Magnetokinetic Effects in Reactions of Br_2^- and $CH_3^{\bullet}$ Radicals with $Ni(Me_2pyo[14]trieneN_4)^{2+}$: Ligand Interchange-Imposed Restrictions on the Reactants Reencounter Probability

G. Ferraudi

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

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Magnetic field effects in reactions of $CH_3^{\bullet}$ and Br_2^- radicals with $Ni(Me_2pyo[14]trieneN_4)^{2+}$ were investigated under magnetic inductions, B, between 0 and 7 T by flash photolysis. The dependences of the normalized rate constants, $k(B)/k(0)$, on B do not conform to the model where the spin motion, Zeeman, and hyperfine and spin−orbit interactions are combined with free reencounters of radical-ion pairs. The experimental observations were better described when the dynamic-probability function was an exponential. The reasons for the observed magnetokinetic behavior in reactions of $Ni(Me_2pyo[14]trieneN_4)^{2+}$, i.e., restrictions imposed by the dynamics of ligand interchange, are discussed.

Introduction

Several studies have shown that the rate of the redox reactions between radicals and (substitution labile) transition metal complexes is controlled by the interchange of a coordinated ligand by the radical.[1−6] Indeed, it has been proposed that free radicals behave in many reactions with transition metals as incoming nucleophile ligands. Since the dissociation of the bond between the ligand and the transition metal, e.g., Mn^{II}, Co^{II}, Ni^{II}, makes a larger contribution to the activation energy than bond formation to the radical, the mechanism has been termed a dissociative interchange, I_d.[1,2] Magnetokinetic effects, MKE, on redox reactions of Ru, Co, and Mn complexes were previously investigated.[3−8] Several steps, eqs 1−3,

$$\underset{\text{bulk species}}{M^{II}L(H_2O)} + X_2^- \rightleftarrows \underset{\text{radical-ion pair}}{[M^{II}L(H_2O), X_2^-]} \tag{1}$$

$$(X_2^- = Cl_2^-, Br_2^-)$$

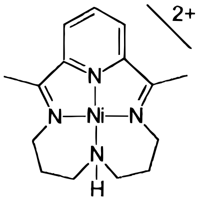
$$[M^{II}L(H_2O), X_2^-] \rightleftarrows \underset{\text{substitution product}}{[M^{II}L(X_2^-), H_2O]} \tag{2}$$

$$[M^{II}L(X_2^-), H_2O] \rightarrow \underset{\text{charge-transfer product}}{[M^{III}LX, X^-]} \tag{3}$$

must be considered when labile coordination complexes react with radicals under any given magnetic induction. Association of the reactants in a radical-ion pair, eq 1, precedes the ligand−radical interchange, eq 2, and displacement of charge, eq 3, to form the final product.[9] A limiting mechanism results when the charge-transfer reaction, eq 3, is faster than the ligand interchange, eq 2. Since the rate of product formation is determined by the rate of eq 2, reactions obeying such a condition are said to have a "substitution-controlled rate".

Although the ligand interchange is expected to be adiabatic, i.e., obeys the conservation of the total electronic angular momentum,[3] no such momentum conservation ensues for the charge-transfer step, eq 3. Under the conditions of the limiting mechanism considered above, the momentum conservation implies that only radical-ion pairs, eq 1, prepared in eigenstates that are correlated with the state of the product, eq 3, will lead to reactive substitution products, namely those that are capable of undergoing the charge-transfer transformation.[3,5−8] It is commonly assumed that evolution of the spin in the radical-ion pair bares resemblance to a similar process of a pair of radicals trapped in the solvent cage. Hence, magnetic field effects (MFE) in the rate of Mn^{II} and Co^{II} reactions were rationalized in terms similar to those of the radical-pair mechanism.[10−12] By contrast to processes with substitution-controlled rates, the charge transfer will be the rate-determining step when evolution of the spin is compelled to occur in the substitution product, eq 2.

