Effect of Applied Hydrostatic Pressure on the Enantioselective Quenching of the Luminescence from *rac*-Tris(2,6-pyridinedicarboxylate)terbium(III) by Resolved Tris(1,10-phenanthroline)ruthenium(II) in Water and Methanol

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The effect of applied hydrostatic pressure on the enantioselective excited-state quenching of *rac*-tris(2,6-pyridinedicarboxylate)terbium(III) [$Tb(DPA)_3^{3-}$] by optically active tris(1,10-phenanthroline)ruthenium(II) [$Ru(phen)_3^{2+}$] is presented. The time dependence of the excited-state luminescence is analyzed in terms of a biexponential decay at pressures from 1 bar to 3 kbar corresponding to the diastereomeric ($\Delta-\Delta$ and $\Delta-\Lambda$) quenching reactions. In water solution it is found that the diastereomeric quenching rates and enantioselectivity increase with pressure, while in methanol solution the quenching rates and enantioselectivity decrease. The results are interpreted in terms of a detailed model for the quenching involving solvation effects within the diastereomeric encounter complexes.

1. Introduction

The excited-state quenching of racemic luminophores by resolved chiral quenchers has been shown to result in the generation of *enantio-enriched* excited states from the initially racemic ground states.[1−17] In these experiments the confirmation that the excited states are not racemic has been verified by the measurement of either steady-state or time-resolved circularly polarized luminescence (CPL).[18] In every case so far reported, the racemic luminophores have been lanthanide complexes which are known to possess luminescent transitions with large dissymmetry ratios, g_{lum}, and, thus, emit light with a high degree of circular polarization, making it possible to detect even small enantiomeric excesses in the excited state. The chiral quenchers that have been employed in these studies have involved a range of chiral resolved transition metal complexes, and, more recently, transition metal centers in biomolecules.[16,17]

In order for the quenching to be efficient there must, of course, be overlap between the appropriate transitions of the donor and acceptor, and there must be an opportunity for the donor and acceptor species to come in reasonably close contact. In a series of recent papers, we have shown that solutions of optically active tris(1,10-phenanthroline)ruthenium(II) [$Ru(phen)_3^{2+}$] effectively quench the luminescence of *rac*-tris(2,6-pyridinedicarboxylate)terbium(III) [$Tb(DPA)_3^{3-}$], and that this quenching, which occurs via excited-state energy transfer, is enantioselective.[4−7] Both of these complexes are known to possess approximate D_3 symmetry in solution. This system is, in fact, the very first system of this type to display enantioselective quenching[1] and one which is particularly amenable to detailed theoretical study, due to the reasonably high symmetry of both species.

The source of the enantioselectivity in the overall chiral quenching processes observed to date is not completely understood; however, several similar mechanistic models have been developed and used to develop an understanding of these experiments.[5,11,15] As presented below, all of the quenching reactions of interest in this work involve the transfer of energy within an excited-state "encounter complex". Clearly, any observed enantioselectivity is going to be due to differences in the net relative rate of this process for the two competing diastereomeric reactions. These differences may be due to unequal concentrations of the diastereomeric encounter complexes, differences in the structure of the complexes, e.g. the distance between donor and acceptor chromophores are not the same, leading to unequal energy transfer efficiencies, or fundamental differences in energy transfer rates due to chiral electronic effects. These effects may be interrelated, and, in general, all of these effects must be considered in order to develop a complete understanding of this chiral phenomenon.

In this work we concentrate on the details of the structure and dynamics of the diastereomeric encounter complexes in water and methanol through the measurement of quenching rates under conditions of high liquid pressure. The effect of pressure on the rates of bimolecular reactions is often used to help elucidate details of reaction mechanisms, and an extensive review of the results from high-pressure measurements on a wide variety of chemical systems is available.[19] Some work on the effect of pressure on energy transfer and electron transfer has been performed,[20] but to our knowledge this work represents the first use of this technique to study differences in the excited-state reactions of optically active molecules. A preliminary account of this work has been recently published.[8]

2. Experimental Section

A concentrated aqueous stock solution of Tb(III) was prepared from $TbCl_3$ (Aldrich) and adjusted to approximately pH 3 with HCl. A stock solution of 2,6-pyridinedicarboxcyclic acid (DPA) (Janssen Chimica) was prepared and adjusted to pH 8 with NaOH. Δ-(−)-$Ru(phen)_3^{2+}$ was prepared and resolved by a procedure previously described.[21] A concentrated aqueous stock solution of $Tb(DPA)_3^{3-}$ was prepared by combining aliquots

