Magnetic Field Effects on the Reactivity of Co-ordination Complexes: A Probe of the Transition-state Magnetic Properties in Outer-sphere Electron Transfers

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The effect of the magnetic field on the rate of the outer-sphere electron-transfer reaction between $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$ has been investigated under fields $0 \leqslant H \leqslant 9$ T. An approximate functional dependence, $k(H)/k(0) = 1 - 0.295H + 0.157H^2 - 0.0281H^3 + 0.0016H^4 + \cdots$ has been found for the ratio of the rate constants determined at H and 0 respectively. The results have been interpreted in terms of a transition state where the magnetic dipoles of the cobalt and ruthenium species are strongly coupled.

A number of recent studies have been concerned with the effect of magnetic fields (intensities between 0 and 9 T) on the rate of chemical reactions.[1–3] In reactions of co-ordination compounds the magnetic field induces accelerations of excited-state processes comprising photosubstitutions, radiationless relaxations, or electron-transfer quenchings.[1,4–6] For example, the rate of the (^{3}c.t.)$[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine, c.t. = charge transfer) radiationless relaxation exhibits a linear dependence on the magnetic field intensity which has been attributed to a field-induced mixing of the excited state with other closely placed electronic states. Such a mechanism provides a better rationale of the experimental observations than one involving a field-induced coupling of the precursor and final states where the rate must exhibit a quadratic dependence on the field.[7]

Previous work suggests, therefore, that intense magnetic fields must perturb the rate of outer-sphere electron-transfer reactions if the reactants and/or products are in electronic states where they behave as magnetic dipoles.[1] In this work we have investigated the functional magnetic field dependence of the rate constant for a typical outer sphere electron-transfer reaction between hexa-ammine complexes of Ru^{II} and Co^{III}.

Results and Discussion

Our observations about the magnetic field effects are given below in sections which respectively provide the theoretical background (*a*), mechanistic features of the electron-transfer reaction (*b*), and the magnetic properties of such a reaction (*c*).

(*a*) *Formulation of the Problem.*—In the quantum theory of outer-sphere electron-transfer reactions, the rate constant is given by equation (1),[8,9] where K_0 is a pre-association equilibrium constant, $|\langle V_{if}\rangle|$ is a Boltzmann-averaged electronic matrix element, and $\Delta G^{\ddagger}{}_{FC}$ includes the Franck–Condon term with vibrational quantization; $\langle V_{if}\rangle$ couples the electronic wavefunctions of the initial state and final state respectively.[8,9]

$$k = K_0|\langle V_{if}\rangle|^2 \cdot \exp(-\Delta G^{\ddagger}{}_{FC}/RT) \qquad (1)$$

Such interactions, defined as Coulomb and exchange in quantum-mechanical formulations, are described by means of operators in a similar manner to that of energy-transfer reactions.[10,11] It should be noted that the operators fully respond to the electrodynamics of the systems only in the presence of extremely weak, *i.e.* earth-size, magnetic fields.[12] When sizeable fields, *i.e.* fields which affect the charges motion, are coupled to the electron transfer, the initial, transition, and final states of the reaction may experience field-induced perturbations. In a limiting case, the Zeeman energies of the reactants and/or products can be much larger than the zero-field electronic matrix elements, $\langle V_{if}\rangle$. The zero-field electronic levels of the various species must first be corrected by incorporating the magnetic field perturbation and then coupled in the electronic matrix element. Experimental evidence, *e.g.* the Zeeman splittings in magnetic circular dichroism (m.c.d.) experiments,[12,13] shows that the electronic matrix elements are larger than or equal to the Zeeman energies for magnetic field intensities up to 9 T. The theory for the motion of charges in an electromagnetic field shows that an operator, $\mathscr{H}^1 = \beta\sum_j \vec{H}(k\hat{l}_j + 2\hat{S}_j)$, where the summation is over all the electrons, must be added to the coupling operators considered above in this other limiting case.[14] This approach has already been discussed in reports about the effect of the magnetic field on the rates of excited-state radiationless relaxations.[2,7]

