

Probing photochemical reactions with assistance of magnetic fields

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ABSTRACT

Magnetokinetic effects in photoredox reactions of Co(III) complexes have been analyzed in terms of changes caused by a magnetic induction on the rates of elementary processes: the excited state relaxations and the cage escape and recombinations of radical-ion pairs. MFE in these ground and excited state redox reactions are rationalized in terms of the radical-pair mechanism and a quantum-mechanical model of outer-sphere electron transfer reactions. Aspects of these mechanisms are illustrated with recent experimental observations of MFE in redox reactions of high and low spin

Fe(II) complexes.

INTRODUCTION

It has been known for some time that rates of thermal and photochemical reactions involving transition metal coordination complexes can be changed when they are exposed to an external magnetic induction, B . [1 - 3] Rates of photochemical and photophysical processes initiated in ligand field, dd, and charge transfer states, CT, exhibit such magnetokinetic effects, MKE. [2, 3]

One example is the effect of the magnetic induction

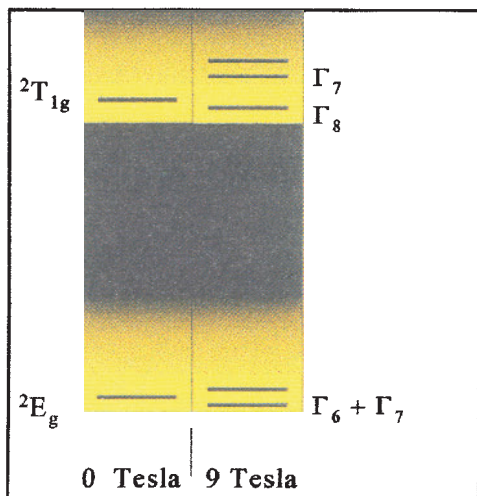
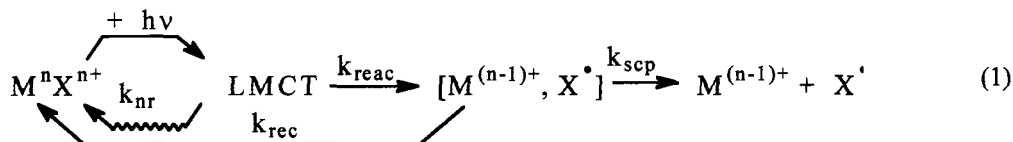
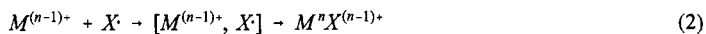


Figure 1. Effect of a 9 Tesla magnetic induction on the lowest lying doublet excited states of a Cr(III) complex.

on the luminescence of Cr(III) complexes.[4] Changes in the Boltzman populations of sublevels with ${}^2T_{1g}\{t_{2g}^3\}$ parentage due to the Zeeman effect, and in the intrinsic rate constants of radiationless relaxation account for experimentally observed MKE, Fig. 1. Radiationless relaxations rate constants of dd and CT states appear to increase monotonically with B, i.e., one approaching the quadratic dependence on B that is expected when MKE are principally dictated by a Zeeman interaction.[5] Rates of product formation from the homolytic bond dissociations that initiated in ligand to metal charge transfer excited states, LMCT, eq. 1,



can be expected to reflect such a dependence of the radiationless rate constant, k_{nr} , on B. The magnetic field effect, MFE, on the rate of product formation will also comprise changes on the rates of primary product recombination, k_{rec} , and separation, k_{sep} , that can be induced by the magnetic induction. Since radical-ion pairs, $[\text{M}^{(n-1)+}, \text{X}^\bullet]$, mediate reactions of radicals with coordination complexes, eq. 2,



the time-resolved study of the MKE in these processes provides a useful tool for the interpretation of similar effects in photoredox reactions, eq. 1. Progress made in the investigation of MKE in this type of redox reaction and in outer-sphere electron transfers between coordination complexes will be discussed in this work.