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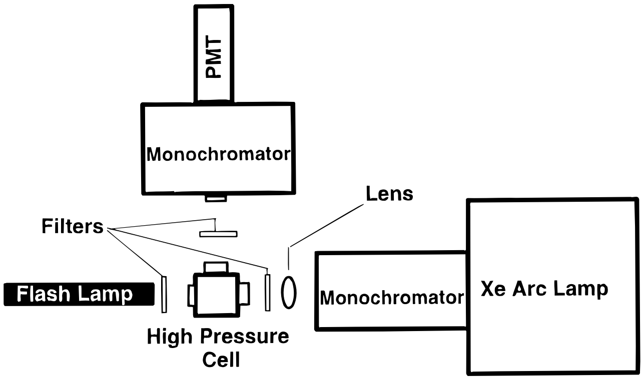

Figure 1. Schematic diagram of instrumentation for measurement of luminescence from liquid solution at high pressure.

of the Tb(III) stock solution with an excess of DPA which was then diluted to volume with water in aqueous samples. Samples of $Tb(DPA)_3^{3-}$ in methanol were prepared by adding very small aliquots of the concentrated aqueous solution of the complex to a cuvette containing methanol (Janssen Chimica). The final water content of the methanol used in this study was estimated to be approximately 0.5%.[4]

A schematic diagram of the luminescence instrumentation is presented in Figure 1. For time decay experiments, the sample was excited with repeated 1 μs pulses at 300 ± 20 nm from an Optitron NR-1B-Xe flash lamp. A 900 W AEG arc lamp was used to excite samples for measurement of total luminescence spectra. The luminescence of Tb(III) was detected at 90.0° to the excitation source. The excitation was set to the maximum of the emission wavelength (543.5 nm) corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition. The detection system consists of a long pass filter, Spex 1681A monochromator, and a cooled photomultiplier tube (PMT) (Hamasutu) operating in photon counting mode. Acquisition of the decay data was terminated when the total number of photon counts in the first time channel reached a value greater than 10^5. The decay curves were analyzed by a nonlinear-least-squares curve fitting procedure using Table Curve (Jandel Scientific). In the absence of quencher the decays were fit to the simple exponential function given in eq 1 where

$$I(t) = A \exp(-k_0 t) + b \tag{1}$$

b denotes a baseline correction. In the presence of chiral quencher, the luminescence decays were fit to the biexponential function given in eq 2. In all cases the luminescence decay

$$I(t) = A\,[\exp(-k_1 t) + \exp(-k_2 t)] + b \tag{2}$$

data were weighted by a factor proportional to $1/I(t)$ as required for random errors due to photopulse noise.[22] It should be noted that the biexponential decay fitting has been shown to be reliable in this analysis, even though the two decay constants differ in some cases by less than 10%. This is due to the fact that the initial concentrations [associated with the preexponential factor in eq 2] of the two emitting species in this racemic solution are exactly equal. The decay constants obtained from Table Curve produced results that were virtually identical to those obtained from a curve-fitting routine written and used previously.[23]

Measurements at greater than atmospheric pressure were accomplished in a custom-made stainless steel NOVA-SWISS high-pressure liquid cell (Figure 2) with three sapphire windows. The sample capsule consisted of a modified 10 mm cylindrical glass tube fitted with a Teflon piston with two O-rings. The solution sample is placed into the capsule, which is then placed inside the high-pressure cell block already filled with hydraulic fluid. The hydraulic fluid used (methanol or water) was the same as the sample solvent. The high-pressure cell is then pressurized to a fixed static pressure and monitored using a Enerpac hydraulic hand pump and gauge. The experimental setup for detection of emission at high liquid pressures is identical to the detection system used at atmospheric pressure described above.

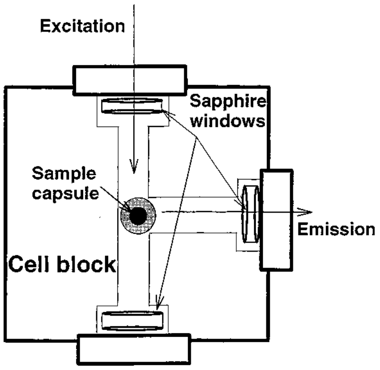

Figure 2. Schematic diagram of the high-pressure liquid cell.

3. Theory and Kinetic Model

The enantioselective quenching reactions involving Δ-Ru(phen)$_3^{2+}$ ≡ (Δ-Ru) and racemic $Tb(DPA)_3^{3-}$ ≡ (Δ,Λ-Tb) may be modeled in terms of the following reaction scheme

$$\Delta\text{-TB} + \Delta\text{-Ru} \underset{k_{-\text{diff}}^{\Delta\Delta}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} [\Delta\text{-Tb}:\Delta\text{-Ru}] \tag{3a}$$

$$\Lambda\text{-TB} + \Delta\text{-Ru} \underset{k_{-\text{diff}}^{\Lambda\Delta}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} [\Lambda\text{-Tb}:\Delta\text{-Ru}] \tag{3b}$$

$$\Delta\text{-TB*} + \Delta\text{-Ru} \underset{k_{-\text{diff}}^{\Delta\Delta}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} [\Delta\text{-Tb*}:\Delta\text{-Ru}] \tag{4a}$$

