

Direct Measurement of Spin-State Lifetimes in Solution for Some Iron(II) Spin Equilibrium Complexes Derived from Hexadentate Ligands^{1a}

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Abstract: The rates of intersystem crossing of the iron(II) spin equilibrium systems [Fe(6-MePy)(Py)₂tren](PF₆)₂ and [Fe(6-MePy)₂(py)tren](PF₆)₂ have been measured by the laser Raman temperature-jump method. Absorbance changes at the charge-transfer band maximum ($\lambda_{\text{max}} \sim 560$ nm) following the temperature-jump perturbation show that the approach to equilibrium occurs by a first-order process. The rate constants for the forward (k_1) and reverse (k_{-1}) steps in the FeL²⁺ (low spin) \rightleftharpoons FeL²⁺ (high spin) reaction in methanol or aqueous solutions are: L = (6-MePy)(Py)₂tren, $k_1 = 4 \times 10^5$, $k_{-1} = 8 \times 10^6$ s⁻¹; L = (6-MePy)₂(Py)tren, $k_1 = 4 \times 10^6$, $k_{-1} = 5 \times 10^6$ s⁻¹ at 25 °C. The kinetics are discussed and it is shown that the results are consistent with the suggestion that a spin-state equilibrium could precede electron transfer in reductions of the hexaaquacobalt(III) ion.

Recently we reported² the synthesis and characterization of a new series of iron(II) spin equilibrium complexes derived from the hexadentate ligands shown in Figure 1. Variable-temperature magnetochemical and electronic spectral results^{2,3} indicated a substantial trigonal distortion of ~ 1000 cm⁻¹ for the series, giving rise to a ¹A (low spin) \rightleftharpoons ⁵A (high spin) equilibrium. Especially noteworthy members of the series are compounds II and III, since they, along with a [Fe(pyrazolylborate)₂] complex,⁴ are the first iron(II) compounds to be well characterized as displaying spin equilibrium *in solution*. Complexes II and III are further distinguished by the fact that they exhibit very similar magnetic moment vs. temperature curves in both the solid and solution states. This behavior is in contrast to the [Fe(pyrazolylborate)₂] series,⁴ where the proportion of the low-spin form obtaining in the solid phase is higher than that present in solution at a given temperature. Theoretical fits for both series^{2,4} indicate that the energy separation between the two spin states is temperature dependent. For II and III, at least, this temperature dependence cannot be attributed to solid-state packing or other forces; the other members of the series, compounds I and IV, are low spin and high spin, respectively, in solution over a >200° temperature range.

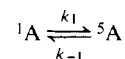
For II, III, and IV, Mössbauer spectroscopy has demonstrated that for a dynamic ¹A \rightleftharpoons ⁵A equilibrium the spin-state lifetimes of the ¹A state, $\tau(^1A)$, and the ⁵A state, $\tau(^5A)$, are $\geq 10^{-8}$ s in the solid state,⁵ whereas ¹H NMR measurements have established an upper limit for τ of $\sim 3.6 \times 10^{-6}$ s in solution.² In this work we wish to report a direct measurement of $\tau(^1A)$ and $\tau(^5A)$ for compounds II and III in solution using the laser Raman temperature-jump technique developed at Brookhaven.⁶ To date, the only other spin equilibrium to be investigated by this technique is the ¹A \rightleftharpoons ⁵A process for the bis(hydrotris(pyrazoyl)borate)iron(II) complex reported by Beattie et al.⁷ In general, metal chelate spin-state lifetime studies of the nature reported here are of interest because of their importance in understanding intersystem crossing phenomena, not only for spin equilibria but also for photochemically excited states and electron-transfer processes where spin conversion may be directly coupled to electron transport.^{8,9}

Experimental Section

The laser Raman temperature-jump apparatus has been described previously.⁶ Sample cells with 0.20–1.60-mm path lengths were em-

ployed and the relaxations were followed at 560 nm. Various hydroxylic solvents and solvent mixtures were tested including methanol, water, water-acetone mixtures (10:1 by volume), methanol-acetone (1:1 to 10:1 by volume), aqueous salt solutions ($\mu \leq 1.0$ M), and Beckman pH buffer solutions ($4 \leq \text{pH} \leq 10$). All experiments were run at 20 ± 2 °C.

