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Spin Chemistry of Ru(II)-Trisdiimine Complex Photooxidation in Magnetic Fields up to 17.5 Tesla

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Abstract

The magnetic field dependence of the efficiency of cage escape η_{ce}, which is due to the magnetic field and spin control of the effective rate of electron backtransfer in geminate pairs of photogenerated Ru(III) complexes and electron acceptor radicals, has been measured for $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ over the entire field range from 0 to 17.5 T. These magnetic field dependent data on η_{ce}, together with the experimental values of the g-tensor components of the Ru(III) complex, allow us to evaluate unambiguously and without recourse to supplementary information, the absolute values of the rate constants of cage escape (k_{ce}), (spin-conserving) backward electron transfer (k_{bet}) and electron spin relaxation time τ_s of the Ru(III) complex.

1 Introduction

The interest in $Ru(bpy)_3^{2+}$ and related complexes as potential sensitizers of photochemical water cleavage has motivated an enormous amount of research. Many investigations have dealt with the spectroscopic properties of the emissive state of these complexes. This is generally classified as a ^{3}MLCT state, although there has been, and still is, controversy about the degree of spin purity or, in other words, the degree of spin-orbit mixing, effective in this state. [1]

Determinations of the efficiency of radical formation in photoelectron transfer reactions of $Ru(bpy)_3^{2+}$ with electron acceptors as methylviologen (MV^{2+}) have revealed that this efficiency, notwithstanding its appreciable ionic strength dependence, is in the order of 20%, indicating the existence of efficient backward electron transfer of the photoelectron to regenerate ground state $Ru(bpy)_3^{2+}$ in immediate succession to the photochemical forward electron transfer, i. e. as a geminate process in the solvent cage. This geminate backward electron transfer (BET) is spin-controlled to an appreciable extent, as we have demonstrated by the magnetic field dependence of the efficiency η_{ce} of cage escape of the radicals from the photogenerated $[Ru(bpy)_3^{3+}\cdots MV^{\bullet+}]$-pair. Because the ground state is singlet, the BET process will select the singlet component from the spin-state ensemble of the radical pair. A magnetic field effect as observed provides evidence that the radical pair is created with predominant triplet spin and that a magnetic field dependent triplet–singlet mixing

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becomes involved in the overall BET process. As a necessary condition for such a magnetic field effect it is mandatory that spin relaxation is not much faster than spin–allowed BET.

2 Theory

Theoretically, we can account for the observed magnetic field effect in a quantitative way [2, 3] by considering the 4×4 spin-orbit density matrix $\varrho_{\theta,\phi}$ of the $[\mathrm{Ru(bpy)}_3^{3+} \cdots \mathrm{MV}^{\bullet+}]$ pair and solving its Stochastic Liouville Equation

$$\frac{d\varrho_{\theta,\phi}}{dt} = -\frac{i}{\hbar}\,[\mathbf{H}_s(\theta,\phi), \varrho_{\theta,\phi}]_- + \mathcal{R}\varrho_{\theta,\phi} - \mathcal{K}\varrho_{\theta,\phi} \tag{1}$$

represented in a basis which is fixed in the molecular frame of the complex. Each orientation of the complex, characterized by the angles θ and ϕ is considered separately. The spin Hamiltonian $\mathbf{H}_s(\theta,\phi)$ governing the coherent motion of the effective spin accounts for the strongly anisotropic Zeeman interaction due to the g-tensor of the Ru(III) complex. This anisotropic Zeeman interaction induces transitions between all four of the spin-orbit states of the pair. Hyperfine interactions can be considered as negligible. The relaxation superoperator $\mathcal{R}$ is determined by the fast spin-relaxation at the Ru(III) complex, whereby it is assumed that the spin relaxation times T_1 and T_2 are equal, viz.