$$\Lambda\text{-TB*} + \Delta\text{-Ru} \underset{k_{-\text{diff}}^{\Lambda\Delta}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} [\Lambda\text{-Tb*}:\Delta\text{-Ru}] \tag{4b}$$

$$[\Lambda\text{-Tb*}:\Delta\text{-Ru}] \xrightarrow{k_{\text{ET}}^{\Lambda\Delta}} [\Lambda\text{-Tb}:\Delta\text{-Ru}'] \tag{5a}$$

$$[\Delta\text{-Tb*}:\Delta\text{-Ru}] \xrightarrow{k_{\text{ET}}^{\Delta\Delta}} [\Delta\text{-Tb}:\Delta\text{-Ru}'] \tag{5b}$$

$$[\Delta,\Lambda\text{-Tb}:\Delta\text{-Ru}'] \xrightarrow{k_{\text{p}}} [\Delta,\Lambda\text{-Tb}:\Delta\text{-Ru}] \tag{6}$$

$$\Delta,\Lambda\text{-Tb*} \xrightarrow{k_0} \Delta,\Lambda\text{-Tb} \tag{7}$$

$$[\Delta,\Lambda\text{-Tb*}:\Delta\text{-Ru}] \xrightarrow{k_0} [\Delta,\Lambda\text{-Tb}:\Delta\text{-Ru}] \tag{8}$$

$$\Lambda\text{-Tb} \underset{k_{\text{rac}}}{\overset{k_{\text{rac}}}{\rightleftharpoons}} \Delta\text{-Tb} \tag{9}$$

where the brackets have been used to indicate presumably "short-lived" encounter complexes; k_{diff} and $k_{-\text{diff}}^{\Delta\Delta}$ are respectively rate constants for diffusion and dissociation; and $k_{\text{ET}}^{\Delta\Delta}$ denotes the rate constant for energy transfer within the $\Delta-\Delta$ encounter complex. Similar definitions apply to the rate constants involving the quenching of (Λ-$Tb(DPA)_3^{3-}$)*. Note that in this model it has been assumed that the diastereomeric diffusion constants, k_{diff}, are equal, but that the dissociation rates may be different for the diastereomeric encounter complexes. We also assume in this model that rate of deactivation of Δ-Ru-

$(\mathrm{phen})_3{}^{2+}$ denoted by k_P in eq 6 is also identical for the two diastereomeric species. The racemization of excited $\mathrm{Tb(DPA)_3}^{3-}$ has not been included since the lifetime of the complex is much shorter than the time required for racemization. Racemization of $\mathrm{Ru(phen)_3}^{2+}$ does not occur under the conditions of these experiments. Finally, we assume that the *unquenched* decay rate of $(\mathrm{Tb(DPA)_3}^{3-})^*$ is independent of whether the species is free (eq 9) or in an encounter complex (eq 8).

Using a steady-state approximation for the concentrations of encounter complexes, the time decay of the enantiomers of $(\mathrm{Tb(DPA)_3}^{3-})^*$ may be expressed as follows

$$\frac{\mathrm{d}[(\Lambda\text{-Tb(DPA)}_3{}^{3-})^*]}{\mathrm{d}t} = -\left(\frac{k_{\mathrm{ET}}^{\Lambda\Delta}k_{\mathrm{diff}}}{k_{\mathrm{ET}}^{\Lambda\Delta}+k_{-\mathrm{diff}}^{\Lambda\Delta}}[\Delta\text{-Ru(phen)}_3{}^{2+}]+k_0\right)[(\Lambda\text{-Tb(DPA)}_3{}^{3-})^*]$$
$$= (k_{\mathrm{q}}^{\Lambda\Delta}[\Delta\text{-Ru(phen)}_3{}^{2+}]+k_0)[(\Lambda\text{-Tb(DPA)}_3{}^{3-})^*]$$
$$= k_{\mathrm{obs}}^{\Lambda\Delta}[(\Lambda\text{-Tb(DPA)}_3{}^{3-})^*] \qquad (10a)$$

$$\frac{\mathrm{d}[(\Delta\text{-Tb(DPA)}_3{}^{3-})^*]}{\mathrm{d}t} = -\left(\frac{k_{\mathrm{ET}}^{\Delta\Delta}k_{\mathrm{diff}}}{k_{\mathrm{ET}}^{\Delta\Delta}+k_{-\mathrm{diff}}^{\Delta\Delta}}[\Delta\text{-Ru(phen)}_3{}^{2+}]+k_0\right)[(\Delta\text{-Tb(DPA)}_3{}^{3-})^*]$$
$$= (k_{\mathrm{q}}^{\Delta\Delta}[\Delta\text{-Ru(phen)}_3{}^{2+}]+k_0)[(\Delta\text{-Tb(DPA)}_3{}^{3-})^*]$$
$$= k_{\mathrm{obs}}^{\Delta\Delta}[(\Delta\text{-Tb(DPA)}_3{}^{3-})^*] \qquad (10b)$$

where these equations serve to define the observed rate constants, $k_{\mathrm{obs}}^{\Lambda\Delta}$, and $k_{\mathrm{obs}}^{\Delta\Delta}$, and the so-called quenching rate constants, $k_{\mathrm{q}}^{\Lambda\Delta}$ and $k_{\mathrm{q}}^{\Delta\Delta}$.