To make an allowance for multiple encounters between partners of the radical-ion pair, an intrinsic feature of the radical-pair mechanism, two assumptions must be made. The interchange of ligands, eq 2, must be labile for a rapid fluxion between the radical pair and the substitution products. Also, the equilibrium in eq 2 must not be displaced toward the substitution product to such an extent that, in a kinetic sense, the process becomes a sink. Departures from these conditions will make MKE in these reactions different from the one exhibited by reactions among free radicals. Recent literature reports,[1a,b] based on the volume of activation of these processes, appear to indicate that departures from these conditions could be expected in reactions of radicals with Ni^{II} macrocyclic complexes. This concern was addressed in this work by investigating the effect of the magnetic induction on the rate of oxidation of a triplet Ni^{II} complex (**I**), by $CH_3^{\bullet}$ and Br_2^- radicals.



(I)

$Ni(Me_2\text{-}pyo[14]trieneN_4)^{2+}$

Experimental Section

1. Kinetic Measurements. Flash irradiations, $\lambda_{exc} = 249$ nm, of the complex $Co(NH_3)_5Br^{2+}$ in aqueous acidic solutions, pH ≈ 3−5, of 0.01 M NaBr were used for the photogeneration

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TABLE 1: Rate Constants for the Oxidation of $Ni^{II}(Me_2pyo[14]trieneN_4)^{2+}$ by Radicals

oxidizing radical	k (M^{-1} s^{-1})	medium conditions[a]
$(SCN)_2^{-}$ [b]	1.4×10^9	pH 4, $I = 10^{-3}$ (NaSCN)
Br_2^{-} [b,c]	1.8×10^9	pH 3, $I = 10^{-2}$ (NaBr)
Br_2^{-} [c]	1.6×10^9	pH 4, $I = 10^{-3}$ (NaBr)
$CH_3^{\bullet}$ [c]	3.2×10^9	pH 4, $I = 10^{-3}$ ($NaClO_4$)

[a] Ionic strength, I, adjusted with a given electrolyte indicated between parentheses. [b] Value in ref 25. [c] This work.

of the anion radical, eq 4,[3,13,14]

$$Co(NH_3)_5Br^{2+} + h\nu \xrightarrow{H^+, Br^-} Co^{2+} + 5NH_4^+ + Br_2^- \quad (4)$$

The methyl radical was photogenerated, eq 5, by 249 nm photolyses of $CH_3Co(dimethylglyoximate)_2OH_2$, anion dimethylglyoximate = DH, in deaerated acidic, pH 4, solutions.[13,15]

$$CH_3Co(DH)_2OH_2 + h\nu \rightarrow Co(DH)_2 + CH_3^{\bullet} \quad (5)$$

Concentrations of the radical scavenger, $Ni(Me_2pyo[14]trieneN_4)^{2+}$ (**I**) were adjusted to such values that made kinetically insignificant the disproportionation of Br_2^- and dimerization of $CH_3^{\bullet}$. Rate constants were calculated by least squares fitting to second-order or pseudo-first-order reaction kinetics. The procedure for the determination of $k(B)/k(0)$, i.e., the ratio of the reaction rate constants respectively measured under magnetic inductions $B \neq 0$ and $B = 0$, and the flash photolysis equipment used for such measurements have been described in earlier studies.[3]

2. Materials. $[Co(NH_3)_5Br]Br_2$ [16] and $CH_3Co(DH)_2OH_2$ [17] were prepared and purified according to a literature procedure. Aldrich $ClCo(DH)_2py$ was purified by a procedure recommended in the synthesis of the material.[17] The $[Ni(Me_2pyo[14]trieneN_4)](ClO_4)_2$ was available from a previous work.[18] Other materials, NaBr, $HClO_4$ and $NaClO_4$, were reagent grade and used without further purification.

Results

1. Reactions of $Ni(Me_2pyo[14]trieneN_4)^{2+}$ with Br_2^- and $CH_3^{\bullet}$. Although a majority of the Ni^{II} macrocyclic complexes in aqueous solutions are diamagnetic or a mixture of singlet and triplet states, $Ni(Me_2pyo[14]trieneN_4)^{2+}$ is one exception with a $^3B_{2g}$ ground state in aqueous solutions.[19-23] The kinetics of oxidation of this complex by various halide and pseudohalide radical anions, e.g., Br_2^- in eq 6,