$$T_1 = T_2 \equiv \tau_s \; . \tag{2}$$

The reaction superoperator $\mathcal{K}$ is assumed to be diagonal in a basis for which the singlet and triplet character of individual substates of the four degenerate spin–orbit states of the $[\mathrm{Ru(bpy)}_3^{3+} \cdots \mathrm{MV}^{\bullet+}]$–pair acquire values which come closest to 0 or 1 respectively. The rate constants used are k_{ce} for cage escape (not substate selective) and $k_{bet}p_s$, where p_s is the singlet character of the respective spin-orbit state of the pair and k_{bet} refers to a hypothetically spin-allowed BET. From the orientation-dependent, time-integrated solution of eq. 1 the orientation dependent contribution to the cage escape efficiency $\eta_{ce}(\theta,\phi)$ is obtained as

$$\eta_{ce}(\theta,\phi) = k_{ce} \int_0^\infty \mathrm{Tr}[\varrho_{\theta,\phi}(t)]dt \; . \tag{3}$$

Finally, the isotropic average of η_{ce} is computed. Altogether, the dynamics encompassing spin and chemical processes are determined by the parameters $g_{\|}$, $g_{\perp}$, τ_s, k_{bet} and k_{ce}. The g-tensor components $g_{\|}$,$g_{\perp}$ of the Ru(III) complex are obtained from the low–temperature ESR spectra of the complexes. The remaining three parameters can be determined from the magnetic field dependence by fitting the observed function $\eta_{ce}(B)$ with the theoretical model.

3 Experimental

The magnet available to us at the High Magnetic Field Laboratory of MPG/CNRS at Grenoble was a Bitter type magnet with a bore of 50 mm diameter, running parallel to the magnetic field. A flow-through system with a solid steel housed, water cooled flow through cell of 5 mm light path and ≈35 μl volume, connected to a 1 mm wide steel capillary flow line was incorporated into the 50 mm bore. The flow cell in the center of the field was accessible to radiation from a 500 W HBO lamp coupled to the cell by a light guide in a 5 mm bore in the direction perpendicular to the field. The 437 nm mercury line was selected for photolysis. The technique applied for determining the magnetic field dependence of the photochemical quantum yield of $MV^{\bullet+}$ radical production was the continuous-flow continuous illumination magnetic field step method described previously [4]. The $MV^{\bullet+}$ radicals produced in the photoreaction were protected against homogeneous reoxidation through Ru(III) complexes by adding $2 \cdot 10^{-2}$ M EDTA as a sacrificial electron donor to reduce Ru(III). The experiments were carried out in aqueous solutions with concentrations of $2 \cdot 10^{-5}$ M for the complexes and $3 \cdot 10^{-3}$ M for MV^{2+}. The solutions were buffered at a pH of 6.2 .

4 Results and Discussion

The magnetic field dependence of η_{ce} for the complexes $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ as measured at the high-field laboratory for the field range of 0 to 17.5 T is shown in Figure 1. The values obtained up to 3.5 T are in good agreement with the ones determined