$$k_{\mathrm{q}}^{\Delta\Delta} = \frac{k_{\mathrm{ET}}^{\Delta\Delta}k_{\mathrm{diff}}}{k_{\mathrm{ET}}^{\Delta\Delta}+k_{-\mathrm{diff}}^{\Delta\Delta}}$$
$$k_{\mathrm{q}}^{\Lambda\Delta} = \frac{k_{\mathrm{ET}}^{\Lambda\Delta}k_{\mathrm{diff}}}{k_{\mathrm{ET}}^{\Lambda\Delta}+k_{-\mathrm{diff}}^{\Lambda\Delta}} \qquad (11)$$

Note that in this approximation the concentration of ground-state species containing $\mathrm{Tb(DPA)_3}^{3-}$ does not appear in the rate equations due to the neglect of eq 3 in the steady-state treatment. This approximation may need to reevaluated in situations in which the amount of available quencher is reduced through encounter complex formation with the $\mathrm{Tb(DPA)_3}^{3-}$ complex.[24]

Since the two enantiomers are emitting simultaneously at the same wavelength, the individual diastereomeric rate constants must be determined either from a measurement of the time dependence of the circularly polarized luminescence (CPL) or from analysis of the biexponential decay of the total emission (TE) from $(\mathrm{Tb(DPA)_3}^{3-})^*$. In the experiments described here, an initial unpolarized excitation pulse is used to excite a sample of $\mathrm{Tb(DPA)_3}^{3-}$ into which a very small amount of chiral quencher has been added. The measurement of CPL reflects differences in the concentration of the two excited enantiomers, whereas the decay of the total emission intensity is related to the sum of the intensities from the two enantiomers. These two experiments are related to the observed rate constants and concentrations as follows

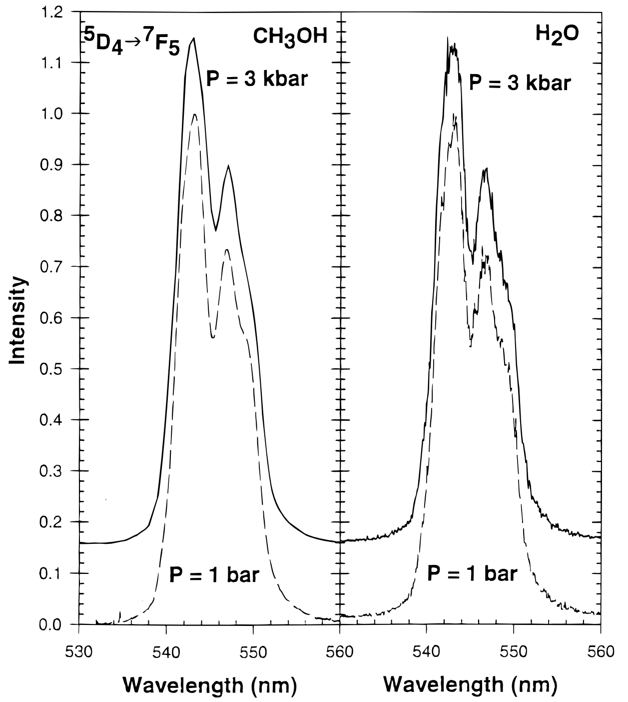

Figure 3. Total luminescence spectra for the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(III) from $\mathrm{Tb(DPA)_3}^{3-}$ in water and methanol.

$$[(\Lambda\text{-Tb(DPA)}_3{}^{3-})^*](t) - [(\Delta\text{-Tb(DPA)}_3{}^{3-})^*](t) = [\Lambda\text{-Tb(DPA)}_3{}^{3-}]_0\mathrm{e}^{-k_{\mathrm{obs}}^{\Lambda\Delta}t} - [\Delta\text{-Tb(DPA)}_3{}^{3-}]_0\mathrm{e}^{-k_{\mathrm{obs}}^{\Lambda\Delta}t} \qquad (\mathrm{CPL}) \quad (12)$$

$$[(\Lambda\text{-Tb(DPA)}_3{}^{3-})^*](t) + [(\Delta\text{-Tb(DPA)}_3{}^{3-})^*](t) = [\Lambda\text{-Tb(DPA)}_3{}^{3-}]_0\mathrm{e}^{-k_{\mathrm{obs}}^{\Lambda\Delta}t} + [\Delta\text{-Tb(DPA)}_3{}^{3-}]_0\mathrm{e}^{-k_{\mathrm{obs}}^{\Lambda\Delta}t} \qquad (\mathrm{TE}) \quad (13)$$

where the subscript "0" is used to indicate initial concentrations. As mentioned above, since the sapphire windows of the high-pressure cell are highly depolarizing, the two diastereomeric decay constants must necessarily be determined from an analysis of the total emission intensity, i.e. eq 13. Confirmation of this analysis through measurement of CPL has been performed under normal atmospheric pressure.[4−7]

