compounds, solvation of the corresponding anion radicals and the charge localization in the CO groups of bipyM(CO)$_4^{\bar{\cdot}}$.

Introduction

Several reports concerning the study of transition metal organometallic anion radicals have appeared in the literature [1–19]. The encyclopedic work of Dessy and collaborators have revealed that when a coordination complex of a transition metal is reduced (or oxidized) the locus of high spin density in the radical anion (or cation) may range between occupation of a predominantly ligand orbital and occupation of a predominantly metal orbital [20,21]. The spin densities in some octahedral [22], trigonal bipyramidal [23], and tetrahedral [22] transition metal coordination complex anion radicals are located in molecular orbitals predominantly ligand in character and much of their charge densities are transmitted via the metal to the metal bonded carbonyls. High spin density in the coordinated π ligands [24,25] and in the

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coordinated metal center [26,27] of organometallic anion radicals have been observed by other authors. However, up to now, there is no good correlation between the different types of transition metals and π ligands with spin and charge delocalization.

Several organometallic systems have shown electrochemical and chemical reversibility upon reduction [1]. Furthermore, some systems have evidenced structural reorganization or anion disproportionation upon reduction [12,20,28,29].

These two events, i.e., charge delocalization and/or structural reorganization, may serve as stabilizing factors in organometallic anion formation relative to its corresponding free ligand anion radical. This stability is suggested by the lower half-wave reduction potentials found in complexed ligands relative to the corresponding half-wave reduction potentials of the uncomplexed ligands [22]. The anion radicals of fumarate and cinnamate esters were produced only transiently by flow and electrochemical techniques [23]. However, when complexed to $Fe(CO)_4$, the corresponding anion radical solutions remained unchanged after one week in sealed ampoules [23].

Unstable anion radicals can also be stabilized if produced in the presence of transition metals [2,30,31]. Determining and understanding the thermodynamics of these differences in stability is mandatory.

There are no reports in the literature regarding the thermodynamics of the following type of equilibrium, eq. 1, where L is a π ligand, M′–L represents the

$$\text{M}'\text{–L}^{\dot{-}} + \text{L} \rightleftharpoons \text{M}'\text{–L} + \text{L}^{\dot{-}} \tag{1}$$

organometallic molecule (where M′ stands for the metal plus other ligands besides L) and $L^{\dot{-}}$ and $M'–L^{\dot{-}}$ are the corresponding anion radicals. Knowing the thermodynamic parameters controlling equilibrium 1 as a function of M′ and L, will be very helpful in understanding the differences in stabilities between $M'–L^{\dot{-}}$ and $L^{\dot{-}}$. In the present work we have just initiated this task by determining the thermodynamic parameters controlling equilibrium 2, where bipy stands for 2,2′-bipyridine and M

$$\text{bipy}^{\dot{-}} + \text{bipyM(CO)}_4 \rightleftharpoons \text{bipy} + \text{bipyM(CO)}_4^{\dot{-}} \tag{2}$$

for Cr, Mo or W. In order to minimize ion pairing complications, this study was carried out in HMPA [32].

Results and discussion

Potassium reduction of HMPA solutions of adequate mixtures of 2,2′-bipyridine and $bipyM(CO)_4$ resulted in ESR spectra where serious overlap between the ESR lines of the corresponding anion radicals existed. Thus, equilibrium 2 was subdivided into two convenient equilibria 3 and 4, where An-d_{10} stands for anthracene-d_{10}.

$$\text{bipy}^{\dot{-}} + \text{An-}d_{10} \rightleftharpoons \text{bipy} + \text{An-}d_{10}^{\dot{-}} \tag{3}$$

$$\text{bipyM(CO)}_4 + \text{An-}d_{10}^{\dot{-}} \rightleftharpoons \text{bipyM(CO)}_4^{\dot{-}} + \text{An-}d_{10} \tag{4}$$

The conveniences of utilizing An-d_{10} is the fact that An-$d_{10}^{\dot{-}}$ presents a single ESR line at the modulation amplitude used, leaving most of the ESR lines of the second anion radical free from overlap (see Fig. 2).

In order to be able to evaluate the ratio of the anion radical concentrations the following procedure was utilized, as exemplified by the case of reaction 4 (M = Mo).

