

A STUDY OF INTRAMOLECULAR ELECTRON EXCHANGE IN COPPER-RADICAL COMPLEXES INVOLVED IN CATALYSIS USING ESR SPECTROSCOPY

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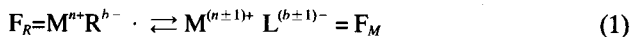
Abstract—ESR simulation and experimental results have been presented to show that transition metal-radical complexes can engage in intramolecular electron exchange and that the exchange gives rise to ESR asymmetric line broadening effect. Depending on the relative concentration of the redox-exchange pair, metal or radical-like spectrum can be obtained. Simulation results show that a metal-radical complex can be masked by its redox counterpart upto a relative concentration of 1:2 at a modest exchange rate of 3×10^8 /s. Asymmetric line broadening was predicted to occur upon such metal-radical complexation. Experimentally, a pronounced ESR asymmetric line broadening was observed for Cu(II) complexes of various redox-active ligands. Cu(II) complex with redox-inert ammonia, however, showed no such evidence. Ligand displacement experiments established the reversibility of metal-radical complexation and the associated ESR line broadening.

Key words: Intramolecular Electron Exchange, Cu(II) Complex, Redox-ligand, ESR Spectroscopy, Asymmetric Line Broadening

INTRODUCTION

There is much indirect evidence in the literature [Tkac et al., 1971; More et al., 1984; Razuvaev et al., 1978; Brown and Hemphill, 1979; Hanaya and Iwaizumi, 1992] which suggests that free radicals and transition metals can form complexes and there is now a growing tendency to look for the involvement of transition metal-radical complexes in organo-metallic and metal catalyzed reactions [Halpern, 1986, 1989; Brown, 1980; Connelly and Geiger, 1984].

Intramolecular electron exchange within the transition metal-radical complex may take place due to the abilities of transition metals and ligands to engage in reversible redox reactions. The exchange process would permit a continuous distribution of metal-like and radical-like forms of a metal complex and add stability to a metal-radical complex as a special case of a electron delocalization. The intramolecular exchange can be formulated generally as:



where F_R and F_M denote, respectively, the radical-like and metal-like forms of the paramagnetic complex in which the unpaired spin is localized on the radical and on the transition metal; M^{n+} and R^{b-} denote, respectively, the transition metal ion with n positive charges and the radical with b negative charges; $M^{(n+1)+}$ denotes the corresponding metal ion formed by a one-electron oxidation ($M^{(n+1)+}$) or reduction ($M^{(n-1)+}$) of M^{n+} , and $L^{(b+1)-}$ denotes the corresponding ligand formed by a one-electron reduction ($L^{(b+1)-}$) or oxidation ($L^{(b-1)-}$) of R^{b-} .

The intermediary of transition metal-radical complexes in many free-radical and electron-transfer reactions has been implicated in kinetic findings such as a rate change or a shift in product distribution. However, direct and definitive evidence such as that which may be provided by ESR spectroscopy is limited. In this study, ESR simulation and experimental findings are presented to show that transition metal-radical complexes can engage in intramolecular exchange and give rise to asymmetric line broadening in their ESR spectra, which can serve as a useful tool detecting the transition metal-radical complexes in solution.

A COMPUTER MODEL SIMULATION OF ESR SPECTRA

A computer simulation was performed using a computer package, DYNESR, developed by J. N. Gex [Gex et al., 1987] to show the possible consequences of intramolecular electron exchange on the ESR spectra of transition metal-radical complexes. A binary exchange equilibrium represented by the Eq. (1) was considered, and for simplicity, attention was given to a single spin system (i.e., $S=1/2$). The unpaired spin is presumed to reside with either R^{b-} in F_R or $M^{(n+1)+}$ in F_M , and M^{n+} is presumed to be diamagnetic. F_R and F_M of the exchange pair are each presumed to have an intrinsic set of ESR parameters (i.e., g -value, hyperfine constants, and line width) characteristic of a radical or a paramagnetic transition metal ion. For the purpose of demonstration, F_R was assumed to have a non-metal nuclear spin of $1/2$ with a hyperfine coupling of 15 G and F_M has a metal nuclear spin of $3/2$ with a hyperfine coupling of 75 G. The forward exchange rate constant

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k_f is varied over a broad range to include the limiting cases of slow and fast exchanges. The exchange equilibrium constant $K(=k_f/k_r=[F_M]/[F_R])$ and the difference in the intrinsic g -values of F_M and F_R are also varied over a wide range to show their effects on the ESR features.