It should be noted that, in this system, it is impossible to distinguish emission from "free" or encounter-complex bound $\mathrm{Tb(DPA)_3}^{3-}$. Therefore, an "exact" treatment would require one to include the time decay associated with Tb(III) emission from encounter complexes, i.e. eq 8, in eqs 12 and 13.[24] However, in this work the concentration of quencher is very small (∼10 μM), and from previous estimates of the *pseudo*-equilibrium constant for formation of encounterion pairs, i.e. $K^{\Delta\Delta} = k_{\mathrm{diff}}^{\Delta\Delta}/k_{-\mathrm{diff}}^{\Delta\Delta}$, and similarly for $K^{\Lambda\Delta}$ (1−1000),[5] and the fact that only a small fraction of species are excited, we conclude that the concentration of excited encounter complexes is negligibly small.

4. Experimental Results

Total emission spectra for the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(III) from solutions of $\mathrm{Tb(DPA)_3}^{3-}$ are presented in Figure 3. In the right-hand side of this figure we plot results for an aqueous solution at 1 bar and 3 kbar external pressure, and on

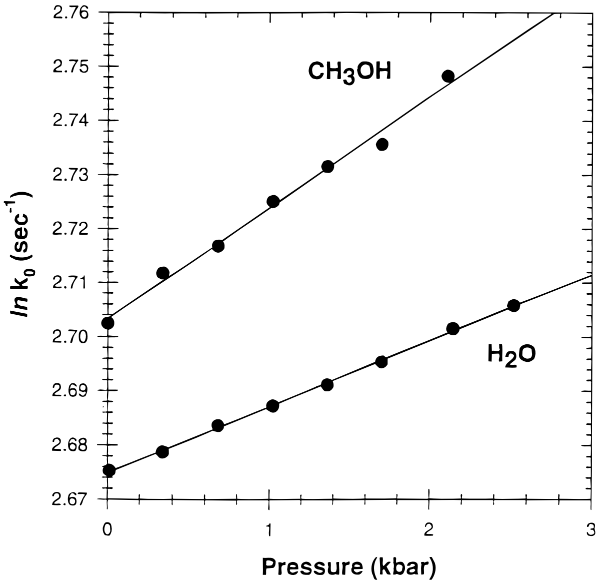

Figure 4. Logarithm of the natural radiative decay rate, k_0, as a function of pressure.

the left-hand side we plot results for the complex dissolved in methanol under similar conditions. Note that these spectra have been normalized to unit intensity at the peak maximum. The important conclusion from this plot is that the spectral line shapes of the four spectra displayed are virtually identical. Thus, we can conclude that the structure of the $Tb(DPA)_3^{3-}$ complex is unchanged and intact in the two solvents and, furthermore, does not change significantly with increasing pressure.

In Figure 4 we plot the measured luminescence decay rates, k_0, for $Tb(DPA)_3^{3-}$ as a function of applied pressure in aqueous and methanol solutions. As can be seen, in both solvents k_0 increases slightly with pressure. If one plots the natural logarithm of the measured rate versus the applied pressure, P, one can determine the volume of activation, $\Delta V^{\#}$, from the slope according to the following equation

$$\Delta V^{\#} = -RT(\partial \ln k/\partial P)_T \tag{14}$$

For the data presented in Figure 4, we obtain activation volumes for the luminescence decay of −0.30 cm^3/mol for the aqueous solution and −0.51 cm^3/mol for the methanol solution. These values are quite small when compared to previously obtained results on various transition metal species[18] and reflect the fact that the $f \leftrightarrow f$ transitions involved are isolated from the solution environment. The negative value for the activation volumes is consistent with an increase in excited-state deactivation as the ligand to metal distances are compressed.

In Figure 5 we plot luminescence decay intensities for a range of applied pressures for aqueous solutions of $Tb(DPA)_3^{3-}$ into which small quantities (13.4 μM) of Λ-$Ru(phen)_3^{2+}$ has been added. In Figure 6 we plot similar results for the complex and quencher (2.5 μM) dissolved in methanol. As can be seen, increasing the pressure on the aqueous solution increases the quenching rate and increasing the pressure on the methanol solution decreases the quenching rate. This effect was unexpected and is the focus of much of the discussion given below. The first few points in the decay have been omitted due to contamination with excitation light.