In the weak-field limit, we have not considered the small field-dependent changes in the standard free energies of the initial, transition, and final states of the reaction. The thermodynamics of magnetic media under thermal equilibrium show that the free energy of magnetization [equation (2)] (χ = magnetic susceptibility) is proportional to the square of the magnetic field.[15] Since the reactants and the transition state of a reaction are in pseudo-equilibrium, the free activation energy of magnetization is as shown in equation (3)[15,16] where $\chi^{\ddagger}$ is the magnetic susceptibility of the transition state and $\delta\chi^{\ddagger}$ can be defined as the magnetic susceptibility of activation by comparison with other activation parameters.[14]

$$\Delta G(H) = -\chi H^2/2 \qquad (2)$$

$$\Delta G^{\ddagger}(H) = -(\chi^{\ddagger} - \Sigma\chi_{\text{reactants}})H^2/2 = \delta\chi^{\ddagger}H^2/2 \qquad (3)$$

In addition, the activation energy $\Delta G^{\ddagger}{}_{FC}$ in equation (1) can be expressed in terms of reorganization energies (inner and outer), coulombic interactions, and the standard free energy of the reaction, $\Delta G^{\ominus}$.[16] For reactions whose rates are far from being diffusion-controlled, the dependence of $\Delta G^{\ddagger}{}_{FC}$ on the magnetic field is approximately given by equation (4), where $\Delta G^{\ddagger}{}_{FC}(0)$ is the

$$\Delta G^{\ddagger}{}_{FC}(H) = \lambda/4 + \Delta G(H)^{\ominus}/2 + [\Delta G(H)^{\ominus}]^2/4\lambda \approx \Delta G^{\ddagger}{}_{FC}(0) - \delta\chi_{PR}H^2/2 \qquad (4)$$

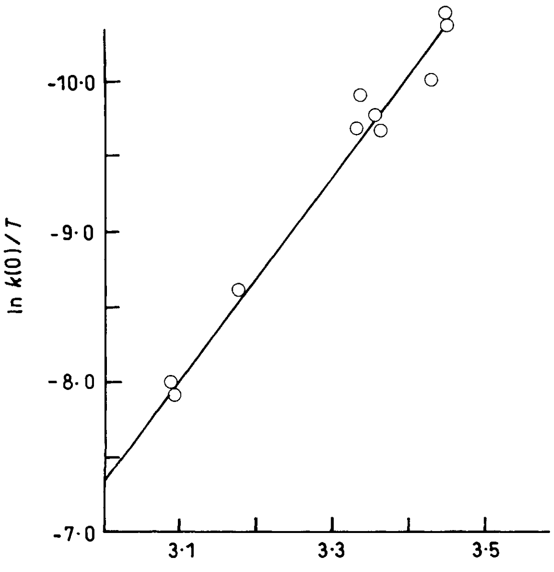

Figure 1. Plot of the Eyring equation showing the dependence of the outer-sphere electron-transfer rate constant, $k(0)$, on the temperature. The reaction rate was determined in the absence of a magnetic field with $I = 0.2$ mol dm^{-3} (NaCl)

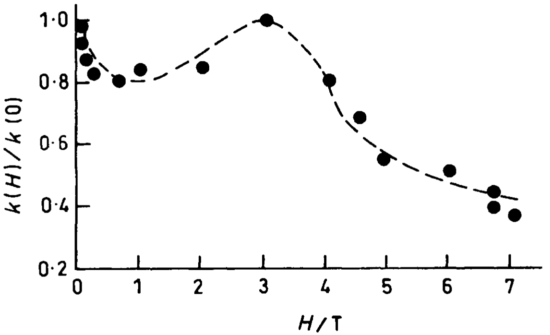

Figure 2. Dependence of the ratio of the rate constants $k(H)$ and $k(0)$ for the reaction driven under H and 0 T respectively. The reaction rates were determined at $T = 298 \pm 0.5$ K with $I = 0.2$ mol dm^{-3} (NaCl). The dashed line shows the fit of the experimental data according to equation (6)

zero-field activation energy and $\delta\chi_{PR} = \Sigma\chi_{\text{products}} - \Sigma\chi_{\text{reactants}}$ is the difference between the magnetic susceptibilities of the reactants and the products.