First, the anion radical of bipyMo(CO)$_4$ alone was generated and the low resolved ESR spectrum (modulation amplitude of ca. 1 Gauss) was recorded, Fig. 1. The first derivative ESR spectrum was double integrated up to the point depicted by X in Fig. 1. This double integration was performed by digitizing the corresponding area coupled to a numerical integration carried out by a computer. The double integrated area of the complete spectrum was also calculated. The ratio of the area up to point X to the area corresponding to the complete spectrum was found to be a constant, independent of the modulation amplitude [33], i.e., 0.020 ± 0.001.

Upon reduction of a 10^{-3} and 10^{-4} *M* HMPA solution of An-d_{10} and bipyM(CO)$_4$, respectively, with a deficient amount of potassium, the simultaneous ESR spectrum of An-$d_{10}^{\bar{\cdot}}$ and bipyMo(CO)$_4^{\bar{\cdot}}$ was generated, Fig. 2. The same position, X, as that in Fig. 1 was located in this ESR spectrum. The An-$d_{10}^{\bar{\cdot}}$ single line ESR spectrum (peak to peak width of ca. 5 Gauss) was far enough from point X so that the perturbation of the An-$d_{10}^{\bar{\cdot}}$ ESR line upon the double integrated area up

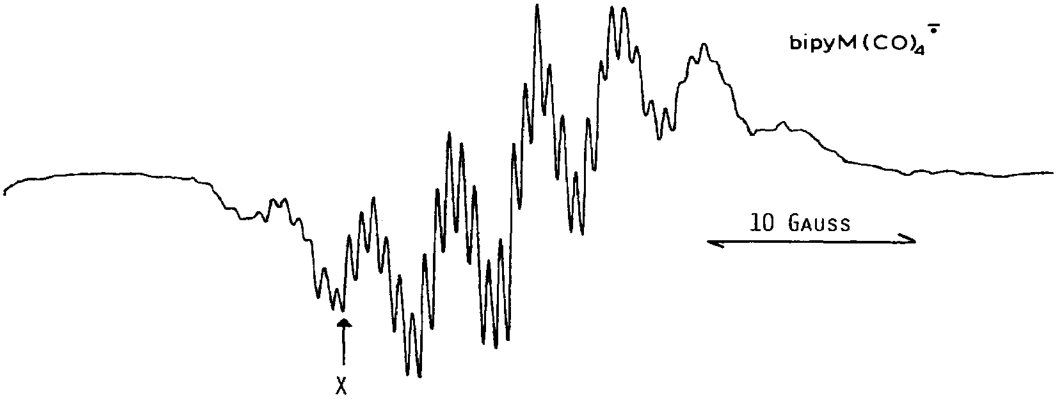


Fig. 1. Low resolved first derivative ESR spectrum of bipyMo(CO)$_4$/K/HMPA. Modulation amplitude of ca. 1 Gauss.

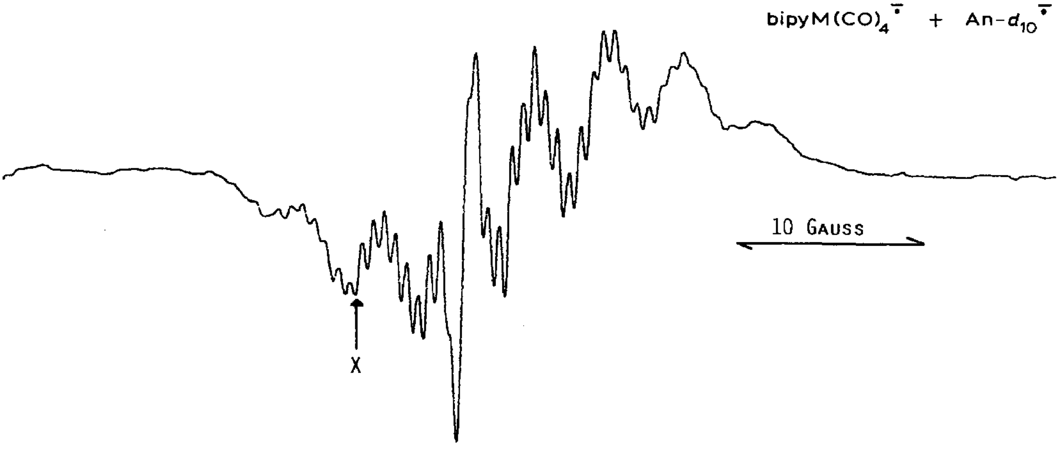


Fig. 2. Low resolved first derivative ESR spectrum of bipyMo(CO)$_4$/An-d_{10}/K/HMPA. Modulation amplitude of ca. 1 Gauss.