To calculate the diastereomeric quenching rate constants from the observed decay constants, eqs 10, it is necessary to determine the effect of solvent compressibility on $Ru(phen)_3^{2+}$ concentration. The volume change for water and methanol was determined from previous measurements of the compressibility of methanol and water at high pressures.[25] These results were used along with the observed pressure dependence of k_0 to calculate the quenching rate constants from the observed rate constant. The logarithm of the resultant quenching rate constants are plotted in Figures 7 and 8 as a function of applied pressure. The solid lines in these figures are least-squares fits to the data, and the slopes have been used to calculate the activation volumes for the quenching reactions. These are listed in Table 1. Consistent with the decays plotted in Figures 5 and 6, the activation volumes for the quenching in methanol are positive, and those measured in water are negative.

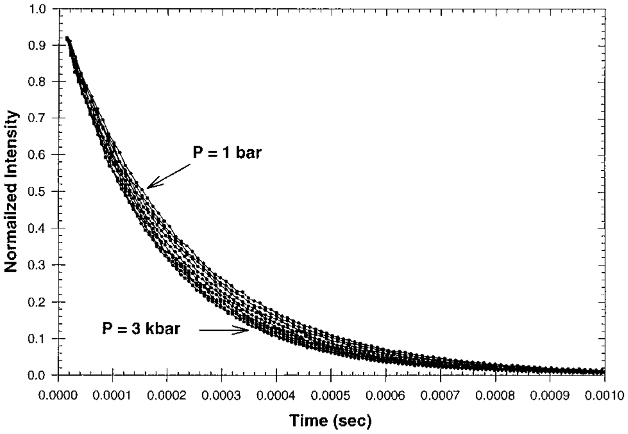

Figure 5. Time decay of the total luminescence from *rac*-$Tb(DPA)_3^{3-}$ in water as a function of pressure.

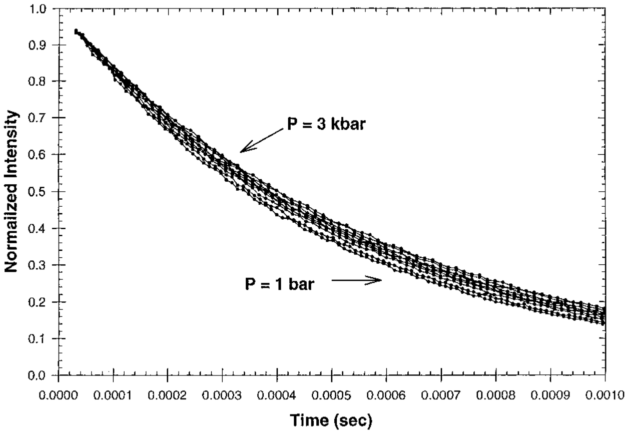

Figure 6. Time decay of the total luminescence from *rac*-$Tb(DPA)_3^{3-}$ in methanol as a function of pressure.

TABLE 1: Calculated Volumes of Activation, $\Delta V^{\#}$ (cm^3/mol), for *rac*-$Tb(DPA)_3^{3-}$

	methanol	water
A. Natural Decay without Quencher (Figure 4)		
$\Delta V^{\#}$	−0.51	−0.30
B. Quenching by Δ-$Ru(phen)_3^{2+}$ in Water and Methanol at Room Temperature (Figures 7 and 8)		
$\Delta V^{\#}$ ($\Delta-\Delta$)	+2.6	−1.9
$\Delta V^{\#}$ ($\Delta-\Lambda$)	+5.2	−0.9

5. Discussion

The effect of pressure on the observed enantioselective quenching rate constants is complicated. As seen in eqs 11, in addition to the effect of pressure on k_0 described above and shown in Figure 4, one also needs to know the effect of pressure on diffusion, dissociation, and energy transfer. The calculation

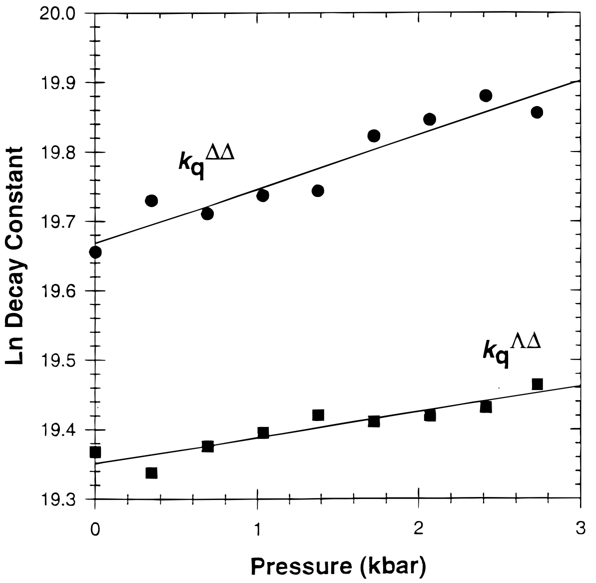

Figure 7. Diastereomeric rate constants for the luminescence quenching of *rac*-Tb(DPA)$_3^{3-}$ by Δ-/Ru(phen)$_3^{2+}$ in water at room temperature as a function of liquid pressure.