The first-order relaxation time for the



spin interconversion process was determined from $\log(I_\infty - I)$ vs. time plots generated from photographs of the oscilloscope traces. Rate constants k_1 and k_{-1} for the spin interconversion processes were calculated from the measured relaxation times ($\tau^{-1} = k_1 + k_{-1}$) and the equilibrium constants for the interconversion (k_1/k_{-1}) previously determined (0.05 and 0.86 for compounds II and III at 20 °C, respectively).² The spin-state lifetimes, $\tau(^1A)$ and $\tau(^5A)$, are then simply k_1^{-1} and k_{-1}^{-1} , respectively.

Results and Discussion

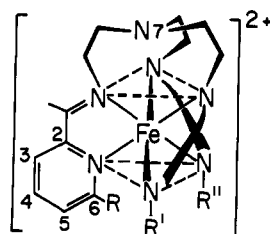
A typical relaxation curve for III in methanol is shown in Figure 2. For the relaxations obtained in these experiments, it can be shown⁶ that electronic band-width considerations for the amplifier-oscilloscope system and the laser pulse width (~ 30 ns) combine to produce an error of <1% in the measured relaxation time.

Both compounds II and III display similar relaxation behavior in water, methanol, and the mixed solvent systems. Results are independent of ionic strength up to 1.0 M using Na₂SO₄ and pH 7 buffer solution. Electronic spectral measurements before and after the experiments indicated no compound decomposition. In buffer with $\text{pH} \geq 8$ or ≤ 6 , no relaxation was observed. Spectral measurements in these cases showed that the absorbance at the band maximum (560 nm) decreased $\sim 2\%$ in the first 15 min after preparation of the solution and continued to decrease somewhat more slowly after that. The initial decrease could be due to a decomposition reaction in the aqueous media. Whatever this reaction is, it is clearly much slower in the other solvent systems studied and, if it is present in those at all, it does not affect the observed kinetics. IV, which should not show any spin relaxation at 25 °C, was too unstable to be studied in aqueous or alcoholic solution. No evidence of a relaxation process was observed when the low-spin compound I (which is stable in aqueous and alcoholic media) was examined at several wavelengths. This fact, along with the absence of an appreciable salt or solvent effect

Table I. Kinetic Parameters for Iron(II) $^1A \rightleftharpoons ^5A$ Spin Interconversion Processes

Compd	Exptl conditions	τ , ns	k_1 , s^{-1}	k_{-1} , s^{-1}
$[\text{Fe}(\text{6-MePy})(\text{Py})_2\text{tren}]^{2+}$ (II) ^a	Methanol, acetone (10%)–H ₂ O (20 ± 2 °C)	120 (20) ^c	4×10^5	8×10^6
$[\text{Fe}(\text{6-MePy})_2(\text{Py})\text{tren}]^{2+}$ (III) ^a	acetone (10%)–H ₂ O acetone (10%)–MeOH (20 ± 2 °C)	110 (30) ^c	4×10^6	5×10^6
$[\text{Fe}(\text{pyrazolylborate})_2]^{2+}$ ^b	MeOH–CH ₂ Cl ₂ (21 °C)	32 (10)	1×10^7	2×10^7

^a This work. ^b Reference 7. ^c τ = measured relaxation time in nanoseconds; numbers in parentheses are calculated standard deviations.



- (I) $[\text{Fe}(\text{Py})_3\text{tren}]^{2+}$; $R=R'=R''=H$
 (II) $[\text{Fe}(\text{6-MePy})(\text{Py})_2\text{tren}]^{2+}$; $R=R'=H$, $R''=CH_3$
 (III) $[\text{Fe}(\text{6-MePy})_2(\text{Py})\text{tren}]^{2+}$; $R=H$, $R'=R''=CH_3$
 (IV) $[\text{Fe}(\text{6-MePy})_3\text{tren}]^{2+}$; $R=R'=R''=CH_3$

Figure 1. Schematic drawing of the coordination of the hexadentate ligands around iron(II) in the spin equilibrium systems.

on the spin lifetimes, strongly suggests that the process responsible for the observed relaxation is indeed the *intramolecular* spin equilibrium process (involving two energy levels) previously characterized.² Therefore, the observed relaxations have been analyzed in terms of a first-order exponential time dependence, although a more complicated relaxation curve could conceivably be masked by noise in the traces.

The low signal intensity is a result of the facts that ΔH is relatively small for these spin equilibrium processes (≤ 5 kcal mol⁻¹)^{2,10} and that the difference in the molar absorptivities for the CT bands of the two magnetic isomers is also relatively small ($\Delta\epsilon \sim 3000$). These considerations lead to a small temperature dependence of the absorbance of the spin system.