EXPERIMENTAL APPARATUS AND PROCEDURE

ESR runs were performed on a Bruker ER 200, X-band spectrometer. Copper(I) radical complexes were generated in situ using suitable combination of copper(I or II), redox ligands, and solvents (water, methanol, chloroform, and methylene chloride). Sodium hydroxide, ammonia, and sodium ethoxide were used as base in aqueous and organic systems, respectively, to effect deprotonation of acidic ligands and to promote radical formation. Crown ether (15-crown-5) was used in organic systems to suppress ion-pair formation between sodium ion and radicals. Reagent grade chemicals were used without further purification. ESR spectra were obtained using a flow technique. Reagent solutions, which were kept under a He atmosphere, were mixed and monitored in a flat cell in the ESR cavity. For a relatively stable copper-radical complex, such as copper-o-semiquinone, a recirculation flow technique was also used. The latter permitted a convenient and quantitative determination of the intensity recovery in radical displacement experiment. The ESR spectrometer was calibrated using DPPH.

RESULTS AND DISCUSSION

Simulated ESR results corresponding to different sets of parameters listed in Table 1 are shown in Fig. 1. It is seen in Fig. 1a that only in the limit of slow exchange ($k_f < 10^7/s$)

corresponding to a low temperature or a large kinetic barrier, F_R and F_M appear as two distinct entities. Except for this slow exchange limit, the simulated spectrum shows only the exchanged average of F_R and F_M as if it were a single entity. The g -value (g) and metal hyperfine constant (A) of the exchange-averaged spectrum are given by the weighted averages of the intrinsic properties of F_R and F_M , i.e.,

$$D_{av} = X_M D_M + X_R D_R = X_M(D_M - D_R) + D_R \quad (2)$$

where D denotes the g -value or metal hyperfine constant, X , the fractional distribution of F_R or F_M , and subscripts R , M , and av refer to F_R and F_M , and their exchanged average, respectively. The simulated results show the masking effect of intramolecular exchange. Depending on whether the relative concentration F_M/F_R is greater or less than unity, F_R may be masked by F_M or vice versa. The simulated spectra in Fig. 1b-1h and 1i-1j correspond, respectively to a large and small presence of F_M ; they all show the masking effect of exchange averaging on the minor component. Fig. 1c shows that at an intermediate exchange rate ($k_f = 3 \times 10^8/s$), the signals for F_R and F_M begin to merge into one. Above this exchange rate, F_R can be masked by F_M at a relative concentration as high as 1:2.

Moreover, except for the limiting cases of slow and fast exchange (1a and 1b), the simulated spectra all show asymmetric line broadening as a distinctive feature; intramolecular exchange is shown to cause the hyperfine lines to have different line widths and peak heights over a broad range of exchange rate ($3 \times 10^8 < k_f < 2 \times 10^{11}/s$). Intramolecular redox exchange is also known to cause proton NMR line broadening [Nielson and Wherland, 1986].

Fig. 1d and 1e show that an increase in the relative pres-

Table 1. Parameter values used to generate the simulated spectra presented in Fig. 1

For the intramolecular electron exchange, $F_R \xrightleftharpoons[k_r]{k_f} F_M$ the relative distribution is given by $\frac{x_M}{x_R} = \frac{x_M}{(1-x_M)} = \frac{k_f}{k_r} = K$