$$Br_2^- + Ni^{II}(Me_2pyo[14]trieneN_4)^{2+} \rightarrow Br^- + Ni^{III}(Me_2pyo[14]trieneN_4)\,Br^{2+} \quad (6)$$

have been previously investigated.[24] In these reactions, Table 1, a fragment of the radical anion or the radical itself is attached to the spin-paired Ni^{III} product whose ground state is a $^2A_1$.[22,23] A similar experimental observation was made in this work when $Ni(Me_2pyo[14]trieneN_4)^{2+}$ reacted with flash photochemically generated $CH_3^{\bullet}$ radicals, eq 7:

$$CH_3^{\bullet} + Ni^{II}(Me_2pyo[14]trieneN_4)^{2+} \xrightarrow{t} Br^- + Ni^{III}(Me_2pyo[14]trieneN_4)\,(CH_3)^{2+} \quad (7)$$

The reaction, followed by means of the product formation at $\lambda_{ob} = 380$ nm, has a rate constant $k = 3.2 \times 10^9$ M^{-1} s^{-1} in 10^{-4} M $HClO_4$. Rate constants for the Ni^{II} reactions in Table 1 show a minimal dependence on the radical redox potential. In this regard, these processes, eqs 6 and 7, like those of Mn^{II} and Co^{II} complexes,[1,3] must have substitution-controlled rates or closely approach to this limiting mechanism.

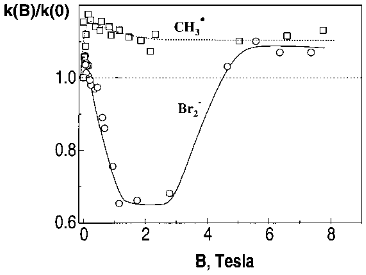

Figure 1. Dependences of the reaction rate on the magnetic induction B for reactions of $Ni(Me_2pyo[14]trieneN_4)^{2+}$ with $CH_3^{\bullet}$, □, and Br_2^-, ○, radicals. The rate constant, $k(B)$, measured under an induction B is normalized with respect to the rate constant at a zero field, $k(0)$. Medium conditions are indicated elsewhere in the text and in Table 1.

2. MKE on the Reaction Rates. The rate constants, $k(B)$, for the oxidation of $Ni(Me_2pyo[14]trieneN_4)^{2+}$, eqs 6 and 7, were measured with samples immersed in a steady magnetic induction, B, equal to or smaller than 7 T. Values of the rate constants, Figure 1, measured with inductions $B > 0$, i.e. $k(B)$, differ considerably from those determined in the absence of the field, i.e., $k(0)$. It must be noted that in both reactions the rate constants increase with magnetic induction for $B \leq 0.1$ T. However, the sense of the MKE on the rate constant for the Br_2^- reaction, eq 6, is reversed in the region $1 < B < 0.1$ T. Another change of the MKE sense takes place at larger magnetic inductions, $B > 2$ T, and raises the value of the rate constant above the zero-field value.

3. Reaction Probabilities. In a zero-order approximation, the eigenstates of $[Ni(Me_2pyo[14]trieneN_4)^{2+}, R^{\bullet}]$ pairs, $R^{\bullet} = CH_3^{\bullet}$ or Br_2^-, were constructed as a multiplication among pure triplet spin and pure doublet spin eigenfunctions of each species in the pair, eq 8:[4,11,12]

$$\langle\phi^i| = \langle\xi^i\,(L, M_L, S, M_S)|\langle\zeta^i\,(I, M_I)| = \langle\xi_A\zeta_A|\langle\xi_B\zeta_B| \quad (8)$$

The subscripts A and B will respectively identify the Ni^{II} complex and the radical throughout the rest of this work. The ξ and ζ functions are, respectively, the spin–orbit and the nuclear spin components of each wavefunction. An electronic wavefunction ξ_A was build with an appropriate set of atomic d orbitals and pure triplet spin functions in accordance to literature reports.[23,25-27] In the wavefunction for the i state of the pair, (L, M_L, S, M_S) denote quantum numbers for the electronic spin and angular momenta and (I, M_I) for the nuclear spin.

