

Dynamics of Interaction between a 1,9-Biradical and Lanthanide Ions

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The lifetime of the triplet 1,9-biradical derived from 2,10-diphenylcyclodecanone was studied in the presence of lanthanide(III) ions (Ln^{3+}) in methanol solvent. The biradical lifetime is greatly decreased in the presence of several of the Ln^{3+} ions. Bimolecular rate constants k_c for the Ln^{3+} -induced biradical decay range from 0 to $2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The Ln^{3+} effect is not due to chemical reaction, since no new products are observed and the product ratio is minimally perturbed. It is proposed that k_c represents *spin exchange* between biradical and Ln^{3+} . As a model for dipolar electronic relaxation by Ln^{3+} , a possible alternative mechanism for Ln^{3+} -induced biradical decay, proton T_1 relaxation times for sodium dodecyl sulfate micelles were measured in the presence of Ln^{3+} ions. The pattern of Ln^{3+} -induced nuclear relaxation enhancements as a function of Ln^{3+} was significantly different from the pattern of k_c vs Ln^{3+} . On the other hand, the known theory of spin exchange accounts qualitatively for the dependence of k_c on Ln^{3+} . The evidence thus suggests spin exchange as the dominant mechanism.

Introduction

The paramagnetic properties of lanthanide(III) ions (Ln^{3+}) have been used extensively in NMR structural investigations. Recently, it has been shown that paramagnetic Ln^{3+} ions increase the rate of decay of triplet radical pairs in micelles,^{1,2} provided the reaction is carried out in a magnetic field, and quench the magnetic field effect of pyrene-dimethylaniline exciplex luminescence.³ No quantitative interpretation of these experiments was given, though qualitative suggestions were made. Several reports over the past decade have dealt with the interaction of triplet biradicals with paramagnetic species such as nitroxides,^{4,5a,b} oxygen,⁶ or $\text{Cu}(\text{acac})_2$.^{5c} In general, the paramagnetic species changed the product distribution (intramolecular^{4,5} and intermolecular⁶) and decreased the biradical lifetime. In addition to chemical scavenging,⁶ the paramagnetic species were reported to catalyze intersystem crossing (ISC) in the biradicals.⁴⁻⁶

In studying the interaction of biradicals with additional paramagnetic species, it is important to establish the mechanism of the interaction. In this paper we report second-order rate constants for Ln^{3+} -induced biradical decay and present evidence that these rate constants represent *spin exchange*⁷ between Ln^{3+} and biradical. To our knowledge, these are the first measurements of bimolecular spin exchange by time-resolved kinetics.

Experimental Section

Lanthanide salts were used as received from commercial suppliers (Aldrich: CeCl_3 , PrCl_3 , SmCl_3 , EuCl_3 , ThCl_3 , YbCl_3 , LuCl_3 ; Alfa: NdCl_3 , EuCl_3 , GdCl_3 , DyCl_3 , TbCl_3 , HoCl_3 , ErCl_3). 2,10-Diphenylcyclodecanone (**1**) was prepared according to our published procedure.⁸ Spectrograde methanol (EM Science Corp.) was used as supplied. Sodium dodecyl sulfate (SDS) was electrophoresis grade from BioRad Laboratories.

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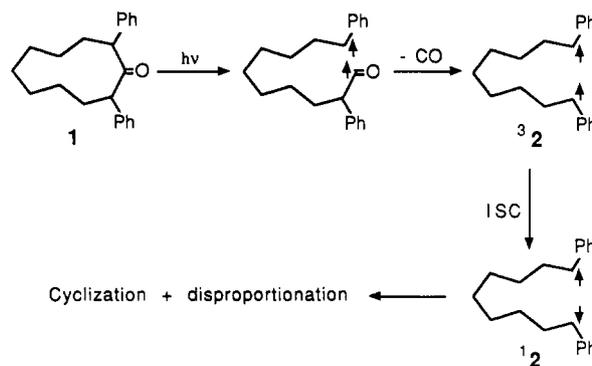
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SCHEME I



SCHEME II

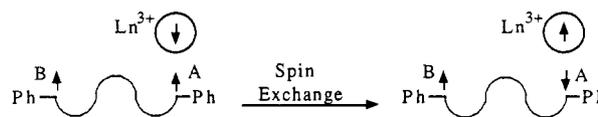


TABLE I: Bimolecular Rate Constants k_c for Ln^{3+} -Induced Biradical Decay

lanthanide	no. of f electrons	ground state ^a $2S+1L_J$	$k_c/10^6 \text{ s}^{-1}$
La	0	1S_0	0 ± 0.5
Nd	3	$^4I_{9/2}$	5.5 ± 0.7
Sm	5	$^6H_{5/2}$	22 ± 2
Eu	6	7F_0	0 ± 0.5
Gd	7	$^8S_{7/2}$	280 ± 30
Tb	8	7F_6	14 ± 1
Dy	9	$^6H_{15/2}$	13 ± 1
Ho	10	5I_8	8 ± 1
Er	11	$^4I_{15/2}$	7.1 ± 0.9
Lu	14	1S_0	0 ± 0.5

^aS = spin, L = orbital angular momentum, J = S + L.