Fig.	Species i	Assumed g -value	Assumed coupling constant A , G	Assumed line-width, G	Assumed mole fraction, X_i	Assumed exchange constant k_f , 1/s
a	F_R	2.003	$A_H=15$	1	0.33	1×10^7
	F_M	2.13	$A_{Cu}=75$	20	0.67	
b	F_R	2.003	$A_H=15$	1	0.33	2×10^{11}
	F_M	2.13	$A_{Cu}=75$	20	0.67	
c	F_R	2.003	$A_H=15$	1	0.33	3×10^8
	F_M	2.13	$A_{Cu}=75$	20	0.67	
d	F_R	2.003	$A_H=15$	1	0.33	2×10^9
	F_M	2.13	$A_{Cu}=75$	20	0.67	
e	F_R	2.003	$A_H=15$	1	0.10	2×10^9
	F_M	2.13	$A_{Cu}=75$	20	0.90	
f	F_R	2.13	$A_H=15$	1	0.10	2×10^9
	F_M	2.003	$A_{Cu}=75$	20	0.90	
g	F_R	2.003	$A_H=15$	1	0.10	2×10^9
	F_M	2.027	$A_{Cu}=75$	20	0.90	
h	F_R	2.003	$A_H=15$	1	0.10	2×10^9
	F_M	2.003	$A_{Cu}=75$	20	0.90	
i	F_R	2.003	$A_H=15$	1	0.99	2×10^9
	F_M	2.13	$A_{Cu}=75$	20	0.01	
j	F_R	2.003	$A_H=15$	1	0.90	2×10^9
	F_M	2.13	$A_{Cu}=75$	20	0.10	

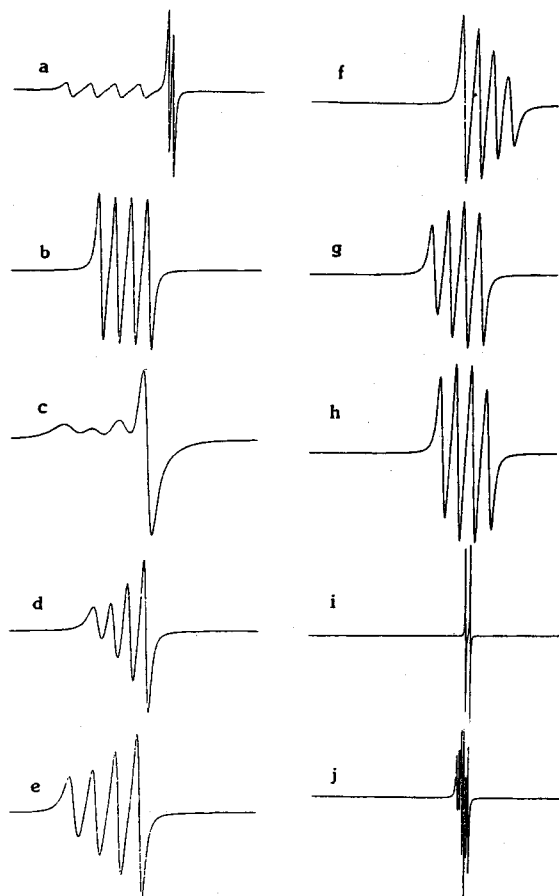


Fig. 1. Results of a parametric simulation study showing the effects of intramolecular exchange on the ESR features of a pair of transition metal complexes. Parameter values corresponding to the different simulated spectra are listed in Table 1.

(a) exchange pair appearing as separate and distinct species in the slow exchange limit, (b) exchange pair appearing as an exchange-averaged entity but showing no asymmetric line broadening in the fast exchange limit, (c) exchange pair beginning to merge at an intermediate exchange rate, (d) exchange pair appearing as an exchange-averaged entity at a normal exchange rate—the F_R form of the exchange pair is masked by the F_M form even at a F_R/F_M ratio as high as 1:2 and sign of asymmetric line broadening, (e) exchange pair appearing as an exchange-averaged entity at a normal exchange rate—symmetric line broadening is clearly evident and the spectrum is F_M -like due to a larger presence of F_M relative to F_R , (f) a variation of case (e) showing a switch in the divergent direction of asymmetric line broadening due to a switch in the relative field positions of F_M and F_R , (g) a variation of case (e) showing the dependence of asymmetric line broadening on the difference in the g -values of F_M and F_R , (h) a variation of case (e) showing that with little or no difference in the g -values of F_M and F_R , asymmetric line broadening may appear in the form of broader edge lines and narrower interior lines, (i) a variation of case (e) showing asymmetric line broadening in a radical-like spectrum, i.e., with F_R in a larger presence than F_M , (j) variation of case (i) showing the projection of the metal's hyperfine coupling on the radical-like spectrum.