In accordance with literature models,[4,11,12] the time-dependent wave function for the ion-radical pair can be expanded:

$$\phi_{RIP}(t) = \sum_{i=1}^{6} C_i(t)\langle\phi^i| = \sum_{i=1}^{6} C_i(t)\langle\xi^i|\langle\zeta^i| \quad (9)$$

The electronic wavefunctions, $\langle\phi^i|$, for the doublet ($i = 1, 2$) and quartet states ($i = 3-6$) of the Ni^{II}-radical pair were described in eq 8. If H_{RIP} denotes the Hamiltonian of the radical-ion pair,[4,11,12] the time dependence of such a function is given in eq 10:

$$i\hbar\frac{\partial\phi_{RIP}(t)}{\partial t} = H_{RIP}\phi_{RIP}(t) \quad (10)$$

The isotropic Zeeman and isotropic hyperfine coupling terms that connect different levels of the pair were included in this Hamiltonian. The exchange interaction was ignored because, based in a previous work,[3a] it is expected to be negligible for this type of radical-ion pair. The probability for the radical-ion pair to be in a given state was calculated by solving six coupled differential equations:

$$\frac{\partial C_i(t)}{\partial t} = \frac{i}{\hbar}\sum_{k=1}^{6} C_k(t)\langle \xi^k \zeta^k\rangle, \quad i = 1...6 \qquad (11)$$

with initial conditions $C_i(0)$.

Terms in the pair's Hamiltonian, H_{RIP}, accounting for isotropic Zeeman and hyperfine couplings must now be considered before a rationale is provided for MKE in eqs 6 and 7. The operator for the Zeeman term η_z is customarily expanded in a sum of two operators, eq 12,

$$\hat{\eta}_z = \hat{\eta}_z^{\ +} + \hat{\eta}_z^{\ -}$$

where

$$\hat{\eta}_z^{\ \pm} = \frac{\beta}{2\hbar}(g_A \pm g_B)(\hat{S}_{zA} \pm \hat{S}_{zB}) \qquad (12)$$

acting upon diagonal, $\hat{\eta}_z^{\ +}$, and off-diagonal, $\hat{\eta}_z^{\ -}$, matrix elements. The spin operators, $\hat{S}_A$ and $\hat{S}_B$, respectively refer to the metal complex and the radical, and operations over the electrons in Ni^{II} were described later by $\hat{S}_{zA} = \hat{S}_{zA}(1) + \hat{S}_{zA}(2)$ where 1 and 2 specify the two free electrons on the metal center. Operation with eq 9 over the doublet and quartet eigenfunctions of the radical-ion pair leads to the relationships

$$\langle \xi^i|\hat{\eta}_z^{\ +}|\xi^j\rangle = \delta(L^i, L^j)\delta(M_s^i, M_s^j\delta(I^i, I^j)\delta(M_I^i, M_I^j), \langle \zeta^i|\hat{\eta}_z^{\ -}|\zeta_j\rangle = 0 \qquad (13)$$

showing that the Zeeman term vanishes over off-diagonal matrix elements. Orthonormality constraints in eq 10 prevent the Faraday mechanism from contributing (in a zero order) to the MKE, i.e., it does not alter the rate of conversion among nondiagonal eigenstates. A weaker effect results when such states are mixed under the *LS* coupling. It is convenient to express the spin−orbit coupling operator by using a formalism commonly used in relation to the coupling of the nuclear and electronic spins, eq 14.

$$\hat{\eta}_{\mathrm{LS}} = (L_{\mathrm{Z,A}}\eta_{\mathrm{Z,A}} + L_{\mathrm{Z,B}}\eta_{\mathrm{Z,B}}) + {}^{1}/_{2}([L_{+,\mathrm{A}}\eta_{-,\mathrm{A}} + L_{-,\mathrm{a}}\eta_{+,\mathrm{A}}] + [L_{+,\mathrm{B}}\eta_{-,\mathrm{B}} + L_{-,\mathrm{B}}\eta_{+,\mathrm{B}}) \qquad (14)$$

In eq 14 the subscripts specify the components of z, the rising, +, and lowering, −, operators for the Ni^{II} complex and the radical. Spin−orbit coupling constants are imbedded in the components of the spin operator, i.e., $\hat{\eta}_{\mathrm{i,k}} = \lambda_k\hat{S}_{i,k}$ with k = A or B. Mixing of two eigenfunctions by the *LS* coupling operator, $\hat{\eta}_{LS}$, is depicted in eq 15.

