

Effect of pressure on the enantioselective quenching of the luminescence from *rac*-tris(2,6-pyridinecarboxylato)terbium(III) by resolved tris(1,10-phenanthroline)ruthenium(II)

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The rate of the enantioselective quenching of the luminescence from *rac*-tris(2,6-pyridinecarboxylato)terbium(III) by resolved tris(1,10-phenanthroline)ruthenium(II) increases with pressure when the reaction is carried out in water, but decreases with pressure in methanol.

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-pyridinedicarboxylato)terbium(III) [Tb(dpa)₃]³⁻, and that this quenching, which occurs *via* an excited-state energy transfer, is enantioselective.¹ Both of these complexes are known to possess approximate D₃ symmetry. This reaction has been modelled in terms of Scheme 1 where braces are used to indicate an encounter complex; *k_d* and *k_d^{ΔΔ}* are, respectively, rate constants for diffusion and dissociation; and *k_{et}^{ΔΔ}* denotes the rate constant for energy transfer within the Δ–Δ encounter complex. A similar equation may be written to describe the quenching of the luminescence of Λ–[Tb(dpa)₃]³⁻. Note that in this model it has been assumed that the diastereomeric diffusion constants, *k_d*, are equal, but that the dissociation rates may be different for the diastereomeric encounter complexes. The rate constant for dissociation of the Λ–Δ encounter complex is denoted *k_d^{ΛΔ}*, and for electronic energy transfer within the Λ–Δ encounter complex, *k_{et}^{ΛΔ}*. Thus, we may define a *pseudo*-equilibrium constant for formation of ΔΔ encounter ion-pairs as *K^{ΔΔ}* = *k_d^{ΔΔ}*/*k_d^{ΔΔ}*, and similarly for *K^{ΛΔ}*.

At room temperature in solution, the Δ and Λ enantiomers of [Tb(dpa)₃]³⁻ interconvert on a 0.1 s timescale, but this is slow enough compared to the lifetime of the excited state (ms) to have a negligible effect on the kinetic analysis presented here.² Using a steady-state approximation for the encounter complex, the observed quenching rate constants, *k_{obs}^{ΔΔ}* and *k_{obs}^{ΛΔ}*, may be related to the rate constants given above by eqns. (1) and (2).

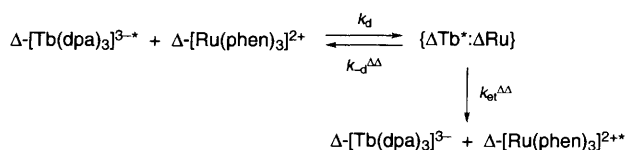
$$k_{\text{obs}}^{\Delta\Delta} = \frac{k_{\text{et}}^{\Delta\Delta} k_{\text{d}}}{k_{\text{et}}^{\Delta\Delta} + k_{-\text{d}}} [\Delta\text{Ru}(\text{phen})_3^{2+}] + k_0$$

$$= k_{\text{q}}^{\Delta\Delta} [\Delta\text{Ru}(\text{phen})_3^{2+}] + k_0 \quad (1)$$

$$k_{\text{obs}}^{\Lambda\Delta} = \frac{k_{\text{et}}^{\Lambda\Delta} k_{\text{d}}}{k_{\text{et}}^{\Lambda\Delta} + k_{-\text{d}}} [\Delta\text{Ru}(\text{phen})_3^{2+}] + k_0$$

$$= k_{\text{q}}^{\Lambda\Delta} [\Delta\text{Ru}(\text{phen})_3^{2+}] + k_0 \quad (2)$$

where these equations define the so-called quenching rate constants, *k_q^{ΔΔ}* and *k_q^{ΛΔ}*, and *k₀* denotes the decay constant for



Scheme 1

[Tb(dpa)₃]³⁻ in the absence of quencher. Since the two enantiomers are emitting simultaneously at the same wavelength, the individual diastereomeric rate constants are determined either from a measurement of the time dependence of the circularly polarized emission or from analysis of the biexponential decay of the total emission from Tb^{III} at the maximum of the emission wavelength (543.5 nm). 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 <10%. This is due to the fact that the initial concentrations (pre-exponential factor) of the two emitting species in this racemic solution are equal.^{1a}