The reported theoretical elaborations for the expressions of the electron-transfer rate constant[8,9] can be modified by using an electronic coupling operator, $\hat{V} + \beta\vec{H}(k\hat{L} + g\hat{S})$, and by adding the magnetization energies to the exponential factor. Such a treatment leads to equation (5), where α and β are

$$k(H) = K_0(\langle V_{\text{if}}\rangle^2 + \alpha H + \beta H^2)\cdot \exp\{-[\Delta G^{\ddagger}{}_{\text{FC}}(0) - 0.5(\delta_{\chi}{}^{\ddagger} + \delta_{\text{PR}})H^2]/RT\} \quad (5)$$

statistically weighted coefficients which gauge the size of the initial to final state Zeeman-induced coupling. It should be noted that equation (5) is reduced to (1) in the zero-field limit.

(*b*) *Activation Parameters for the* $[Ru(NH_3)_6]^{2+}$–$[Co(NH_3)_6]^{3+}$ *Electron Transfer*.—In order to investigate the effect of the magnetic field on the rate of outer-sphere electron-transfer reactions, we selected the reduction of $[Co(NH_3)_6]^{3+}$ by $[Ru(NH_3)_6]^{2+}$ [equations (6) and (7)]. Some interesting

$$[Co(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+} \longrightarrow [Co(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \quad (6)$$

$$[Co(NH_3)_6]^{2+} \xrightarrow{H^+} Co^{2+}(aq) + 6NH_4{}^+ \quad (7)$$

features of this process are that the magnetic dipole of the reactants is negligible, *i.e.* $\Sigma\chi_{\text{reactants}} = 0$ in equation (3), but is large in the products,[17] and that the electron transfer undoubtedly proceeds by an outer-sphere mechanism. We have calculated the rate of the reaction with the Marcus square-root relationship, $k_{ab} = (k_{aa}k_{bb}K_{ab}f_{ab})^{\frac{1}{2}}$, where k_{ii} are self-exchange rate constants, K_{ab} is the equilibrium constant of the cross-reaction, $\log(f_{ab}) = (\log K_{ab})^2/4\log(k_{aa}k_{bb}/A_{aa}A_{bb})$, and A_{ii} are the pre-exponential factors of the respective self-exchange reactions.[18,19] The retardation factor, β_{ab},[10] defined as a ratio between the experimental, $k_{\text{obs.}}$, and calculated, $k_{\text{calc.}}$, constants, *i.e.* $\beta = (k_{\text{obs.}}/k_{\text{calc.}}) = (6 \pm 4) \times 10^{-3}$, suggests that the reaction is slightly 'non-adiabatic'. The large error in β is associated with an order of magnitude uncertainty in the value of the $[Co(NH_3)_6]^{3+}$–$[Co(NH_3)_6]^{2+}$ self-exchange rate constant rather than experimental error in the determination of $k_{\text{obs.}}$,*[20] We have also determined the rate at temperatures between 278 and 340 K, a range where the logarithmic representation of the results, Figure 1, is in accord with Eyring's equation.[14] An activation enthalpy, $\Delta H^{\ddagger} = 56.1$ kJ mol^{-1}, and an intercept, $[(\Delta S^{\ddagger}/R) + \ln(\kappa k/h)] = 13.3$, were calculated by the least-squares method. Such activation parameters and the retardation factor give an activation entropy, $\Delta S^{\ddagger} \approx -0.93$ J K^{-1} mol^{-1}, whose value suggests opposed entropic contributions from the Coulombic interaction and the outer-sphere reorganization respectively.[16]