ence of F_M causes the exchange-averaged spectrum to become more F_M -like i.e., the metal hyperfine constant and the g -value move closer to the intrinsic parameters of F_M in accord with the Eq. (2). Fig. 1d and 1f show that a switch in the relative field position of F_M to F_R reverses the direction of asymmetric line broadening. Fig. 1d, 1g and 1h show that the asymmetric line broadening becomes less pronounced as the difference in the g -values of F_M and F_R gets smaller. When F_M and F_R have the same or very close g -values, asymmetric line broadening appears in the form of broad edge lines and narrow interior lines (Fig. 1h). Fig. 1i shows that when F_R has a dominant presence of F_M , the exchange-averaged spectrum becomes F_R -like, but asymmetric line broadening is still evident in the spectrum for as small as a presence of F_M as 1%. Fig. 1j shows that intramolecular exchange can project metal splitting onto a radical-like spectrum, even when F_R itself does not have any intrinsic metal splitting.

Eq. (2) implies that the average metal hyperfine constant (A_{av}) and g -value (g_{av}) of the exchange pair should correlate linearly, i.e.,

$$A_{av} = \frac{(A_M - A_R)}{(g_M - g_R)} g_{av} + \frac{(g_M A_R - g_R A_M)}{(g_M - g_R)} = m \cdot g_{av} + c \quad (3)$$

$$\text{where } m = \frac{(A_M - A_R)}{(g_M - g_R)}$$

$$c = \frac{(g_M A_R - g_R A_M)}{(g_M - g_R)}$$

Eq. (3) was derived from the A - and g -forms of Eq. (2) by eliminating the mole fraction. It is stipulated that as the relative distribution of F_M and F_R is varied with a shift in the exchange equilibrium, the exchange-averaged parameters, A_{av} and g_{av} should correlate linearly. Since the exchange equilib-

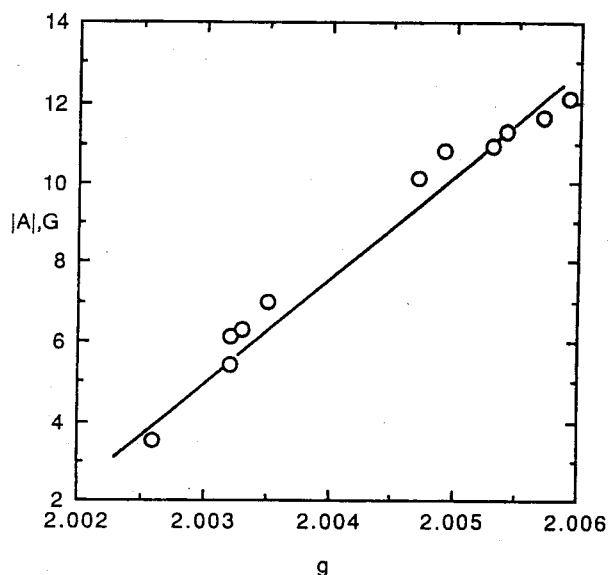


Fig. 2. Literature data showing the correlation between the shifts in g -value and copper hyperfine constant of copper(1)-3,5-di-tert-butyl-o-semiquinone complex in the presence of different co-ligands in tetrahydrofuran [Razuvaev et al., 1978].

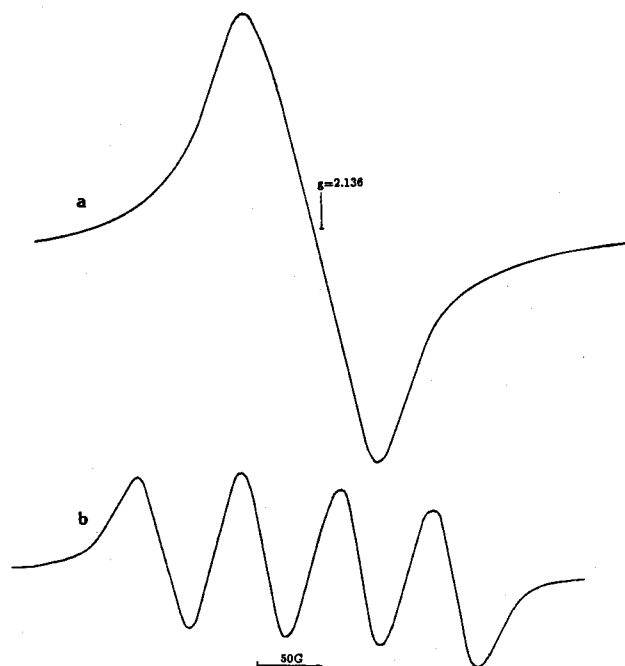


Fig. 3. ESR spectra of (a) copper(II) and (b) copper(II)-ammonia complex in aqueous solutions.