One of the most remarkable observations seen in these previous studies has been that the identity of the enantiomer that is quenched more rapidly is different when the reactions are carried out in methanol as compared to studies in water. The temperature dependence of the quenching rate constants has been determined under a variety of conditions in both methanol and water, and it has been concluded that the observed differences between the competitive reactions in water and methanol are due to differences in the relative contributions of entropy and enthalpy to the diastereomeric free energies of activation.^{1d} The origin of these solvent effects is not completely understood. The observations may be a result of differential solvent effects on encounter complex formation (*K*), or on the rate of formation of a 'precursor' transition-state structure within the encounter complex (*i.e.* the reaction step described by *k_{et}*). In order to probe these solvent differences in more detail, we have very recently undertaken measurement of the quenching rate constants under conditions of high liquid pressure. These measurements were carried out in a specially constructed high-pressure stainless-steel liquid cell equipped with three sapphire windows. Since these windows are highly depolarizing the individual quenching rate constants were necessarily determined from the biexponential analysis of the total luminescence decay.

The results from the high pressure measurements are given in Fig. 1. In these experiments, excitation of racemic [Tb(dpa)₃]³⁻ at 330 nm was accomplished *via* a pulsed Xe arc lamp, and the time-dependence of the luminescence at 90° to the excitation beam was detected after wavelength selection by a cooled photomultiplier operating in photon counting mode. In order to calculate the quenching rate constants from the observed decay constants using eqn. (1), it was first necessary to determine the pressure dependence of *k₀*, and also the effect of solvent compressibility on [Ru(phen)₃]²⁺ concentration. Although *k₀* did increase with increasing pressure in both solvents, the change was insignificant compared to the magnitude of the first terms in eqn. (1). The volume change of water and methanol was determined from previous measurements of the compressibility of methanol and water at high pressures,³ and these corrections have been applied to the data plotted in Fig. 1.

Comparison of the results for water and methanol shows that the pressure dependence on the quenching rate constants is opposite for these identical reactions in these two achiral

solvents. In water both diastereomeric rate constants increase, however they increase at different rates, and result in increasing enantioselectivity as pressure increases. In methanol, however, increasing pressure results in a decrease in the quenching rate constants, and also decreasing enantioselectivity. The measurement of reaction rates at high liquid pressure has been used to investigate the mechanisms of electron transfer, energy transfer, and many other types of chemical reactions.⁴ In most applications the natural logarithm of the measured reaction rate, k , is plotted vs. the applied pressure, P , and the volume of activation, ΔV^\ddagger is calculated from the slope according to eqn. (3)

$$\Delta V^\ddagger = -RT \left(\frac{\partial \ln k}{\partial P} \right)_T \quad (3)$$

Linear least-squares fitting of the data given in Fig. 1 yields the activation volumes given in Table 1. We have also listed in this Table differences between the same diastereomeric reaction in different solvents, and differences between the diastereomeric reactions in the same solvent. The opposite sign of the activation volumes in the two solvents for identical diastereomeric chemical reactions is an unexpected result, and clearly shows the importance of solvation, desolvation, electrostriction, and other solvent effects in the intimate details of the reaction mechanisms.

The calculation of diffusion rates for these ionic species 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.^{1b} Estimating the diffusion rates in these solvents at the highest pressures used (from the pressure dependence of the viscosity)³ show that in all cases the reaction rates are substantially lower than the diffusion-control limit. In this kinetic regime the quenching rate constants may be expressed by eqns. (4) and (5) and, thus, the