The previously determined⁷ spin-state lifetimes for the $^1A \rightleftharpoons ^5A$ spin equilibrium compound, bis(hydrotris(pyrazolyl)borate)iron(II), along with the lifetimes for the II and III systems determined in this work are summarized in Table I. Although lifetimes for the 1A and 5A states fall within a 10^{-6} – 10^{-8} -s range for all these $^1A \rightleftharpoons ^5A$ processes, those for compounds II [$\tau(^1A) = 2.5 \times 10^{-6}$, $\tau(^5A) = 1.3 \times 10^{-7}$ s] and III [$\tau(^1A) = 2.5 \times 10^{-7}$, $\tau(^5A) = 2 \times 10^{-7}$ s] are significantly *longer* than for the $[\text{Fe}(\text{pyrazolylborate})_2]$ complex [$\tau(^1A) = 1 \times 10^{-7}$, $\tau(^5A) = 5 \times 10^{-8}$ s]. The full implication of these results is not yet clear, since these three samples of a $\Delta S = 2$ spin change may not span the entire range of lifetimes that will be realized for other spin equilibrium systems of differing electronic structure (metal ion and oxidation state) and molecular geometry (coordination number and ligand environment).¹¹ It may be, for example, that the hexadentate ligand environments in compounds II and III are mainly responsible for the *longer* 1A and 5A spin lifetimes as compared to those observed for the $[\text{Fe}(\text{pyrazolylborate})_2]$ complex. Whatever the details of the electronic crossing may be, it will of necessity take place on the multidimensional translational-vibrational surface connecting the two electronic states of the system. Even in the absence of any mechanical restrictions by the ligand,

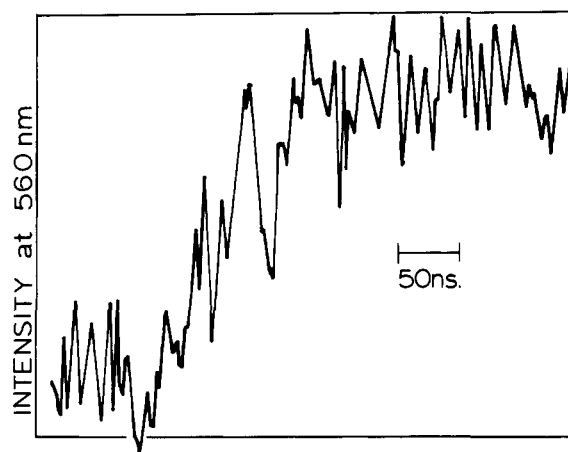


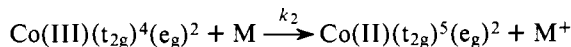
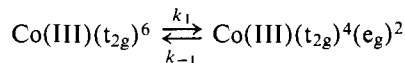
Figure 2. Typical oscilloscope trace obtained from laser Raman temperature-jump system for the iron(II) spin equilibrium complexes: sweep time = 50 ns per major division, $[\text{FeL}^{2+}] = 5 \times 10^{-4}$ M.

some adjustments in the activation parameters are expected as the crossing point of the microstate energies is changed.¹² The magnitude of these effects and the constraints due to such conformational restrictions in compounds II and III as H–H nonbonding interactions between methylene protons on the tren backbone or methyl group–pyridine ring steric interactions in the lower polyhedral face are difficult to assess. Probably, both play a role. It is clear, however that *shorter* lifetimes are encountered for the $[\text{Fe}(\text{pyrazolylborate})_2]$ species, where molecular models suggest that steric interactions are not important. This difference in the two systems seems reasonable if in the present systems nonbonding steric interactions within the chelated multidentate ligand are energetically restrictive to the primary coordination sphere reorganizational processes known to accompany spin conversion;^{2,13} no similar stereochemical restrictions to structural change are present in the bistridentate $[\text{Fe}(\text{pyrazolylborate})_2]$ species.

While the anomalous magnetism associated with spin equilibria is only observed when the energies of the two spin states are within a few hundred wavenumbers of each other, it is possible that a kinetically significant population of a higher energy state may be present even when the energy difference between the two states is considerably larger. For example, even with a 2000 cm^{-1} separation, a Boltzmann distribution gives a 6×10^{-5} equilibrium population of the high energy state at 30 °C. If the rate constant for electron transfer to or from the more stable spin state is small, it may well be that excitation to a higher energy electron configuration becomes the preferred pathway for electron transfer. In this case, the active species is the small equilibrium population of the high energy state present in solution. The observed rate constant is then the product of the two terms K_{th} , the equilibrium constant for population of the excited spin state, and k_2 , the sec-

ond-order rate constant for transfer of an electron from or to the excited spin state.