rium can be shifted by varying the temperature, solvent, or a substituent group in the radical ligand, it follows that Eq. (3) may provide a quantitative test of the intramolecular exchange model for the transition metal-radical complexes. Fig. 2 shows the shifts in g -value and copper hyperfine constant of Cu(I)-3,5-ditertbutyl-o-semiquinone complex in the presence of different co-ligands, taken from Razuvaev et al. [1978], and it is clear that such a linear correlation was experimentally observed very closely. Much the same trend was reported for semiquinone complexes of molybdenum [Hanaya and Iwaizumi, 1991].

Fig. 3 shows a broad, featureless ESR spectrum of aqueous Cu(II) (a), and in the presence of redox-inert ammonia, aqueous Cu(II) gave a well-resolved four-line spectrum that shows no apparent sign of asymmetric line broadening (b). According to Fig. 4, on the other hand, the combination of a redox-active ligand with copper (I or II) consistently produced a well-resolved spectrum that shows asymmetric line broadening (a-h). The only attribute in common among the different ligands in the second group of complexes that distinguishes them from ammonia is the redox propensity, and evidently, taken in conjunction with the known ability of copper to engage in redox exchange, the redox-active ligands can each undergo an intramolecular electron exchange with Cu(II) to form the corresponding ligand radicals. The same ESR signal that was generated by copper (I) addition to an o-semiquinone solution could also be generated by copper (II) addition to a catecholate solution, and it is consistent with the known abilities of catecholate and o-semiquinone to engage in reversible redox reactions. Fig. 5a shows a ESR spectrum of o-semiquinone radical anion generated by adding catechol (=0.01 M) to a dry dichloromethane solution that contained sodium ethoxide (=0.02 M) and crown ether (=0.05 M). The

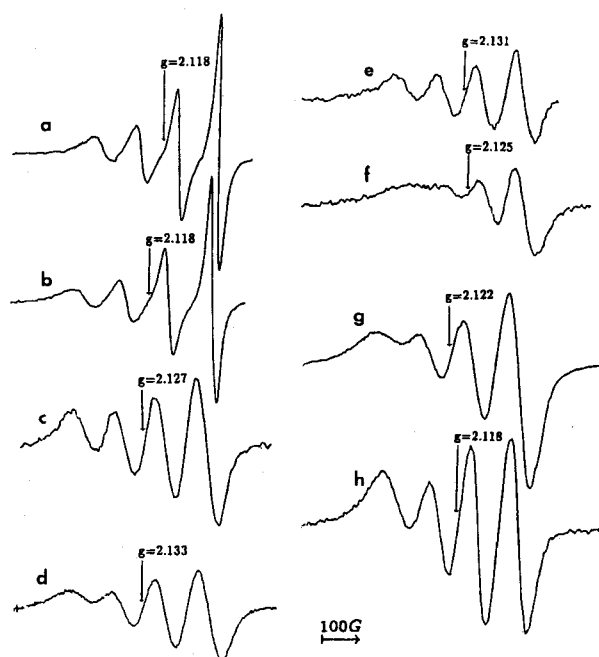
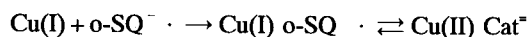


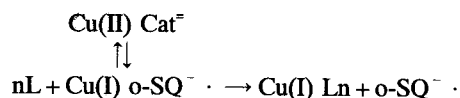
Fig. 4. Asymmetric line broadening in the ESR spectra of copper complexes in solutions at room temperature.