The biradical lifetimes were measured in methanol at ca. 23 °C on a nanosecond transient absorption apparatus previously described.⁹ Excitation by a Lambda Physik excimer laser at 308 nm (15-ns fwhm, <20 mJ per pulse) was monitored at 320 nm. NMR T_1 measurements were performed on a Bruker 250-MHz spectrometer at 25 °C using a 180- τ -90 pulse sequence.

Results and Discussion

In CH_3OH solution at 25 °C, photolysis of **1** (Scheme I) generates a transient which decays with a rate constant of $1.58 \times 10^6 \text{ s}^{-1}$. From its transient absorption spectrum ($\lambda_{\text{max}} = 320$

± 2 nm) and the insensitivity of its decay rate to addition of diene, we assign the transient to $^3\mathbf{2}$. Under the conditions of these experiments, the observed decay is the rate constant for intersystem crossing (ISC) from the triplet to the singlet biradical, k_{ISC} .⁹ Addition of paramagnetic Ln^{3+} ions to a methanol solution of $\mathbf{1}$ increases the observed rate constant for decay (k_{obsd}) according to

$$k_{\text{obsd}} = k_{\text{ISC}} + k_e[\text{Ln}^{3+}] \quad (1)$$

where k_e is the second-order rate constant for lanthanide-induced quenching of the biradical. Table I lists the k_e values for a variety of LnCl_3 salts. We suggest spin exchange⁷ as a reasonable mechanism for the quenching. In this mechanism, a collision between Ln^{3+} and the biradical gives rise to an exchange interaction with predominantly one of the radical centers ("A" in Scheme II). The mutual exchange of electron spin states between Ln^{3+} and radical center A constitutes an ISC mechanism for the biradical spins. Spin exchange is represented by the operator $J_{\text{ex}}(g_J - 1)\mathbf{J}\cdot\mathbf{S}_A$,¹⁰ where J_{ex} is the net exchange interaction between lanthanide and radical center A of the biradical, $(g_J - 1)\mathbf{J}$ is the projection of the total angular momentum \mathbf{J} of the lanthanide onto the spin \mathbf{S} ,¹¹ g_J is the Landé g factor, and \mathbf{S}_A is the electron spin operator for radical center A.

The assignment of spin exchange is based on the following observations. (1) The quenching is not due to chemical reaction since no new products are observed,¹² and no reactions have ever been reported between Ln^{3+} ions and alkyl radicals under these conditions. (2) Rapid, reversible electron transfer is ruled out by the relative redox potentials of lanthanides¹³ and 1-phenylethyl radicals.¹⁴ (3) Ln^{3+} -induced dipolar electronic relaxation predicts the wrong pattern of k_e vs Ln^{3+} . (4) The relative k_e values are qualitatively in accord with the theory of spin exchange.⁷ These observations are now discussed in more detail.

The quenching rate constants fall into three groups. In the first group, there is no detectable quenching ($k_e < 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) for La^{3+} and Lu^{3+} , both diamagnetic with empty or filled 4f shells, and also for Eu^{3+} , which has a $J = 0$ ground state. Of the lanthanides with nonzero k_e , all members of the second group lie within a factor of 2 of $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ —except for Gd^{3+} , the only member of the third group, which has by far the largest k_e . All k_e values fall well below the bimolecular diffusion limit, which suggests that the quenching occurs in the weak exchange limit, $J_{\text{ex}}^2 \tau_c^2 \ll 1$, where τ_c is the lifetime of the solvent-caged encounter pair during which repeated collisions take place ($\approx 10^{-11}$ – 10^{-10} s).¹⁵ Equation 2 shows expressions for the rate constant k_e for spin exchange between a spin $1/2$ radical and a lanthanide of total angular momentum \mathbf{J} in the weak exchange limit,¹⁶ obtained from the original formulas¹⁶ by replacing the spin angular momentum \mathbf{S} by $(g_J - 1)\mathbf{J}$, the projection of \mathbf{J} upon \mathbf{S} .¹⁰

$$k_e = [F(g_J - 1)^2 J(J + 1) J_{\text{ex}}^2 \tau_c^2] k_{\text{diff}}, \quad \tau_c < T_{1e} \quad (2a)$$

$$k_e = [F'(g_J - 1)^2 J(J + 1) J_{\text{ex}}^2 \tau_c T_{1e}] k_{\text{diff}}, \quad T_{1e} < \tau_c \quad (2b)$$