$$\langle \xi^{i'}| = \langle \xi^i| + \frac{\langle \xi^i|\hat{\eta}_{LS}|\xi^j\rangle}{\Delta E_{ij}} \qquad (15)$$

Operating by the right with $|\hat{\eta}_{LS}|\xi^j\rangle$ leads to the magnetic induction dependent term,

$$\langle \xi^{i'}|\hat{\eta}_z|\xi^j\rangle = \frac{\langle \xi^i|\hat{\eta}_{LS}|\xi^j\rangle}{\Delta E_{ij}}\Delta g\, \beta\, B\delta(I^i, I^j)\delta(M_I^i, M_I^j) \qquad (16)$$

If the spin−orbit coupling is only strong in the radical, i.e., the *LS* coupling constants obey the relationship $\lambda_A = 0$ and $\lambda_B \neq 0$, the Zeeman term, eq 13, will make conversions between $\phi_1 \leftrightarrow \phi_2$, $\phi_3 \leftrightarrow \phi_4$, and $\phi_5 \leftrightarrow \phi_6$ dependent on the magnetic induction. Otherwise, when $\lambda_A \neq 0$ *and* $\lambda_B \neq 0$, the selection rules for $\phi_i \leftrightarrow \phi_j$ conversions are the following: $i = 1, j = 2, 3$; $i = 2, j = 1, 4$; $i = 3, j = 1, 4, 6$ with analogous counterparts for symmetrically placed states (Figure 2).

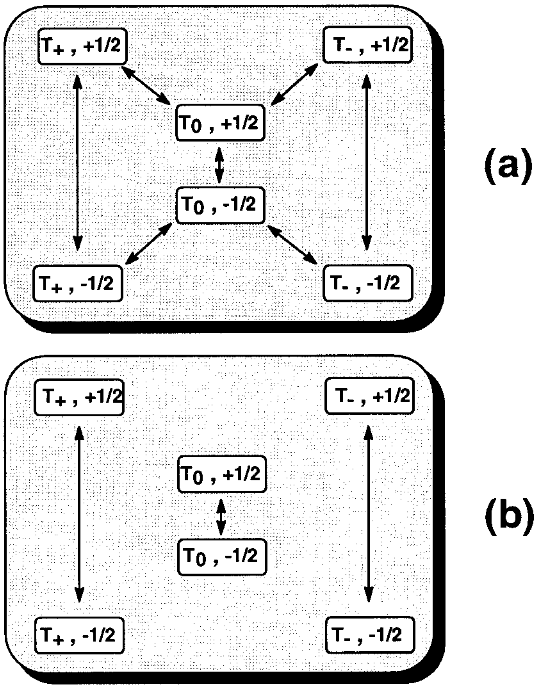

Figure 2. Diagrams for the hyperfine (a) and LS coupling (b) nondiagonal couplings of electronic states in encounter complexes of Ni(Me$_2$pyo[14]trieneN$_4$)$^{2+}$ and a doublet radical. The electronic state of the complex is summarily represented by the triplet components, $T_{\pm,0}$.

TABLE 2: Selected Values of Paramagnetic Properties for Various Reactants[29]

reactant	$A_{\mathrm{iso}} \times 10^3$ (T)	$A_{\parallel}/A_{\perp} \times 10^3$ (T)	g_{iso}	$g_{\parallel}/g_{\perp}$
Cl_2^-	4.0	10.4/1.27	2.03	2.001/2.043
Br_2^-	9.6	46/8.1	2.11	2.00/2.17
$CH_3^\bullet$	2.3	$A_{\parallel} = A_{\perp}$	2.003	$g_{\parallel} = g_{\perp}$
$(^3A_1)$Ni^{II}			2.22	$g_{\parallel} = g_{\perp}$in D_{4h}
(Γ_6)Co^{II} (high spin)	10	11./8.7	3.1	6.78/2.392/3.345
Co^{II} (low spin)	3.2	2.2/4.28/3.04	2.1	2.017/2.323/2.343