(a) copper(I)-o-semiquinone in water. [Cu(I)]=0.0002 M, [o-SQ]=0.0001 M, [NaOH]=0.001 M. (b) copper(II)-catecholate in methanol. [Cu(II)]=0.0006 M, [catechol]=0.020 M, [NaOEt]=0.025 M. (c) copper(I)-o-chloranil in methanol. [Cu(I)]=0.0003 M, [o-chloranil]=0.004 M. (d) copper(II)-N₂H₄ in water. [Cu(II)]=0.10 M, [N₂H₄]=2.5 M, [HCl]=0.5 M. (e) copper(II)-ascorbate in water. [Cu(II)]=[ascorbic acid]=0.006 M, [NH₃]=0.05 M. (f) copper(II)-glutathione in water. [Cu(II)]=[glutathione]=0.003 M, [NH₃]=0.05 M. (g) copper(I)-tert-butylhydroperoxide in methanol. [Cu(I)]=0.02 M, [t-butylhydroperoxide]=2.0 M, [NH₃]=0.05 M. (h) copper(II)-o-phenylenediamine in water. [Cu(II)]=0.005 M, [o-phenylenediamine]=0.010 M.

solution was continuously circulated through the ESR cavity by a peristaltic pump while being kept under a He atmosphere. Upon adding copper(I) chloride (=0.01 M), a new asymmetrical signal downfield from the free semiquinone signal is observed in 5b, which can be assigned to Cu(I)-semiquinone complex and its exchange counterpart, Cu(II)-catecholate complex, i.e.,



Deaerated triphenylphosphite was then added to the solution to provide a stoichiometric excess (=0.1 M) over copper, and the spectrum 5c was then obtained. Evidently, triphenylphosphite caused the displacement of the semiquinone radical from Cu(I), which disrupted the intramolecular exchange equilibrium. The changes can be described as follows ;



where L denotes triphenylphosphite. The quantitative recovery of the semiquinone radical (=90 %) demonstrates the reversi-

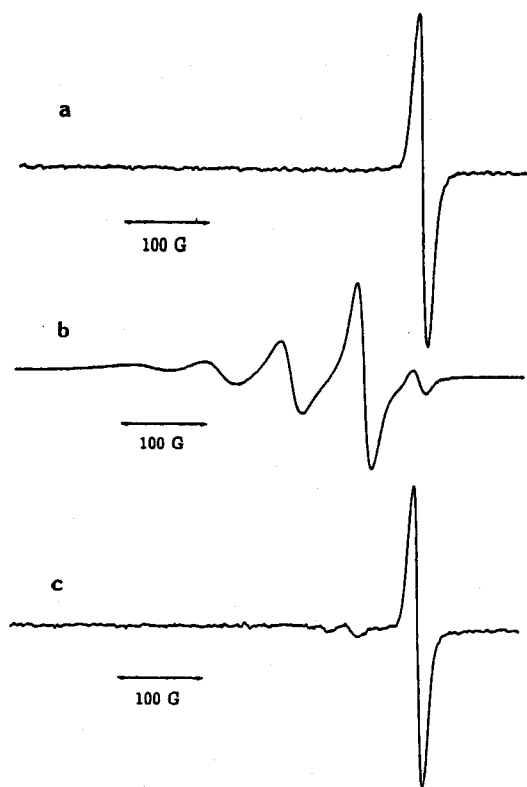


Fig. 5. The reversibility of copper(I)-o-semiquinone complexation.

- (a) dichloromethane solution containing o-semiquinone radical anion alone. (b) addition of copper(I) chloride to (a). (c) addition of excess triphenylphosphite to (b).

bility of the metal-radical complexation and the associated line broadening, and this validates the fact that the presence of a metal-radical complex can be unmasked by the use of a displacement ligand.

CONCLUSIONS

ESR simulation, experimental results, and literature evidence have been presented to show that transition metal-radical complexes can engage in intramolecular electron exchange and that the exchange can give rise to ESR asymmetric line broadening. Simulation results show that a transition metal-radical complex can be masked by its redox counterpart up to a relative concentration of 1:2 at a modest exchange rate of 3×10^8 /s. Asymmetric line broadening, however, provides a clear indication of the masked presence of the radical complex and its involvement in intramolecular exchange. Cu(II) complexes of various redox-active ligands showed all significant ESR asymmetric line broadening, whilst Cu(II) complex with redox-inert ammonia showed no such evidence. Ligand displacement experiments established the reversibility of metal-radical complexation and the associated ESR line broadening.

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