(*c*) *Magnetic Field Effects*.—The rate constant of the electron-transfer reaction, [equations (6) and (7)], was measured at a constant temperature, $T = 298.0 \pm 0.5$ K, and given magnetic field intensities, Figure 2. In individual determinations of the rate constants the relative 'most probable error' of the rate constants and the ratio, $k(H)/k(0)$, are 3 and 6% respectively. The points in Figure 2 are averages of five individual determinations with a standard deviation $\leqslant 3\%$. The non-linear dependence of $k(H)/k(0)$ on the magnetic field is in accord with the mathematical complexity of equation (5). The exponential factor in the expression of $k(H)/k(0)$ deduced from equations (1) and (5) was series-expanded in powers of H, *i.e.* $k(H)/k(0) = \Sigma_{n=1}^{\infty} a_nH^n$, under approximations that are commonly used in the theory of magnetic susceptibilities.[17] Values for the coefficients, equation (8), were calculated by a least-squares

$$k(H)/k(0) = 1 - 0.295H + 0.157H^2 - 0.0281H^3 + 0.0016H^4 + \cdots \quad (8)$$

polynomial fitting of the experimental data in Figure 2. Correlations of the coefficient values with their analytical expressions allowed us to calculate $(\delta\chi^{\ddagger} + \delta_{\text{PR}}) \approx 10^2$ J dm^3 mol^{-1} T^{-2}. Since literature values of the magnetic susceptibilities show that the contribution of δ_{PR} is negligible, *i.e.* $\delta_{\chi\text{PR}} \ll 10$ J dm^3 mol^{-1} T^{-2}, the transition state of the reaction, equation (1), must be strongly paramagnetic. Such strong paramagnetism suggests strong coupling of the magnetic dipoles of Co and Ru as expected for an exchange mechanism. In a qualitative sense, a similar magnetic behaviour has been observed in other electron-transfer reactions of low-spin d^6 and d^7 metal ions, *e.g.* reactions involving complexes of low-spin Co^{II}, Co^{III} and Ru^{II}.

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* Note that a probable error, $\delta\beta/\beta = [(\delta k_{\text{obs.}}/k_{\text{obs.}})^2 + (\delta k_{bb}/k_{bb})^2]^{\frac{1}{2}}$ can be derived from the expressions of β and k_{bb}, respectively.[20] The relative errors, $(\delta k_{\text{obs.}}/k_{\text{obs.}}) \approx 0.07$ and $(\delta k_{bb}/k_{bb}) \approx 0.3$, were estimated from the magnitudes and uncertainties of the respective rate constants.

Experimental

Reaction rates were measured for pseudo-first-order kinetics with $[Ru(NH_3)_6]^{2+}$ in at least ten-fold excess of $[Co(NH_3)_6]^{3+}$. The reactant solutions were handled under anaerobic conditions by using a syringe procedure. Moreover, the accuracy of the measurements was optimized by adding a given volume of the ruthenium(II) solution to a weighted and deaerated sample of the cobalt(III) stock solution already placed in the reaction cell. The reactant concentrations were calculated from the weight of the mixture, the weight of the $[Co(NH_3)_6]^{3+}$ solution, and the concentrations of the complexes in the stock solutions. A modified gas-tight spectrophotometer cell enabled placing of the reaction mixture inside the cavity of an American Magnetics superconducting magnet which was able to generate fields between 0 and 9 T. Solutions in the cavity were kept at constant temperature which experienced insignificant fluctuations ($\Delta T < 0.2$ °C) during the experiments. The reaction was followed by reading the optical density (o.d.) with an error Δ(o.d.) = ± 0.0002 at 279 nm. Each individual value of the rate constant was calculated from 50 measurements of Δ(o.d.) in time intervals equivalent to reactant-to-product conversions less than or equal to 20%. Moreover, the o.d. changes for more than 99.99% reactant to product conversions were measured for times greater than or equal to 9.5 reaction half-lives.

The compounds $[Ru(NH_3)_6][ClO_4]_2$ and $[Co(NH_3)_6]Cl_3$ were available from previous work and their purity was assessed from their u.v.–visible spectra; $[Ru(NH_3)_6][ClO_4]_2$(Alfa) was purified according to a literature procedure and its purity established by means of its absorption spectrum.[21] Other materials were reagent grade and used without further purification.

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