EXPERIMENTAL

Flash photolysis experiments for the study of MFE in redox reactions of Fe(II) complexes were

carried out with an apparatus and procedures described elsewhere.[6] The reaction cell was placed in the cavity of a solenoid. Steady state magnetic inductions of 0 to 7 Tesla and a 2 ms lifetime were generated by the discharge of a capacitor bank on the RL circuit. The Fe(II) complex, $[\text{Fe}(\text{Me}_2\text{-}[15]\text{pyaneN}_5)](\text{ClO}_4)_2$, was prepared and purified by a literature procedure.[7] $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$, R. G. Smith, was purified by recrystallization with NaClO_4 from its aqueous solution. Other materials were reagent grade and used without purification.

RESULTS AND DISCUSSION

MFE in the LMCT Photochemistry of Co(III) Complexes: The geminate products of the bond photodissociation are said to be "spin correlated," i.e., the spin label of such a radical or radical-ion

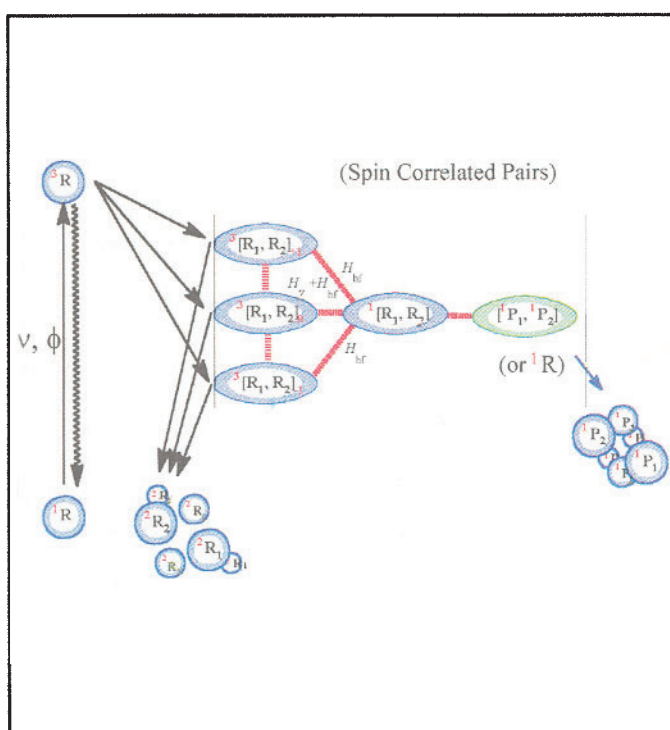


Figure 2. Pathways for the evolution of the spin (inside brackets) in a geminate radical pair prepared by decay from a triplet excited state. Dissociation of the triplet and escape of the radicals are indicated with black arrow. Conversion to singlet products is indicated with a blue arrow. Some of the perturbations mixing given sublevels are shown by the side of each path.

pair is the same one of the excited state where they have originated.[1, 8] This is shown in Fig. 2, where radical pairs $^3[\text{R}_1, \text{R}_2]_j$ in a sublevel $j=\pm 1, 0$ of the triplet state, are generated from a triplet excited state, ^3R . The changes of the spin state of the pair over a period of time can be conveniently described by the time dependent perturbation theory of quantum mechanics. In Fig. 2, the curly brackets give a graphic description of the "spin evolution" under various perturbations having finite non-diagonal matrix elements. For example, the evolution from the