It is possible to describe the contact interaction within the pair by the operator

$$\hat{H}_{\mathrm{hfc}} = {}^{1}/_{2}(\hat{S}_A - \hat{S}_B)(\sum_i A_{i,A}\, \hat{I}_{i,A} - \sum_j A_{j,B}\, \hat{I}_{j,B}) \qquad (17)$$

where these summations involve every nuclei, i in A and j in B, with corresponding nuclear spin operators $\hat{I}_{i,A}$ and $\hat{I}_{j,B}$. It must be noted that the isotopes ^{58}Ni and ^{60}Ni, 67.76% and 26.16% abundance, have $I = 0$ while ^{61}Ni with $I = 3/2$ has a natural abundance too small, 1.25%, to contribute to the MKE associated with eqs 6 and 7. In this regard, only nuclei in the ligand, i.e., N and H, will make a contribution to the summation over the Ni^{II} complex in eq 17. The A_{iso} values for $CH_3^\bullet$ and Br_2^- radicals, Table 2, can be considered as a result of contributions from equivalent H and Br nuclei. Transitions induced by the isotropic hyperfine coupling among eigenstates of the pair, Figure 2, will be cut off with increasing magnetic inductions.

Under a double group treatment, the doublet state of the pair is correlated with the $^2A_1$ of the Ni^{III} products in eqs 6 and 7. The probability, $|C_D(t)|^2$, of being in such a doublet state is the added probabilities, eq 18, of being in one of the sublevels with $M_s = \pm 1/2$.

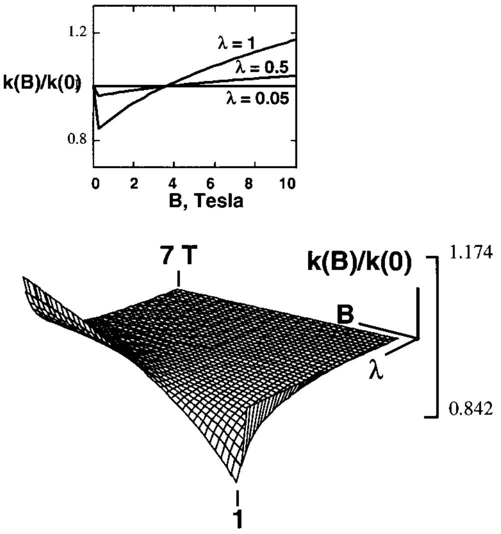

Figure 3. Typical dependence of the normalized reaction rate constant, $k(B)/k(0)$, on the magnetic induction, $0 \leq B \leq 7$ T, and the probability, $0 \leq \lambda \leq 1$, of product formation in a single encounter. Values in literature reports were used for the parameters in the Noyes probability of a first reencounter, $f(t)$. Values of $|C_D^F(t)|$ were calculated with parameters in Table 2 for the Ni^{II} complex and Br_2^- radical and mathematical expressions for the Faraday and hyperfine couplings of various electronic states. Cross sections of the surface for several values of λ are shown at the top. The calculation does not incorporate contributions from a relaxation mechanism.

$$|C_D(t)|^2 = |C_1(t)|^2 + |C_2(t)|^2 \qquad (18)$$

Probabilities, $|C_D^D(t)|^2$, $|C_D^Q(t)|^2$, and $|C_D^F(t)|^2$ for a doublet, $C_1 = C_2 = 1$, $C_3 = C_4 = C_5 = C_6 = 0$, and quartet, $C_1 = C_2 = 0$, $C_3 = C_4 = C_5 = C_6 = 1$, and F precursor were defined by analogy with the singlet, triplet and F precursors of reacting doublet radicals.[4,11,12] In the F precursor case, i.e., reactants with uncorrelated spins, reaction probabilities were calculated as an average over an exponential distribution of lifetimes, eq 19:[11a,29]

$$\frac{k(B)}{k(0)} = \frac{\int_0^\infty |C_D^F(t)|^2\, e^{-t/\tau}\, dt}{\lim_{B\to 0}\int_0^\infty |C_D^F(t)|^2\, e^{-t/\tau}\, dt};\quad |C_D^F(t)|^2 = 1/2\,[(1-\lambda)|C_D^D(t)|^2 + |C_D^Q(t)|^2] \qquad (19)$$