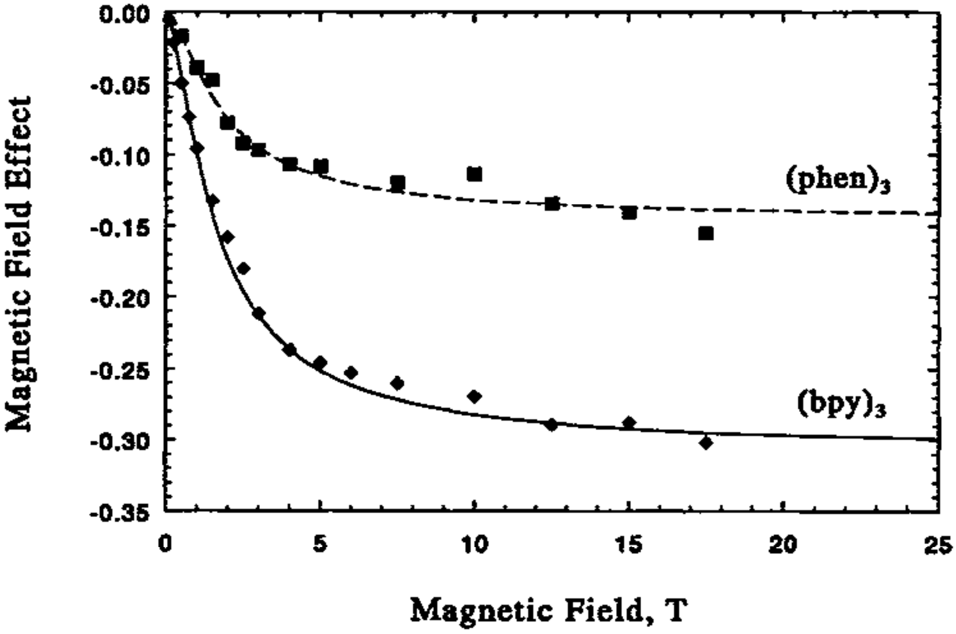

Figure 1: Magnetic field effects for $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$. The curves correspond to theoretical calculations of the magnetic field dependence using the parameters given in Table 1.

Table 1: Elementary reaction rate parameters k_{ce}, k_{bet}, τ_s obtained from the magnetic field dependence of η_{ce} for the primary Ru(III) complex $MV^{\bullet +}$ radical pair[a,b]

Ru-ligands	k_{ce}, ns^{-1}	k_{bet}, ns^{-1}	τ_s, ps	$(4\tau_s)^{-1}$, ns^{-1} [c]
$(bpy)_3$	2.5 (5.0)	90 (241)	23.6 (21)	10.6
$(phen)_3$	1.5 (5.0)	34 (140)	15.2 (9)	16.4

[a] The values previously obtained (cf. ref [3]) from the analysis of the limited field range 0 – 3.5 T and prefixing k_{ce} to $5 \cdot 10^9$ s^{-1} are given in parentheses. [b] Other input data used are $\eta_{ce} = 0.19$, and g–tensor components $g_{\parallel} = 2.71$, $g_{\perp} = 1.12$ (cf. ref [3]) [c] Corresponds to rate constant of T → S relaxation in the radical pair (cf. ref [3]).

previously with the conventional electromagnet in our laboratory. Above this field value the curvature of the field dependence increases; then the magnetic field dependence levels off at ca. 7 T, with only very gentle rise continuing up to 17.5 T, the highest field strength applied. To our knowledge this is the highest magnetic field at all, applied so far in the study of kinetic spin–chemical effects.

The curves drawn in Figure 1 result from a theoretical simulation of the magnetic field effect, based on the experimental values of the g-tensor components, the measured absolute value of η_{ce} and the values of k_{ce}, k_{bet} and τ_s given in the Table 1. As can be seen, the fit is as good as can be expected with the given scatter of the experimental data points. What must be emphasized, however, is that the information available from the full magnetic field dependence, together with the experimental values of η_{ce} and the g-tensor of the Ru(III) complex set rather narrow bounds to the *absolute* values of *all three* parameters k_{ce}, k_{bet} and τ_s which can therefore be determined through the magnetic field effect without any accessory information on them at hand. The same did not hold true when only data from the field range of 0 to 3.5 T were available and the ambiguity in the possible parameter set had to be removed by fixing the value of k_{ce} by making use of an estimation based on the Eigen-Debye equation (cf. ref. [3]).

In Figure 2 we give a demonstration how the extended field range, over which data are now available, sharpens the conditions for assessing the kinetic parameters. Here k_{ce} is fixed to the previously used value of $5 \cdot 10^9$ s^{-1}. With all the other parameter values previously used for $Ru(bpy)_3^{2+}$ (cf. Table 1), the theoretical curve (the one corresponding to the strongest magnetic field effect in Figure 2) clearly deviates from the experimental data points at fields higher than 4 T. On the other hand for $k_{ce} = 5 \cdot 10^9$ s^{-1} there is no appropriate value of τ_s to yield an acceptable fit of the experimental data (note that after fixing the values of k_{ce} and τ_s the value of k_{bet} is fixed by the condition that the correct value of η_{ce} at zero field must be reproduced). Only setting k_{ce} equal to $2.5 \cdot 10^9$ s^{-1} (±20%) allows to find values of τ_s and k_{bet} for which the experimental magnetic field effect is satisfactorily reproduced over the full field range. The absolute values of k_{ce} thus obtained being by about a factor of 2 to 3 smaller (cf. Table 1) than previously estimated on the basis of the Eigen–Debye equation, are still within the limits reasonably expected for the applicability of the diffusion model, where the effective radius of dissociation is not very