to position X (AX) was considered to be negligible. If AX is divided by the constant 0.020, the double integrated area corresponding to bipyMo(CO)$_4^{-}$ is obtained. If this area is substracted from the total simultaneous ESR spectrum, the area corresponding to An-d_{10}^{-} can be obtained. In this manner, the ratio {bipyMo(CO)$_4^{-}$}/{An-d_{10}^{-}} was obtained. The overmodulated area of the simultaneous ESR spectra were compared to that corresponding to a galvinoxyl standard in HMPA and the total spin concentration {An-d_{10}^{-}} + {bipyMo(CO)$_4^{-}$} was determined. From the ratio and the summation of the corresponding anion radical concentrations the actual concentration of each radical species was determined. Upon subtracting the anion radical concentrations from the corresponding initial concentration of the neutral compounds, the equilibrium concentration of the neutral species was obtained. Thus, the equilibrium constant for reaction 4 (M = Mo), K_{eq}, was evaluated, eq. 5. The equilibrium constants corresponding to reaction 3 and to the other reactions type 4 were determined in the same manner. A minimum of eight equilibrium constant determinations were performed for each case.

$$K_{eq} = \{\text{An-}d_{10}\}\{\text{bipyMo(CO)}_4^{-}\}/\{\text{An-}d_{10}^{-}\}\{\text{bipyMo(CO)}_4\} \tag{5}$$

The equilibrium constants corresponding to equilibrium 2 is equal to the product

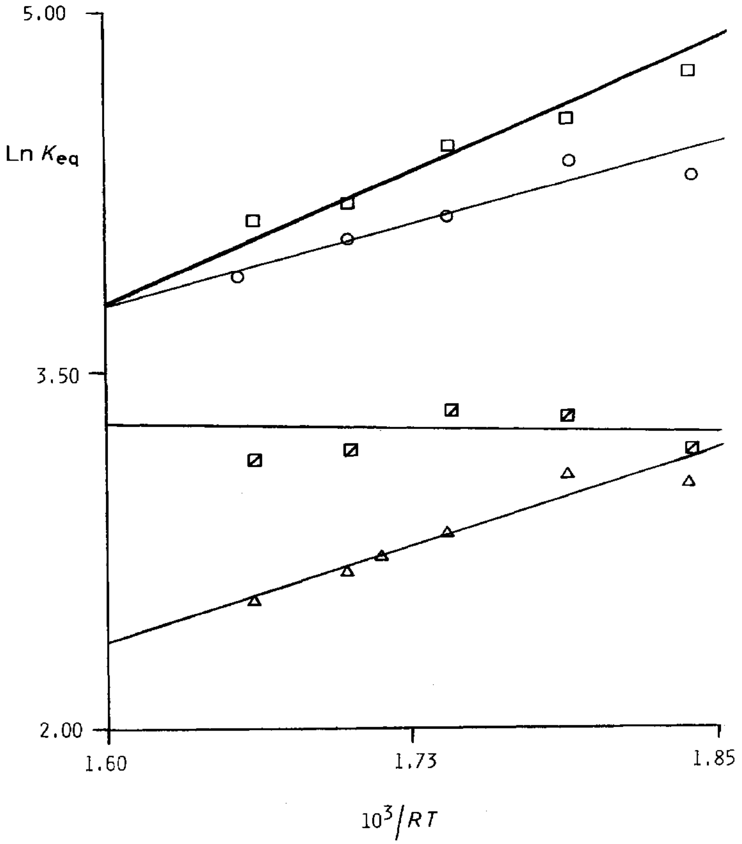


Fig. 3. Representative Van't Hoff plots corresponding to equilibria 3 (Δ) and 4 (▨ Cr, □ Mo, ○ W).

$K_{eq.3} \times K_{eq.4}$. The ΔH^0 values corresponding to equilibria 3 and 4 and, thus, that corresponding to equilibrium 2 were determined by at least three different Van't Hoff plots of $\ln K_{eq}$ vs. $10^3/RT$ for each case, Fig. 3. The thermodynamic parameters are tabulated on Table 1.