triplet sublevels of the pair, $^3[R_1, R_2]_{\pm 1}$, to the singlet, $^1[R_1, R_2]$, is allowed under mixing of such states by the hyperfine coupling, H_{hf} . Mixing between $^3[R_1, R_2]_0$ and $^1[R_1, R_2]$ is also fostered by the Zeeman perturbation, H_z . The mixing by a B-independent perturbation, spin-orbit and/or hyperfine couplings, is effective while the magnitude of the energy gap, ΔE , between levels that are being mixed is equal to or less than the magnitude of the perturbation, e.g., $\Delta E \leq H_{\text{hf}} = \langle 3, \pm 1 | H_{\text{hf}} | 1 \rangle$. When the magnetic field-induced separation of the levels obeys the opposite relationship, e.g., $\Delta E > H_{\text{hf}} = \langle 3, \pm 1 | H_{\text{hf}} | 1 \rangle$, such mixing is no longer possible and $^3[R_1, R_2]_{\pm 1}$ pairs experience transformations different from the conversion to the reactive singlet. By contrast, mixing of $^3[R_1, R_2]_0$ and $^1[R_1, R_2]$ by the B-dependent Zeeman mechanism is reinforced by the magnetic induction. Because this Zeeman mechanism is proportional to the difference in the g values of the reactants, eq. 3,

$$\mathcal{H}_z = \beta h^{-1}(g_1 - g_2) \cdot B (\hat{S}_{1z} - \hat{S}_{2z}) \quad (3)$$

\hat{S}_{iz} = z-projection of the spin operator
for each reactant in the pair

B = magnetic induction

g_i = g-factor for each reactant in the pair

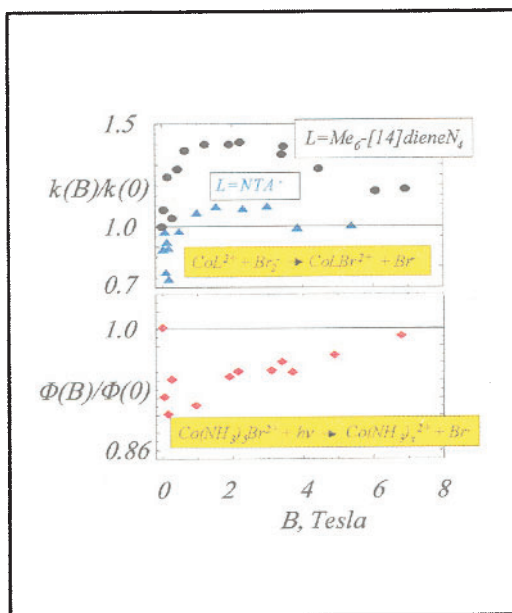


Figure 3 Dependence of the normalized reaction rate constant, $k(B)/k(0)$, on the magnetic induction, B, (top two curves) in reactions of high and low spin Co(II) complexes. The bottom curve shows the dependence on B of the normalized quantum yield, $\Phi(B)/\Phi(0)$, in 248 nm photolyses of $Co(NH_3)_6Br_2$.

its contribution to MFE in reactions between radicals and coordination complexes can be very large. In addition to the "spin evolution" problem, several models for the "statistics of encounters" have been considered for photochemical reactions. Indeed, pairs in $^3[R_1, R_2]_{\pm 1}$ that fail to achieve the correct spin state may undergo reencounters while keeping memory of their geminate spin state; with each reencounter providing a new opportunity for

conversion to the $^1[R_1, R_2]$. Other pairs that escape to the bulk will react later as "spin uncorrelated pairs." They will be considered below in connection with outer-sphere electron transfer reactions. MFE in the charge transfer photochemistry of Co(III) complexes, Fig. 3, appear to be determined by those interactions of the magnetic induction with radical-ion pairs that were described above. [5, 9, 10] Notice that a rapid change of quantum yield for $B < 1$ Tesla and a diminished effect for $B > 1$ Tesla cannot be rationalized in terms of the expected monotonic change of the rates of the excited state radiative and radiationless relaxation when magnetic inductions are increased from 0 to 8