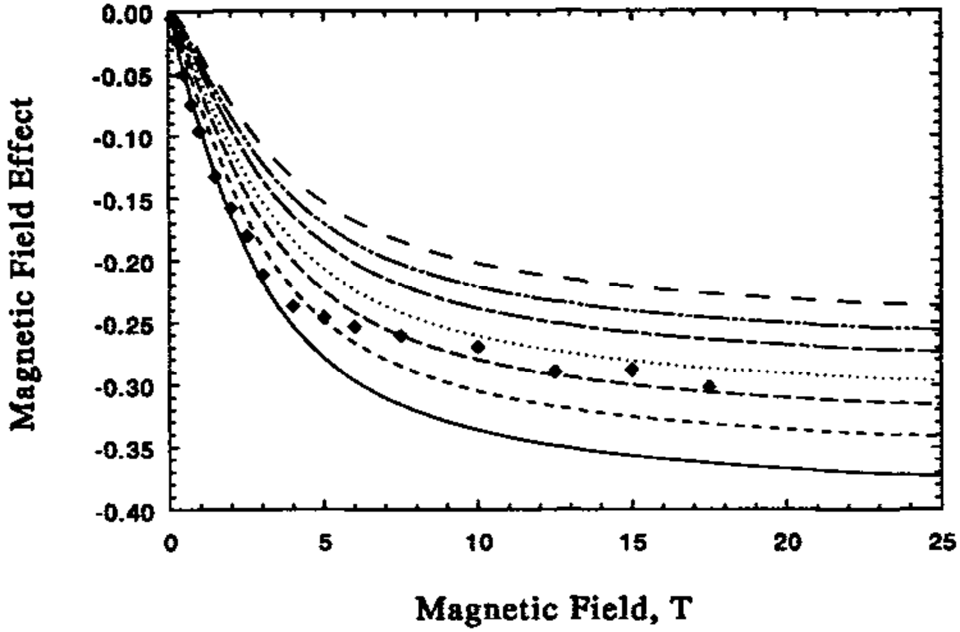

Figure 2: Magnetic field effects calculated with k_{ce} fixed to $5 \cdot 10^9$ s^{-1} and τ_s varied through the series from 21 ps (strongest field effect) to 9 ps (weakest field effect). For each τ_s the value of k_{bet} was determined to comply with a value of $\eta_{ce} = 0.19$ at zero field (cf. ref [3])

sharply defined and enters into the expression of k_{ce} with the inverse of its third power. However, it is important to note that the k_{ce} values are now direct results of the experiment and not incorporated into the model in an ad hoc fashion.

In assessing the significance of the present results, it must be emphasized that direct time–resolved observation of the decay of the $[Ru(bpy)_3^{3+} \cdots MV^{\bullet +}]$–pair is impossible for principal reasons when freely diffusing reactants are involved because by a diffusion controlled reaction the pair cannot be created in less than ca. 1 ns, whereas it decays in several tens of picoseconds. In this case, the magnetokinetic approach seems to be really unique. Furthermore, our analysis has clearly shown, that the overall rate of the backward electron transfer process is in fact largely determined by the rate of spin relaxation (cf. Table 1: compare the values of $(4\tau)^{-1}$ with those of k_{bet}!). We want to point out that this aspect of spin control has been overlooked in recent ps time–resolved investigations of photoelectron transfer reaction occurring in chemically linked $Ru(bpy)_3^{2+}$—MV^{2+}–pairs [6]. In that work, time constants of backward electron transfer in the range of 10 to 60 ps have been found. These values are of the same order of magnitude as determined in our work here and provide direct evidence that our analysis of the magnetic field effect is correct. However, the authors of ref. [6] discussed their results exclusively in terms of the ΔG–dependence of the electron transfer rate according to current electron transfer theory. In view of the important role of the spin process, which our work has demonstrated, it appears now that such a discussion of the effective rate constant of backward electron transfer (which is a measure of the rate of the overall process i. e. spin relaxation plus subsequent electron backward transfer) may be inconclusive, if it does not properly take into account the kinetic contribution of the spin process.

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