In eq 2, k_{diff} is the diffusion-controlled rate constant for bimolecular contact, T_{1e} is the electronic spin–lattice relaxation time for the lanthanide, τ_c is the same as described above, and F, F' are steric factors that include the effects of anisotropic exchange interaction and orientational averaging during the collision.¹⁵ Although no theory has been published for spin exchange between biradicals and lanthanides, eq 2 should serve as a qualitative guide

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(11) In lanthanides, efficient coupling of spin (\mathbf{S}) and orbital angular momentum (\mathbf{L}) implies that the relevant quantum number is the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

(12) The intramolecular product ratio is modified slightly as a result of added Ln^{3+} (cf. ref 4–6). The change in product ratio is partly a salt effect.

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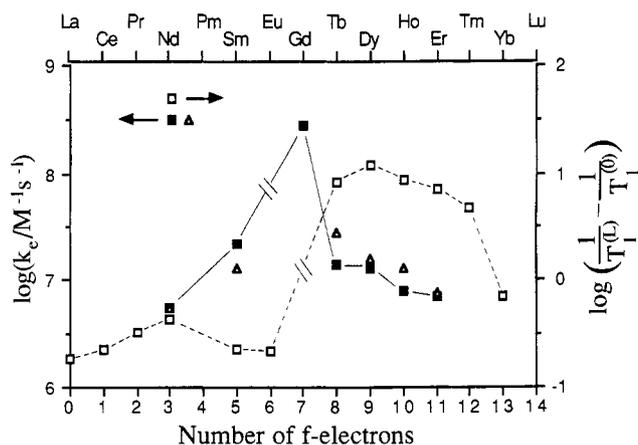


Figure 1. Solid squares: nonzero experimental k_e values; triangles: relative theoretical k_e values normalized to Nd^{3+} , computed from relative G values (see text); hollow squares: proton relaxation enhancements. Experimental and theoretical k_e values refer to the left ordinate, and nuclear relaxations to the right ordinate.

for what to expect. All Ln^{3+} ions except Gd^{3+} have short T_{1e} times (10^{-13} – 10^{-12} s),¹⁷ and their quenching is governed by eq 2b. Equation 2a is appropriate only for Gd^{3+} , which has $T_{1e} \approx 3 \times 10^{-9}$ s.¹⁸ The factor of 13–50 separating the value for Gd^{3+} from the other paramagnetic ions (Table I) can be attributed to the much longer relaxation time of Gd^{3+} and is the right order of magnitude predicted by eq 2. Most of the difference is due to τ_c/T_{1e} , which, from estimates given above, probably lies within half an order of magnitude of 100.

With the approximation that the steric factors and T_{1e} values are not grossly different among the lanthanides,¹⁹ eq 2 suggests that k_e ought to correlate roughly with $G = (g_J - 1)^2 J(J + 1)$. Figure 1 compares the nonzero k_e (filled squares) with the relative G values (triangles), and the correlation is reasonable.

An alternative mechanism for Ln^{3+} -induced ISC in the biradical is dipolar electronic relaxation of radical center A (Scheme II), which would also be expected to be increased by a very long T_{1e} . In nonviscous solution at room temperature, the dipolar relaxation rate is given by²⁰

$$T^{-1} = \frac{4}{3\hbar^2} \frac{\gamma^2 \mu_{\text{eff}}^2}{r^6} \tau \quad (3)$$

$$\tau = T_{1e} \text{ for } T_{1e} < \tau_0, \quad \tau = \tau_0 \text{ for } \tau_0 < T_{1e}$$

In eq 3, τ_0 is the correlation time for motion that modulates the dipolar interaction, γ is the magnetogyric ratio of the radical, r is the interelectronic distance from Ln^{3+} to the radical, and μ_{eff} is the effective magnetic moment of Ln^{3+} . For the ground J state, $\mu_{\text{eff}}^2 = g_J^2 \beta^2 J(J + 1)$, where g_J is the Landé g value and β is the Bohr magneton. The separation of the contributions of dipolar relaxation and spin exchange is nontrivial,¹⁵ but the known values of μ_{eff} can be used as a rough guide to the expected relative k_e values if k_e were due exclusively to dipolar relaxation. In units of β^2 , the literature values²¹ of μ_{eff}^2 for Nd^{3+} and Sm^{3+} are 30–40 times smaller than μ_{eff}^2 for Tb^{3+} or Dy^{3+} , but k_e for Nd^{3+} and Sm^{3+} is within a factor of 2 of k_e for the other two ions. Thus, dipolar relaxation does not appear to account for the variation in k_e as a function of Ln^{3+} ion, but an independent experiment would be helpful.