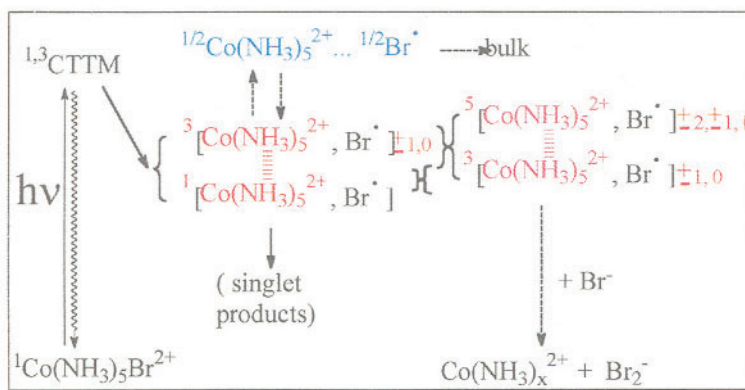


Figure 4 Possible pathways for the evolution of the spin in pairs generated from singlet and triplet LMCT excited states. Low spin Co(II) (red) forms triplet and singlet pairs. Some sublevels are mixed with sublevels triplet and quintuplet pairs with high spin Co(II) (magenta). Partners (blue) with memory of the pair's spin state may undergo reencounters or escape.

shown by the quantum yield of radical Br^\bullet formation, $\phi(B)/\phi(0)$, in photolyses of $Co(NH_3)_5Br^{2+}$. In order to rationalize MFE in the charge transfer photochemistry of $Co(NH_3)_5Br^{2+}$ the mechanism of Fig. 2 can be recast into the scheme in Fig. 4. Perturbations that mix states of the radical-ion pair, i.e., the triplet of low spin parentage with quintet and triplet of the high spin parentage, will increase the rate of dissociation in $Co(NH_3)_x^{2+}$ ($x \leq 5$) and Br^\bullet . Only the low spin singlet pairs are rapidly consumed by recombination processes somewhere in manifolds of the singlet products. The Zeeman mechanism, in the manner shown in Fig. 2 for the mixing of $^3[R_1, R_2]_0$ and $^1[R_1, R_2]$, will accelerate

Tesla. Reactions of radicals with low and high spin Co(II) complexes exhibit rapid changes of their rate constants with magnetic inductions for $B < 1$ Tesla. [10] In this regard, MKE in a reaction of

the low spin $Co(Me_6- [14] diene N_4)^{2+}$ complex, Fig. 3, are near the reverse of those

the rate of recombination. This is the magnetokinetic behavior exhibited by reactions between radicals and low spin Co(II) complexes, e.g., like one shown for the reaction of $\text{Co}(\text{Me}_6\text{-[14]dieneN}_4\text{)}^{2+}$ in Fig. 3.

MFE in Reactions of Radicals with Coordination Complexes: It has been noted above that, in the mechanisms of Fig. 2 and 4, radical-ion pairs may separate before they react. These species keep no memory of the initial spin state when they react, sometimes in the same manner of geminate pairs, at

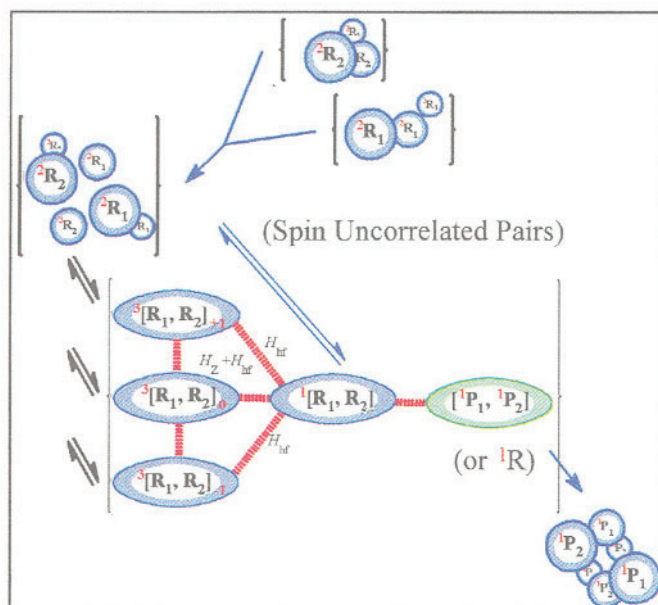


Figure 5. Pathways for the evolution of the spin in radical pairs form in random encounters (double arrows) and conversion of the singlet pair in singlet products.