having τ as the mean value of the pair's lifetime. The reaction probabilities were also calculated on the basis of a model where reactants undergo multiple encounters, eq 20:[11a,12,30]

$$\frac{k(B)}{k(0)} = \frac{\lambda/3 + A\int_0^\infty |C_D^F(t)|^2 f(t)\, dt}{\lim_{B\to 0}(\lambda/3 + A\int_0^\infty |C_D^F(t)|^2 f(t)\, dt};\quad A = \frac{\lambda/6}{1 - P[1-\lambda/2(1-\lambda)]} \qquad (20)$$

The relationship $k(B)/k(0)$ in eq 20 depends on the probability λ for product formation in a single encounter on $|C_D^F(t)|^2$ and the Noyes probability of a first reencounter $f(t)$. The cumbersome eqs 19 and 20 were numerically integrated with literature values given to parameters of $f(t)$. Typical results of these calculations, Figures 3 and 4, reveal that the exponential model, eq 17, accounts for the experimental observations in Figure 1.

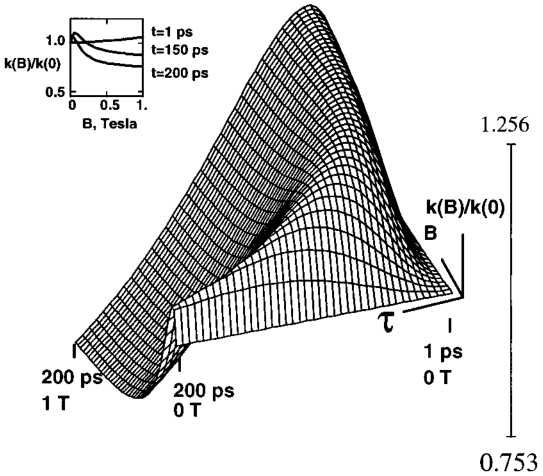

Figure 4. Typical dependence of the normalized reaction rate constant, $k(B)/k(0)$, on the magnetic induction, $0 \leq B \leq 7$T, and the lifetime, 1 ps $\leq \tau \leq$ 200 ps, of the encounter complex. Values of $|C_D^F(t)|$ were calculated with parameters in Table 2 for the Ni^{II} complex and Br_2^- radical and mathematical expressions for the Faraday and hyperfine couplings of various electronic states. Cross sections of the surface for several values of τ are shown at the top. The calculation does not incorporate contributions from a relaxation mechanism.

Discussion

Magnetic properties of the Ni^{II} complex described above and the radicals in eqs 1 and 2 are summarized in Table 2. Values for the g_{iso} and A_{iso} suggest that MKE for $B < 1$ T in Figure 1 must result from a combination of contributions, i.e., the Faraday mechanism and the suppression of hyperfine coupling-induced transitions. In experimental terms, curves shown in Figure 1 do not exhibit the functional dependence on B that is expected when such contributions are associated with a model for multiple encounters of the reactants. When experimental results are modeled by using literature values for nuclear and electronic spin properties of the reactants, the expected mathematical dependence of $k(B)/k(0)$ on B and λ, Figure 3, is similar to the one described in the literature for pairs of doublet radicals.[4,12] It must be noted that the functional dependencies of $k(B)/k(0)$ in Figure 3 were previously observed with reactions of various radicals with Co^{II} compounds. Such an observation suggests that the failure of the model in these Ni^{II} reactions can be ascribed to the dynamic probability factor, i.e., the dynamics of RIPs generation and consumption in eqs 6 and 7 instead of particularities in the spin evolution. In this regard, the statistics for encounters in radical-ion pairs of the Ni^{II} complex appear to resemble those of radical pairs in "a microreactor", e.g., micelles or microemulsion nanodroplets or those kinetically reacting under conditions of strong scavenging.[31-34] Either of these dynamic conditions will prevent the Noyes function in eq 20 to be a good approximation of the reencounter statistics. A simplistic "exponential model" in eq 19 leads, therefore, to a much closer representation of the experimental results, Figure 4. This result suggests that in $[Ni(Me_2pyo[14]trieneN_4)]^{2+}$ dynamic conditions on the ligand−radical interchange, eq 2, are different from those in previously investigated reactions of Co^{II} and Mn^{II} complexes.[3,6,7] Such conditions could cause the Ni^{II} complex and radical to lose memory of the spin state when they separate from the (first encounter) radical-ion pair. In eq 2, an equilibrium largely displaced toward either the substitution product or the radical-ion pair will prevent successive reencounters where the spin polarization is preserved. Also, a slow back-dissociation into a radical-ion pair, i.e., in a process that possesses a significant activation energy, may result in conditions similar to those in biradicals.[11] This option appears to be in better agreement with conclusions drawn in literature reports from the effect of the pressure on the reaction rate of these redox processes.[1b,c]