The $K_{eq.2}$ values are large, as expected, indicating the greater stability of bipyM(CO)$_4^{\bar{\cdot}}$ as compared to bipy$^{\bar{\cdot}}$. This greater stability if favored by both, the enthalpy and the entropy changes although the entropy changes are surprisingly small.

It has been previously observed that the carbonyl force constants of bipyM(CO)$_4$ are lowered upon reduction [24]. This has been explained in terms of electronic charge delocalization into the π anti-bonding orbitals of the carbonyl groups via the metal center. This localization of charge into the carbonyl groups (mostly into the oxygen atoms) stabilizes the transition metal complex anion radical since more charge is localized in a larger number of electronegative atoms as opposed to bipy$^{\bar{\cdot}}$.

The thermodynamic parameters ΔH^0 and ΔS^0 can be explained, basically, in terms of the solvation of the anion radicals and/or the gas phase electron affinities of the neutral species.

The small entropy changes can possibly be attributed to a slightly more ordered solvation of bipy$^{\bar{\cdot}}$ versus that corresponding to bipyM(CO)$_4^{\bar{\cdot}}$.

The enthalpy changes are due to differences in the gas phase electron affinities between bipyM(CO)$_4$ and bipy, and differences in the heats of solvation of the corresponding anion radicals (assuming essentially the same heats of solvation of the neutral compounds when compared to those expected for the anion radicals). The experimental data show that a summation of these two processes (the solution electron affinity) is more exothermic in the case of the transition metal complex than in the case of the free ligand 2,2′-bipyridyl.

From Table 1 it is observed that an increase in the exothermicity of reaction 2 occurs when going from Cr to Mo and stays practically unchanged when going from Mo to W. A similar behavior is also observed for the change in the entropy of reaction 2. The entropy change become less positive when going from Cr to Mo but stays practically unchanged from Mo to W. These two effects produce an analogous variation in $K_{eq.2}$.

Dessy and Wieczorek found the carbonyl groups situated *trans* to the ligand as being more affected than the carbonyl groups *cis* to the ligand upon reduction [24].

TABLE 1 [a]

THERMODYNAMIC PARAMETERS CONTROLLING EQUILIBRIA 3, 4 AND 2

Equilibrium	M	$K_{eq}{}^{b}/10^2$	ΔH^0 (kcal mol^{-1})	ΔS^0 (eu)
3	–	0.15 ± 0.02	-1.3 ± 0.4	1
4	Cr	0.25 ± 0.06	-0.7 ± 0.2	8
4	Mo	0.77 ± 0.18	-2.5 ± 0.7	0
4	W	0.77 ± 0.25	-1.9 ± 0.4	2
2	Cr	4 ± 1	-2.0 ± 0.2	9
2	Mo	12 ± 3	-3.8 ± 0.8	1
2	W	12 ± 5	-3.2 ± 0.6	3

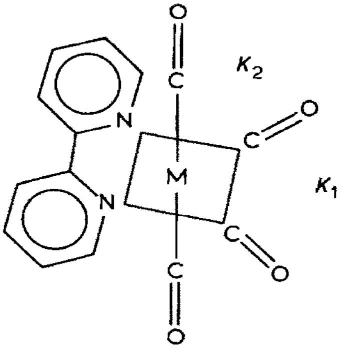
[a] Potassium is the counterion. [b] 25°C.

TABLE 2

CARBONYL FORCE CONSTANTS[a] OF bipyM(CO)$_4^-$ [24]

Metal	K_1	K_2	ΔK_1[b]	ΔK_2[b]
Cr	14.03	15.20	0.50	0.34
Mo	14.09	15.15	0.66	0.35
W	14.07	15.16	0.69	0.48

[a] The force constants are in mdyn/Å. [b] $\Delta K = K$ (neutral) $- K$ (reduced).



Thus, the changes in the carbonyl force constants which are *trans* to the ligand (ΔK_1) are larger than the corresponding changes in the force constants of the carbonyl which are *cis* to the ligand (ΔK_2) upon reduction, Table 2.