longer times. A similar situation exists when two reactants are mixed, e.g., in the stop-flow experiment shown in Fig. 5, or in radiochemically generated reactants. Radical-ion and radical pairs formed under this regime are regarded as "spin uncorrelated pairs" because one reactant has no prior knowledge of the other reactant's spin state. Unless spin-orbit interactions induce large differences among the zero-field energies of the spin states in the pair, each

sublevel has the same Boltzman weigh. In the example of Fig. 5, one quarter of the pairs will be in a given triplet sublevel and one quarter in the singlet state. Since singlet pairs are rapidly consumed in the product's singlet manifold, the rate constant of the reaction, $k(\text{B})$, is determined by a factor, $\text{F}(\text{t}, \text{B})$, that measures the "spin evolution" toward the appropriate spin state and a statistics of reencounter, $\text{W}(\text{t})$, as shown in eq. 4.

$$k(B) = \int_0^{\infty} W(t) \cdot F(t, B) dt \quad (4)$$

Counteracting contributions from the B-independent perturbations, e.g., hf or LS couplings, and the Zeeman perturbation may give a typical extreme to $k(B)$. Either a monotonic growth or decrease of $k(B)$ with B is observed when one or the other type of interaction dominates. Good examples of these expectations are provided by the contrasting magnetokinetic behavior of low and high spin Co(II)

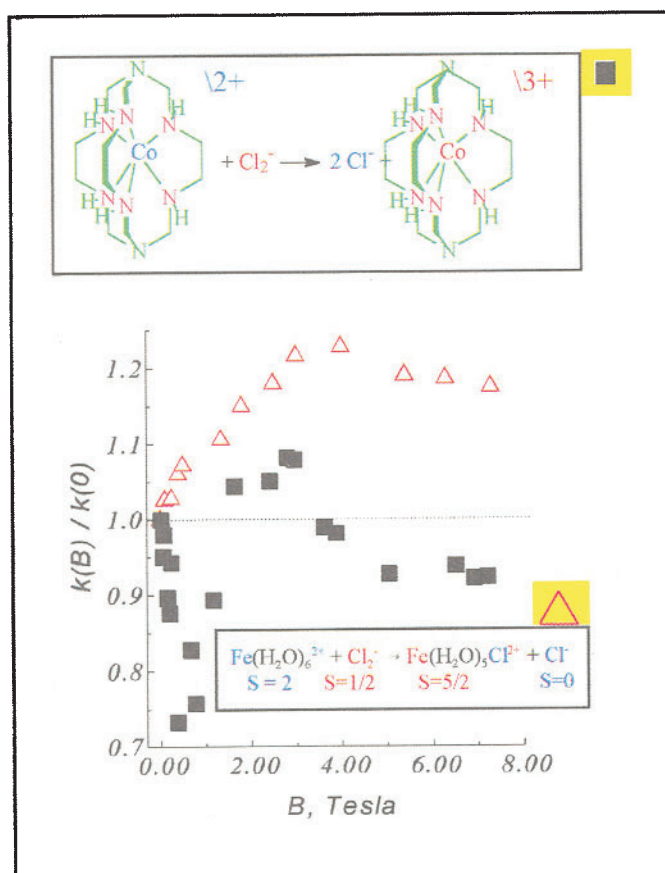


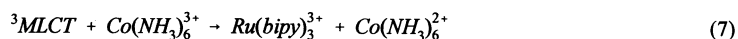
Figure 6. MKE in reactions of high spin Co(II) and Fe(II) complexes with an inorganic radical.