$$k_q^{\Delta\Delta} = k_{et}^{\Delta\Delta} K^{\Delta\Delta} \quad (4)$$

$$k_q^{\Lambda\Delta} = k_{et}^{\Lambda\Delta} K^{\Lambda\Delta} \quad (5)$$

activation volumes can be further approximated by a sum of contributions from energy transfer and encounter-pair equilibrium. Separation of the observed effects into contributions due to differences between $K^{\Delta\Delta}$ and $K^{\Lambda\Delta}$, or differences in the rate of energy transfer is very difficult. In general, one expects that the activation volume associated with the formation of an ion-pair would be positive due to reduced electrostriction, and this is generally what is observed.⁴ For the system studied here, however, it is expected that these effects will be quite small since the individual ions and ion-pairs are so large. We conclude, therefore, that the differences in activation volumes between the identical reactions in the two solvents are associated with the processes described by $k_{et}^{\Delta\Delta}$ and $k_{et}^{\Lambda\Delta}$. In the formal energy-transfer step, the charge of the ions does not change, and, in addition, electronic relaxation is not expected to affect the charge distribution of the lanthanide complex. The effect of excitation of $[\text{Ru}(\text{phen})_3]^{2+}$ through radiationless energy transfer is not clear, although it has been shown that the transition rate from the charge-transfer excited state to the ground state in water shows a small pressure dependence.⁵ Overall electrostriction effects in this step are, therefore, predicted to be small, and, since the quencher is identical in the two diastereomeric reactions, differences in ΔV^\ddagger in a particular solvent reflect volume changes associated with formation of diastereomeric transition states for energy transfer.

For water, the negative activation volumes for both quenching reactions are consistent with a situation in which the precursor structure prior to energy transfer is a more tightly bound encounter complex. In this simple picture, as the distance between the donor and quencher decreases, the quenching rate constant increases. In methanol, a much different situation exists, and this must be due to solvation effects. From Table 1, it is seen that $\Delta V_{\text{MeOH}}^\ddagger - \Delta V_{\text{water}}^\ddagger$ is $+6.2 \text{ cm}^3 \text{ mol}^{-1}$ for the $\Delta\Delta$ reaction and $+5.1 \text{ cm}^3 \text{ mol}^{-1}$ for the $\Lambda\Delta$ quenching reaction. The results presented here are consistent with a scheme in which methanol molecules are 'trapped' in an encounter complex preventing the donor and quencher from close contact and more effective quenching. The positive activation volume is a result of desolvation being more important in methanol than in water. At increasing pressure, it becomes more difficult to remove the solvent and, hence the quenching rate decreases.

This increased enantioselectivity seen in the aqueous solutions, and the decreasing enantioselectivity seen in the methanol solutions is a result of the different pressure dependence of the diastereomeric quenching rate constants. These differences are small, and, although they certainly reflect structural aspects of the solvated diastereomeric encounter pairs, a precise explanation awaits further study.

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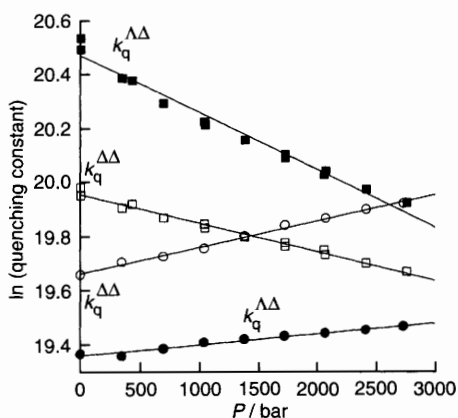


Fig. 1 Diastereomeric rate constants for the luminescence quenching of $\text{rac}[\text{Tb}(\text{dpa})_3]^{3-}$ by $\Delta\text{-}[\text{Ru}(\text{phen})_3]^{2+}$ in water (○, ●) and methanol (□, ■) at room temperature as a function of liquid pressure

Table 1 Calculated volumes of activation, ΔV^\ddagger , for quenching of $\text{rac}[\text{Tb}(\text{dba})_3]^{3-}$ by $\Delta\text{-}[\text{Ru}(\text{phen})_3]^{2+}$ in water and methanol at room temperature

	Methanol	Water	Methanol-water
$\Delta V^\ddagger (\Delta\text{-}\Lambda)/\text{cm}^3 \text{ mol}^{-1}$	+2.6	-2.5	+5.1
$\Delta V^\ddagger (\Delta\text{-}\Delta)/\text{cm}^3 \text{ mol}^{-1}$	+5.2	-1.0	+6.2
$\Delta V^\ddagger (\Delta\text{-}\Lambda) - \Delta V^\ddagger (\Delta\text{-}\Delta)/\text{cm}^3 \text{ mol}^{-1}$	-2.6	-1.5	—

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