Equation 3 is quite general and describes the dipolar interaction of Ln^{3+} ions with either radicals or nuclei. Thus, the relative k_e values produced by the dipolar mechanism should basically coincide with the relative dipolar spin–lattice relaxation rates for

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nuclei interacting with Ln^{3+} ions (in which case γ in eq 3 refers to the nucleus and r to the electron-nuclear distance). As part of an NMR study of lanthanide-bound micelles, we have measured the proton T_1 relaxation times for SDS micelles (0.07 M surfactant) to which a variety of Ln^{3+} ions (0.002 M) had been added.²² The quantity of interest, plotted as hollow squares in Figure 1, is the relaxation enhancement for the CH_2 group in SDS bound directly to the sulfate, defined as $(1/T_1^{(\text{L})}) - (1/T_1^{(0)})$, where $T_1^{(\text{L})}$ and $T_1^{(0)}$ are the proton spin-lattice relaxation times in the presence and absence of lanthanide, respectively. (Gd^{3+} was not included because it produced line widths too broad to measure properly.) For Ln^{3+} ions the dipolar interaction typically dominates the Fermi contact term.^{19,23} Note that the pattern

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of dipolar T_1 enhancements (hollow squares) does not match the pattern of k_e values (filled squares). This argues against a significant dipolar contribution to k_e .

Conclusion

We have measured bimolecular quenching rate constants k_e for interaction of lanthanide ions with the 1,9-biradical **2**. The evidence so far suggests that spin exchange is the principal quenching mechanism. The dipolar mechanism does not appear to have a major influence on the quenching. Further investigations, including the magnetic field dependence and chain length dependence of k_e , and lanthanide effect on intramolecular product ratios, are in progress.

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A Realistic $\text{HO}_2(\tilde{X}^2A'')$ Potential Energy Surface from the Double Many-Body Expansion Method

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A double many-body expansion potential energy surface reported previously for $\text{HO}_2(\tilde{X}^2A'')$ and referred to here as DMBE I is modified to produce thermal rate coefficients for the reaction $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ in good agreement with experiment. This new potential energy surface will be referred to as DMBE II. By the further imposition that the potential function should reproduce the experimental spectroscopic force field data for the hydroperoxyl radical, another potential energy surface has been obtained, DMBE III. Both of these improved DMBE II and DMBE III potential energy surfaces preserve the functional form used previously for DMBE I except for the long-range $\text{O} \cdots \text{OH}$ electrostatic interaction, which is defined in the spirit of a more satisfactory adiabatic theory.

1. Introduction

The potential energy surface for the electronic ground state of the hydroperoxyl radical, $\text{HO}_2(\tilde{X}^2A'')$, is important in understanding the chain-branching reaction (i) $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ of many combustion processes¹ and its reverse (ii) $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$, both of which are also important in the HO_x cycle of atmospheric chemistry.^{2,3} Connected with reactions (i) and (ii) are studies of isotope exchange⁴ in $\text{O} + \text{OH}$ and the vibrational relaxation⁵ of O_2 in collisions with H. It is also important for theoretical studies of the vibrational-rotational spectroscopy of $\text{HO}_2(\tilde{X}^2A'')$ and, as a building block, for construction of the potential energy functions of larger polyatomics (which have ground-state HO_2 as a dissociation fragment) from the many-body expansion (MBE)⁶ and double many-body expansion (DMBE)^{7,8} methods. Thus, it is not surprising that there has been a considerable theoretical effort to arrive at a reliable potential energy surface for the electronic ground state of the hydroperoxyl radical, with use of both ab initio⁹⁻¹⁴ and semiempirical¹⁵⁻¹⁷ methods.

On the experimental side, the dissociation energy,^{18,19} the geometry,^{6,20,21} and the quadratic force constants^{6,20} of the hydroperoxyl radical have also been reported. An extensive list of references to spectroscopic studies by a variety of techniques covering a wide range of the spectra can be found in ref 14.

Once a reliable three-dimensional (3D) working potential energy surface is available, it can be used for dynamics calculations by

using either the classical trajectory method^{14,5,22-29} or approximate quantum mechanical theories^{30,31} and for variational transition

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