When magnetic inductions are above 1 T, Figure 1, MKE can be related to the relaxation mechanism,[35-37] a contribution to MKE already addressed in previous literature reports.[3,38−42] This mechanism is more strongly manifested in the reaction of Br_2^-, eq 6, than in the $CH_3^\bullet$ one, eq 7, because of the large anisotropies characterizing the **A** and **g** tensors of the halide radical anions. Since the **A** and **g** tensors of the $CH_3^\bullet$ radical are isotropic, results in Figure 1 show the expected lesser contribution of the relaxation mechanism to the MFE in the rate of the reaction between this radical and $Ni(Me_2pyo[14]trieneN_4)^{2+}$, eq 7. The isotropy of **g** in the Ni^{II} complex is somewhat dependent on the presence of a moderate zero-field splitting.[25] Measurements of the $Ni(Me_2pyo[14]trieneN_4)^{2+}$ ESR spectrum support the presence of such small anisotropies in **g**. It is possible, therefore, to ascribe the partial quenching of the MKE for $B > 1$ T in the rate of the $CH_3^\bullet$ reaction to the anisotropic Zeeman mechanism.

Conclusions

In this work and elsewhere in the literature, the overall experimental evidence signals that an effective rationalization of MKE on reactions between radicals and substitution labile complexes must combine features of the radical-pair mechanism with those of the ligand interchange mechanism. Although the sense of the MKE on the rate of these processes does not seem to be largely determined by the dynamics of ligand interchange,[44] this mechanism has a significant shaping effect on the dependence of $k(B)$ on B. Departures from this magnetokinetic behavior could be expected in those reactions, not yet investigated, where the rate is controlled by the electron transfer rather than the ligand interchange.

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$$M^{II}L(H_2O) + R^\bullet \rightleftarrows [M^{II}L(H_2O), R^\bullet] \text{ radical-ion pair}$$

$$(R^\bullet = CH_3^\bullet, CO_3^{\bullet-})$$

$$M^{II}L(H_2O), R^\bullet \rightleftarrows [M^{III}L(R^-), H_2O] \text{ product}$$

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(19) The Ni^{II} complex has been reported to have a high spin configuration and to be the bis(aquo) species, e.g., $Ni(Me_2pyo[14]trieneN_4)(H_2O)_2^{2\bullet+}$.[20,21] Therefore, a ground state $^3B_{2g}$ results under the ligand field approximation in a D_{4h} symmetry.[22,23] The ground state of the Ni^{III} complex, $^2A_{1g}$, results in a similar approximation.[22,23]

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(25) Electronic levels of Ni^{II} in octahedral, O_h, and tetragonal, D_{4h}, symmetries have been a matter of considerable research.[23,26,27] In an O_h point group symmetry, the spin−orbit coupling perturbation does not remove the three-fold degeneracy of the $\Gamma_5(^3A_{2g})$ ground state in the Ni^{II} complex. A weak tetragonal distortion will be effective in removing such a degeneracy and in causing the zero-field splitting of the $\Gamma_5(^3A_{2g})$ state into the $\Gamma_5(^3B_{1g})$ and $\Gamma_4(^3B_{1g})$ levels. The separation between them is $-2D/3$ and $D/3$ where D is of a moderate magnitude. Other electronic triplet and singlet levels with energies above the corresponding ground states are too high to mix with ground states and/or to achieve Boltzman populations relevant to the observed MFE.

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