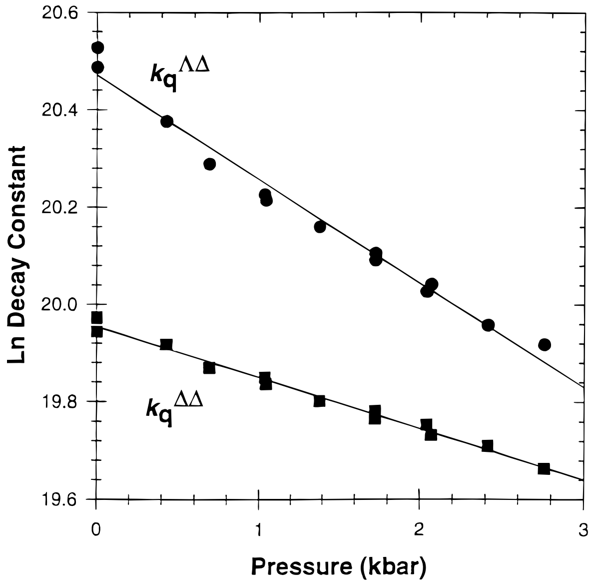

Figure 8. Diastereomeric rate constants for the luminescence quenching of *rac*-Tb(DPA)$_3^{3-}$ by Δ-/Ru(phen)$_3^{2+}$ in methanol at room temperature as a function of liquid pressure.

of diffusion rates for these ionic species using the Debye–Smolukowski equation under the conditions of these experiments show that, at room temperature and 1 bar, the diffusion rate in water is approximately 100 times larger than the observed quenching rates, and for methanol it is more than 20 times larger.[5] It should be noted that under conditions of very low temperature in methanol, these reactions do become diffusion controlled and the enantioselectivity vanishes.

At room temperature and atmospheric pressure, it has been demonstrated that the enantioselective quenching for the system studied here can accurately be described by "preequilibrium" kinetics.[7] In relation to the specific model introduced above, this means that $k_{-\mathrm{diff}}^{\Delta\Delta} \gg k_{\mathrm{ET}}^{\Delta\Delta}$, and similarly for the other diastereomeric encounter pair. Therefore, we may rewrite eqs 11 as follows

$$k_q^{\Delta\Delta} \cong k_{\mathrm{ET}}^{\Delta\Delta} k_{\mathrm{diff}} / k_{-\mathrm{diff}}^{\Delta\Delta} = k_{\mathrm{ET}}^{\Delta\Delta} K^{\Delta\Delta}$$

$$k_q^{\Delta\Lambda} \cong k_{\mathrm{ET}}^{\Delta\Lambda} k_{\mathrm{diff}} / k_{-\mathrm{diff}}^{\Delta\Lambda} = k_{\mathrm{ET}}^{\Delta\Lambda} K^{\Delta\Lambda} \qquad (15)$$

where $K^{\Delta\Delta}$ and $K^{\Delta\Lambda}$ are pseudoequilibrium constants for the formation of the diastereomeric encounter complexes. One can estimate[5] values for $K^{\Delta\Delta}$ and $K^{\Delta\Lambda}$ to be no larger than 10^3, so k_{ET} must be on the order of 10^5.

The major effect of pressure on k_{diff} and $k_{-\mathrm{diff}}$ is through an increase in solution viscosity. At a pressure of 4 kbar the viscosity of water is approximately 50% larger than at 1 bar, and that of methanol is larger by a factor of almost 3.[26] The Debye–Smolukowski equation, which has been used to estimate k_{diff}, and the Eigen equation, which can be used to estimate $k_{-\mathrm{diff}}$, both have an inverse dependence on viscosity, so the effect of solution viscosity is to decrease k_{diff} in water by a factor of 2/3 and in methanol by a factor of 1/3. This variation does not alter the assumptions that these quenching reactions are far from diffusion controlled and may be described by preequilibrium kinetics. Since the dependence of k_{diff} and $k_{-\mathrm{diff}}$ on viscosity is the same, one expects the variation of $K^{\Delta\Delta}$ and $K^{\Delta\Lambda}$ with pressure, due to the influence of viscosity, also to be small.