The differences in ΔK_1 when going from Cr to Mo (0.66–0.50 = 0.16) is greater than from Mo to W (0.69–0.66 = 0.03). The opposite occurs between the ΔK_2 values when going from Cr to Mo (0.35–0.34 = 0.01) as compared to going from Mo to W (0.48–0.35 = 0.13). This reveals that essentially the same amount of charge is going into the *trans* carbonyls in the Mo and W complex anion radicals upon reduction whereas less charge is transferred to the *trans* carbonyls in the Cr complex anion radical as compared to the Mo or W complex anion radicals. The opposite occurs regarding the *cis* carbonyl groups. If this observation is related to our work, it could explain the similarities between the thermodynamic parameters controlling reaction 2 when Mo and W are involved and the disimilarities of these two systems with that corresponding to Cr. Apparently, solvation effects on the *trans* carbonyls and/or delocalization of charge into these carbonyls contributes more to the solution electron affinities of bipyM(CO)$_4^-$ than the same processes occurring in the *cis* carbonyls. However, more data is needed before this preferential charge delocalization or any other event is utilized in explaining this curious trend in the stability of bipyM(CO)$_4^-$ upon change of the transition metal.

Experimental

The compounds bipyM(CO)$_4$ were synthesized as described in the literature and characterized by IR spectroscopy [4,23]. 2,2′-Bipyridine was purchased from Aldrich Co. and sublimed out at vacuum (10^{-6} torr). Anthracene-d_{10} was purchased from Aldrich and stored in a desiccator until used. HMPA, purchased from Aldrich, was distilled from calcium hydride and stored over molecular sieves.

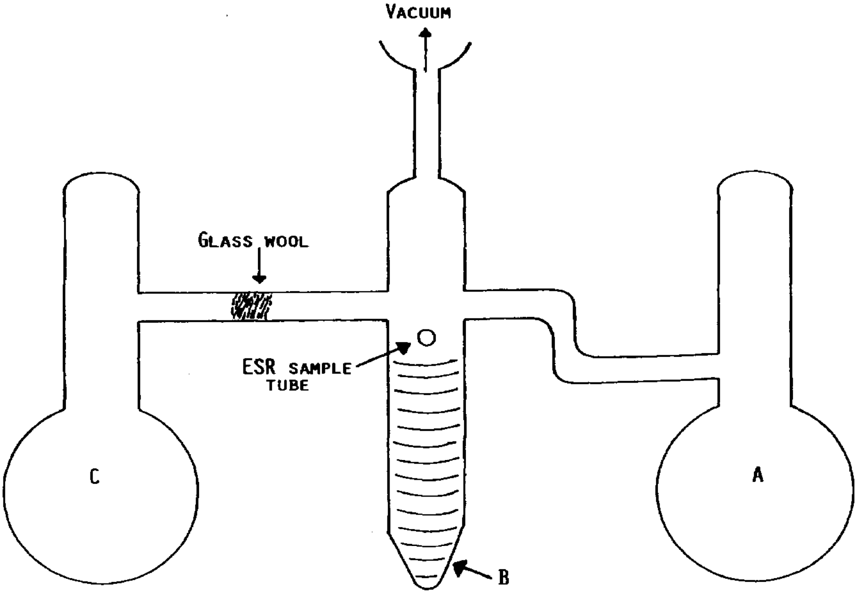


Fig. 4. Apparatus utilized in the potassium reduction of the compounds studied in this work.

The anion radicals were generated via potassium reduction under high vacuum as follows. An all-glass apparatus was used for the anion radical generation, Fig. 4. A weighed amount of the two different neutral compounds were added into the calibrated tube B and HMPA distilled, from potassium, from bulb A into bulb B. Subsequently, bulb A was sealed off from the apparatus. The HMPA solution was then transferred to a deficient amount of K in bulb C. This amount of K was weighed to be less than the amount of moles of the less concentrated compound in solution. After completed dissolution of the potassium, the solution was homogenized in concentration throughout bulbs B and C and an ESR sample tube was sealed off from the apparatus. This procedure was repeated with new proportions of the corresponding compounds until a simultaneous ESR spectra was observed for the corresponding anion radicals.

ESR spectra were recorded on the X-band of a Varian E-9 ESR spectrometer. Constant temperature in the ESR cavity was maintained with a Varian V-4557 variable temperature controller calibrated against a copper-constantan thermocouple.

Anion radical concentrations were determined using the dual cavity ESR technique comparing the areas under the over modulated spectra with that of a standard galvinoxyl radical solution in THF [34].

The first derivative ESR spectra were doubly integrated by digitizing the lines coupled with a numerical integration carried out by a computer.

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