complexes below 3 Tesla, Fig. 3, 6. The same can be said for the oxidation of high spin $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ by Cl_2^- , Fig. 6. A monotonic growth of $k(B)$ with B could be indicative of a very strong Zeeman mechanism, i.e., relative to the B-independent perturbations. This situation is caused by a large difference between the g values of the reactants, e.g., $g \sim 3.4$ for Fe(II) and $g \sim 2.0$ for Cl_2^- . Features in the magnetokinetic behavior of reactions between radicals and coordination complexes, Fig. 3 and 6, with magnetic inductions above 3 Tesla cannot be explained only in terms of the

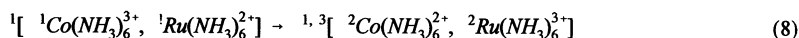
isotropic interactions considered above. Some perturbations induce transitions among the spin

sublevels over short periods, i.e., the "autocorrelation time." This phenomenon is based on the theory of relaxation and requires a magnetic induction fluctuating at the appropriate frequency.[11] In organic radicals the relaxation is caused by rotation, i.e., the spin-rotation interaction.[1, 11, 12] Relaxations caused by anisotropy of the g-tensor (anisotropic electronic Zeeman) and the anisotropic hyperfine (dipolar interaction) must also be considered in the mechanism, i.e., the "relaxation mechanism." All contributions to the MFE on the reaction rate make $k(B)/k(0)$ approach a limiting value when B is greater than 5 Tesla. This functional behavior becomes evident in Figs. 3 and 6 for Co(II) and Fe(II) reactions.

MFE in Ground and Excited: State Electron Transfer Reactions: Recent studies have shown the existence of MFE in outer-sphere electron transfer reactions involving one excited state reactant, i.e., the metal to ligand charge transfer state MLCT in eq. 5-7.



The investigation of MKE may be complicated, however, by competing processes with B-dependent rates, eq. 6, 7. Problems presented by parallel reactions are more easily circumvented when the studies are conducted on thermal electron transfer reactions. The detection of MFE in the reduction of the low-spin Co(III) complex, eq. 8,



shows that MKE in outer-sphere electron transfers must be rationalized in terms of the models (semiclassical or quantum mechanical) developed for these processes rather than those (above)

applied to reactions of radical and radical-ion pairs.[13] Indeed, encounter pairs are formed in only in a singlet state which is correlated to the successor complex singlet state. Contrary to the