Although the above scheme has been suggested previously,¹⁴⁻¹⁶ its ramifications have not always been appreciated. Applied to certain cobalt(III) reactions the pre-equilibrium scheme takes the form



A rate saturation is expected for the more rapid reactions at high concentrations of the reducing agent. It arises naturally in the above scheme when the rate of electron transfer becomes competitive with the rate of spin change. Failure to observe rate saturation in reductions of Co(III) is, however, not necessarily evidence against the above mechanism, since rate saturation will not occur if $k_{-1} > k_2[M]$. As for the iron(II) systems discussed above, the spin change for the cobalt(III) system is also a $\Delta S = 2$ transition and the data in Table I show that such a spin change can be very rapid. For the above scheme to provide the main pathway for the oxidation of M by Co(III), it is also necessary that the product $K_{th}k_2$ be larger than the rate constant for the direct (nonadiabatic) electron transfer between $\text{Co(III)}(t_{2g})^6$ and M. Finally, K_{th} cannot be too small, since this would require an unreasonably high value of k_2 .

The above considerations may be illustrated by considering the reactions of $\text{Co(H}_2\text{O)}_6^{3+}$. It has been found¹⁷ that the rate of reduction of $\text{Co(H}_2\text{O)}_6^{3+}$ by a series of reducing agents remains second order, but "saturates" below the diffusion-controlled limit as ΔG° becomes very negative. From this rate saturation, the value of K_{th} for $\text{Co(H}_2\text{O)}_6^{3+}$ can be estimated to be 10^{-5} (the maximum rate in terms of this model is $K_{th}k_{diff}$).^{12,18} Although this estimate seems reasonable,¹⁹ the rate saturation of the $\text{Co(H}_2\text{O)}_6^{3+}$ reactions can also be rationalized in terms of nonadiabatic factors.^{12,18,20,21}

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References and Notes

(1) (a) Presented in part at the Southwest Regional Meeting of the American

- Chemical Society, Houston, Texas, December 1974; (b) School of Chemical Sciences, University of Illinois; (c) William Marsh Rice University; (d) Brookhaven National Laboratory.
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 - (5) Preliminary variable temperature (153–300 K) ESCA data taken on IV shows no observable change in the high-spin Fe(2p) ionization pattern with decreasing temperature, even though by 153 K the bulk property magnetic moment measurement ($\mu_{eff} \approx 0.6 \mu_B$) indicates nearly complete $^5A \rightarrow ^1A$ spin conversion. Since the Fe(2p) binding energies for the high-spin form [for IV with μ_{eff} (300 K) = 5.0 μ_B , $2p_{3/2} = 710.1$ eV, and $2p_{1/2} = 723.2$ eV relative to C(1s) peak] and the low-spin form [for I with μ_{eff} (300 K) = 0.5 μ_B , $2p_{3/2} = 708.0$ eV, and $2p_{1/2} = 720.5$ eV] are measurably different in position and peak shape [the high-spin Fe(2p) peaks have shake-up structure and the low-spin Fe(2p) peaks do not], the lack of temperature dependency in the spectrum of IV suggests the possibility of local domains in the lattice consisting of static 5A or 1A molecules with the ESCA detectable 5A "surface" molecules being among the last to undergo the $^5A \rightarrow ^1A$ spin conversion. Thus, the Mössbauer experiment may not be monitoring a dynamic $^1A \rightleftharpoons ^5A$ process at all, making the discussion of τ from this solid-state technique less meaningful. In solution no such ambiguity exists and the spin interconversion process can reasonably be assumed to be dynamic, permitting direct measurement of τ as described herein. Complete variable-temperature ESCA work on these and other variable-spin metal complexes will be reported subsequently: E. V. Dose, M. G. Simmons, M. F. Tweedle, C. D. Wagner, and L. J. Wilson, submitted for publication.
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 - (10) Attempts to measure these rates at -5°C indicated no measurable change in the first-order relaxation time. From this, we estimate that $\Delta H \leq \Delta H^\ddagger \leq 5$ kcal mol $^{-1}$.
 - (11) The only other $\Delta S = 2$ spin interconversion rate data available are for some ferric myoglobin hydroxides where a conventional temperature-jump experiment has established a lower limit of 2×10^5 s $^{-1}$ on the sum of the forward and reverse rate constants [J. K. Beattie and R. J. West, *J. Am. Chem. Soc.*, **96**, 1933 (1974)]. Of course, direct laser temperature-jump spin state lifetime measurements for spin equilibrium heme proteins would be especially intriguing, since the spin change should be intimately related to the movement of the iron atom into or out of the plane of the porphyrin ligand.
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