To discuss further the observed pressure dependence in this system it is useful to expand the important steps of the kinetic model as follows

$$(\mathrm{Tb}^*)^{3-} + \mathrm{Ru}^{2+} \underset{k_{-\mathrm{diff}}}{\overset{k_{\mathrm{diff}}}{\rightleftharpoons}} [\mathrm{Tb}^*{:}\mathrm{Ru}(\Omega)]^- \qquad (16)$$

$$[\mathrm{Tb}^*{:}\mathrm{Ru}(\Omega)]^- \underset{k_{-\mathrm{r}}}{\overset{k_{\mathrm{r}}}{\rightleftharpoons}} [\mathrm{Tb}^*{:}\mathrm{Ru}(\Omega')]^- \qquad (17)$$

$$[\mathrm{Tb}^*{:}\mathrm{Ru}(\Omega')]^- \xrightarrow{k_{\mathrm{ET}}} [\mathrm{Tb}^*{:}\mathrm{Ru}'(\Omega')]^- \qquad (18)$$

where for the moment we have ignored the enantioselective aspects of the quenching. In eq 16 we have used Ω to indicate a generalized orientation of the donor to acceptor encounter complex. In eq 17, k_{r} denotes the rate of rearrangement to an orientation Ω′ which describes a donor:quencher configuration from which energy transfer (eq 18) is highly probable In general, one expects that the activation volume associated with the formation of an ion pair (eq 16) would be positive due to reduced electrostriction associated with the reduced charge, and this is generally what is observed.[18] For this donor:acceptor system, however, it is expected that these effects will be quite small since the individual ions and ion pairs are so large. It is also expected that this contribution to the overall activation volume would be identical for the two diastereomeric reactions.

In the formal energy transfer step given in eq 18, the charge of the ions does not change, and electronic relaxation within the f orbitals is not expected to affect the charge distribution of the lanthanide complex. The effect of excitation of Ru(phen)$_3^{2+}$ through radiationless energy transfer is not as clear, although it has been shown that the transition rate from the charge-transfer excited state to the ground state in water shows only a small pressure dependence.[27] We conclude, therefore, that the effect of applied pressure on the overall reaction is mainly due to the rearrangement step described by eq 17.

This model may be employed to explain the observed pressure dependence of the quenching in water. The orientation from which energy transfer occurs is associated with a more compact fit of the donor:quencher encounter pair, and as the pressure is increased, the probability that the encounter pair attains this orientation increases. Thus, as shown in Figure 7, the quenching rates increase. The enantioselectivity in this case is due to differences in the rates $k_r^{\Delta\Delta}$ and $k_r^{\Delta\Lambda}$ or equilibrium constants $K^{\Delta\Delta}$ and $K^{\Delta\Lambda}$. It is, of course, possible that both of these effects are important and that these diastereomeric differences are related.

As described below, the observed differences between the quenching in methanol versus aqueous solution must be ascribable to some sort of solvation or desolvation process that is different in the two solvents. With this in mind we modify the kinetic model as follows

$$(\mathrm{Tb}^*)^{3-} + \mathrm{MeOH{:}Ru}^{2+} \underset{k_{-\mathrm{diff}}}{\overset{k_{\mathrm{diff}}}{\rightleftharpoons}} [\mathrm{Tb^*{:}MeOH{:}Ru}]^- \tag{19}$$

$$[\mathrm{Tb^*{:}MeOH{:}Ru}]^- \underset{k_{-\mathrm{r}}}{\overset{k_{\mathrm{r}}}{\rightleftharpoons}} [\mathrm{Tb^*{:}Ru}]^- + \mathrm{MeOH} \tag{20}$$

$$[\mathrm{Tb^*{:}Ru}]^- \xrightarrow{k_{\mathrm{ET}}} [\mathrm{Tb{:}Ru'}]^- \tag{21}$$

where we have explicitly included a solvent molecule (MeOH) in the encounter complex. We again predict little or no pressure dependence in eqs 19 and 21, but in this case an increase in pressure will decrease the forward rate of eq 20 due to the positive volume of activation for this step. As a result the overall quenching rate decreases, and this is what is seen in Figure 8. Thus, the observed opposite behavior for the identical chemical system is ascribed to a difference in solvation. This conclusion is under further study through modeling and other spectroscopic investigations. Note that, for simplicity, we have not put solvation in the model for rearrangement in water solution, nor explicit orientation dependence in the model for the quenching in methanol.

Although the exact source of the enantioselectivity seen in this system cannot be unequivocally assigned to the equilibrium step or to the rearrangement step in the above mechanism, it is clear that the source of the difference in quenching rates between the two enantiomers is structural in origin. The increased enantioselectivity observed as a function of pressure in water is consistent with the expectation that as the donor and acceptor are forced closer together, the diastereomeric interactions will become more important. Of course, the opposite is true for the quenching in methanol. If the solvent molecule inhibits the close approach of the two species, then on average the energy transfer will be occurring under conditions where the discriminatory diastereomeric interactions will be reduced. Previous work on the observation that the sign of the enantioselectivity is opposite in these two solvents has also led to the conclusion that differences exist in the rearrangement required within the donor to acceptor complex to attain the transition-state geometry.[7]

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