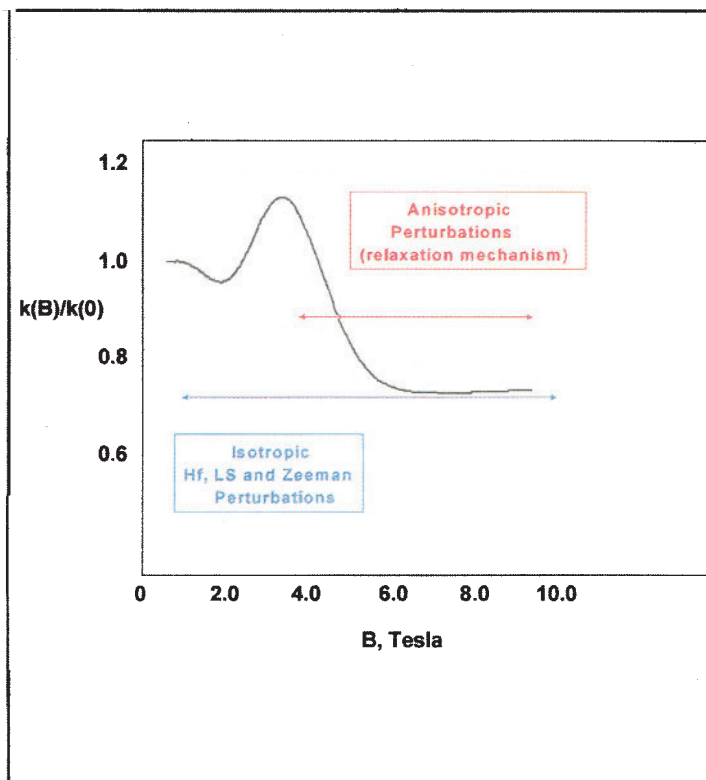


Figure 7. Dependence of the normalized rate constant, $k(B)/k(0)$, on B for the reduction of $\text{Co}(\text{NH}_3)_6^{3+}$ by $\text{Ru}(\text{NH}_3)_6^{2+}$, eq. 5. Color coded horizontal bars span ranges of B where contributions to the MFE from isotropic perturbations and the relaxation mechanism respectively dominate.

experimental observations, the model discussed above for MFE in radical-coordination complex reactions predicts no dependence of the rate constant on B . A theoretical interpretation of MKE has been rationalized on a modification of the quantum mechanical treatment for electron transfers.[14] Terms (perturbations) reflecting interactions of the spin (nuclear and electronic) and electronic angular momentum with one another and with a magnetic induction were appended to the exchange Hamiltonian of the model. Separation of the

isotropic and anisotropic contributions to the Hamiltonian successfully accounted for the functional dependence of $k(B)$ on B in various reactions of $\text{Co}(\text{II})$ complexes, Fig. 7. Extremes in the plot of $k(B)/k(0)$ vs. B are the result of the field-induced separations and crossings of various spin levels. This model is presently being applied to newly recorded MFE in electron transfer reactions of $\text{Fe}(\text{II})$ complexes. Typical MKE in the reactions of a high and a low spin $\text{Fe}(\text{II})$ complex are shown in Fig. 8. In the oxidation of the high spin macrocyclic complex, the functional dependence of $k(B)$ on B

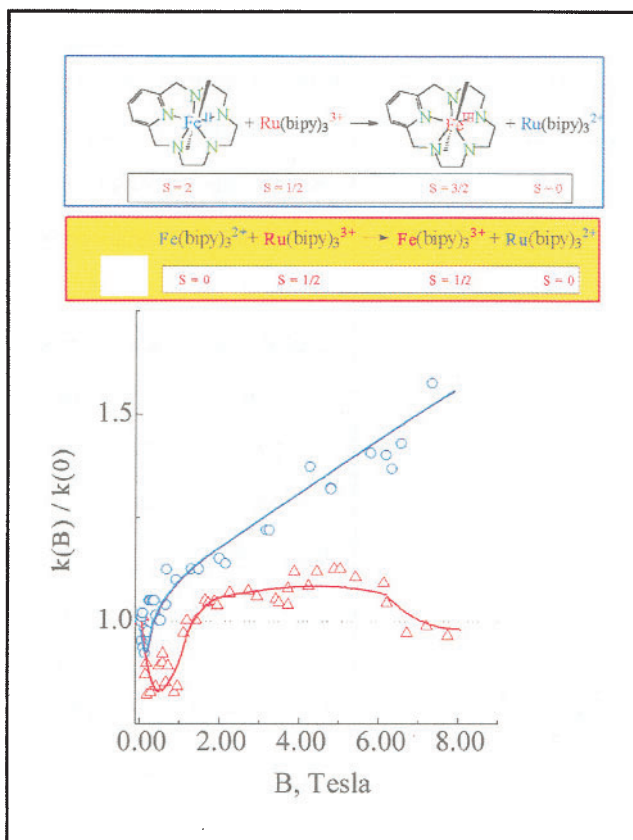


Figure 8. MKE in outer-sphere electron transfer reactions of high and low spin Fe(II) complexes. The insets show reactions and the spin of each reactant and product.

resembles those, shown above, for high-spin complexes when $B < 3$ Tesla, Fig. 3 and 6. This behavior can be rationalized by assuming counter posed contributions of the B-independent mechanisms, e.g., LS and hf couplings, and the Zeeman mechanism respectively decreasing and increasing the rate of the reaction. Spin levels of the pair must be also very symmetrically distributed, i.e., the sextet manifold with respect to the quartet manifold, in the encounter complex. Such a condition will eliminate the type of level crossings that lead to extremes in plots of $k(B)/k(0)$ vs. B in Fig. 7.

The continuous growth above 5

Tesla can be related to the vibronic-induced relaxations into the quartet manifold. While this feature has not yet been experimentally observed in reactions of Co(II) complexes, it was predicted nevertheless by the model for MFE in outer-sphere electron transfers. The effect of the magnetic induction on the rate of oxidation of the low-spin $\text{Fe}(\text{bipy})_3^{2+}$ by $\text{Ru}(\text{bipy})_3^{3+}$, Fig. 8, is remarkable because the doublet spin states of reactant and product pairs are correlated. Either adiabaticity must be introduced by mixing excited states into the ground state or a fraction of the Fe(II) population could be in a spin state, e.g., the low ligand field 3T_1 or 5T_2 states, different from the singlet ground state.[15] The two reaction pathways are illustrated in Fig. 9. In (a), LS coupling mixes the excited

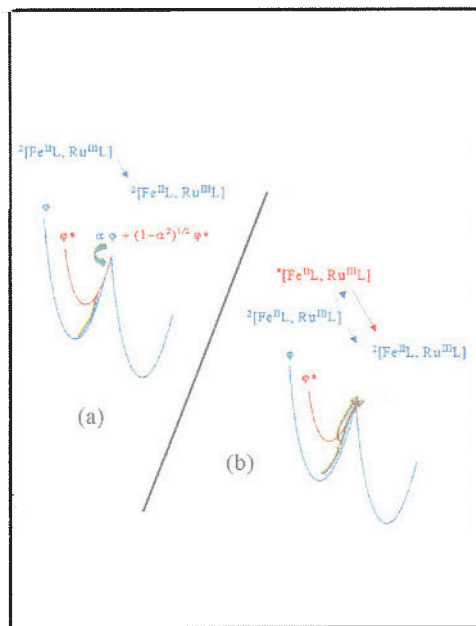


Figure 9. Possible participation of excited states in reactions of low spin Fe(II) complexes. In (a), ground and excited states are mixed along the reaction coordinate (horizontal axis). Two separate potential surfaces, one for the ground state and other for the excited state, are considered in (b).

states and the ground state at a reaction coordinate domain where energy gaps are equal to or smaller than the off diagonal matrix element. The type of first order wave function shown in Fig. 9 must be used in the description of the encounter complex electronic state which is no longer a doublet. Evolution of the spin among the new levels accounts for the experimentally observed MFE. The process in (b) has a fraction of the Fe(II) population reaching an excited state, eg. 5T_2 or 3T_1 in O_h symmetry.[15] This crossover may occur either through an adiabatic jump between surfaces, assisted or not by collisions with the other reactant in the pair, or by thermal equilibrium between two populations. A jump between surfaces in (b) or the state mixing in (a) give a more realistic explanation

of the MFE in the $Fe(bipy)_3^{2+}$ reaction. Indeed, these mechanisms do not suffer the limitation imposed by a large energy gap between states, i.e., one which makes the population of the upper state too small for the size of the observed MFE.

CONCLUSIONS

The experimental observations presented above indicate that MKE are a common phenomenon in thermal and photochemical reactions involving transition metal coordination complexes. In some type of processes, i.e., outer-sphere electron transfers, MFE must be rationalized on the basis of a modified semiclassical or quantum-mechanical model; one that is different from the radical-pair mechanism that has successfully accounted for such effects in reactions between radicals and coordination complexes. Since MKE have been found in a variety of reactions involving Co, Ni, Mn and Fe complexes, it is almost certain that they will be also observed in some biological relevant processes of transition metal metalloenzymes.

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