

NMR study of electron transfer between paramagnetic complexes

Kinetics of the self-exchange reaction $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{+/0}$ (py = pyridine)

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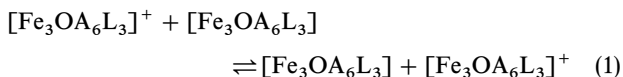
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The kinetics of the electron transfer self-exchange reaction $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+ + [\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3] \rightleftharpoons [\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3] + [\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+$ have been measured by NMR line broadening. Both reactants are paramagnetic and it was possible to measure broadening of lines of each component by exchange with the other. In dichloromethane at 23 °C the second-order rate constant is $(3.7 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The ligand exchange reactions of $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{n+}$ with pyridine are rapid for the mixed-valence complex ($n = 0$) but slow for the oxidised complex ($n = 1$).

1 Introduction

Although NMR line-broadening is a standard technique for kinetic measurements on quasi-symmetrical reacting systems,¹ its application to electron transfer 'self-exchange' reactions has mainly been to systems in which at least one of the reagents is diamagnetic, so that the effect measured is that of kinetic broadening on the resonances of the diamagnetic species. The principal exceptions to date have been a few studies of electron transfer in biological systems, using NMR of protons remote from the site of electron transfer.^{2a,3} In studies of reactivity of polynuclear transition metal clusters, especially the important family of exchange-coupled trinuclear complexes,⁴ we required rate constants for self-exchange reactions of the type $[\text{M}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^{+/0}$, where M is a first row transition metal, and in all cases both the oxidised and reduced forms are paramagnetic. However, the complexes are strongly antiferromagnetic, and the distances of the protons of the R and L groups from the magnetic centres are quite large. We found that good quality proton NMR spectra could be obtained with clearly resolved resonances for both reactants. Here we report a study of self-exchange involving the mixed-valence iron(III, III, II) complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$ (py = pyridine). Spectra were obtained for both the oxidised and the reduced species, and this made it possible to study the kinetics by independently varying the concentrations of both species. This proved to be an essential precaution since it disclosed a complication due to ligand dissociation, which would otherwise have caused a large systematic error.

The reaction of interest is



where A = pivalate, $\text{Me}_3\text{CCO}_2^-$, and L = $\text{C}_5\text{H}_5\text{N}$. In the solid state, both complexes have the well known ligand-bridged structure (Fig. 1),^{4,5} and NMR and IR studies show that the oxo-centred trinuclear cluster is stable in solution in various non-polar and moderately polar solvents.⁶ The reduced complex contains the mixed valences iron(III, III, II). At room temperature the valences are fully delocalised on the Mössbauer timescale (in the solid)⁵ and on the NMR timescale (in solution)⁷ but all indications are that this is due to a rapid internal electron transfer and that the iron sites are correctly described as high-spin iron(III) and iron(II), the spins being antiferromagnetically coupled.^{8,9}

2 Experimental

The complexes^{8,9} were weighed dry into the NMR tubes and dissolved under nitrogen in degassed perdeuteriodichloromethane (with 0.1% TMS). Tubes were sealed with Parafilm while spectra were run. Oxidation of the mixed-valence complex, estimated from intensities of resonances due to the fully oxidised complex in the spectra of the mixed valence sample, did not exceed 2%.

All spectra were recorded on a JEOL 270-EX spectrometer covering a total frequency range of 49 019.6 Hz, corresponding to $\delta -45$ to 135 with 32 000 data points and 128 scans. A 90° pulse and a pulse repetition rate of 1 s were used. The spectrometer magnets were shimmed manually. Temperature was controlled to ± 0.2 °C using the spectrometer cryogenic unit, and the rate of temperature equilibration between the contents of the tubes and the surroundings was found by experiment to be rapid. Bandwidths $\nu_{1/2}$ of the resonances, defined as full width at half height, were measured by hand on suitably enlarged hard copies. This was found to be the most reliable and reproducible method: values obtained using the instrument software were found to vary by up to 10% in an apparently random way, and it was not possible to transfer data to a format suitable to allow independent curve fitting. Errors due to uncertainties in measurement of line width were checked in the following ways. Phasing was tested by deliberately altering the phasing of a peak and measuring the apparent FWHH. The effects were small, about 0.02 Hz per 5°, and

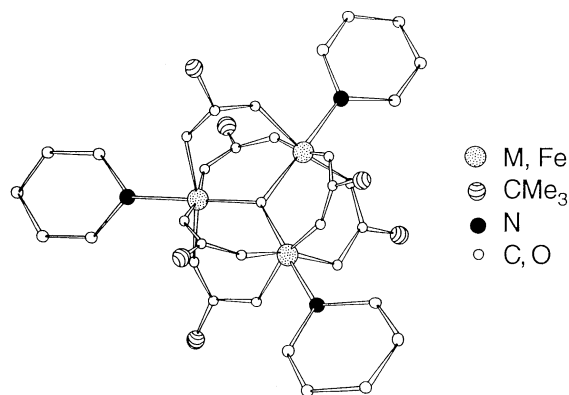


Fig. 1 Basic structural unit of the complexes $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{+/0}$

the correct phasings of lines could easily be estimated visually. Varying numbers of scans also had little effect on band width, *e.g.* an increase of 0.02 Hz on doubling the number of scans. The largest error that could not be controlled was that of measuring widths directly when the width was large and the height of the signal such that baseline noise was significant. This restricted the range of measurement of some resonances, especially the β -H (pyridine) resonance of the mixed-valence iron complex.

3 Results

3.1 Spectra

Typical ^1H spectra of the oxidised and reduced iron trimer complexes are shown in Fig. 2. For the oxidised complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+$, three resonances were observed as reported and assigned previously⁷ [the resonance of γ -H(py) is obscured by that of H(Me)]. They are all broad singlets, second order coupling effects between the pyridine protons being lost due to paramagnetic broadening. Selective proton decoupling measurements showed very small effects on line width, typically a narrowing of 2–3 Hz was observed, consistent with suppression of second order effects. From comparisons with spectra of the free ligand it is clear that paramagnetic shifts arising from coordination to the iron centres increase in the order $\text{H}(\text{Me}) < \gamma\text{-H}(\text{py}) < \beta\text{-H}(\text{py}) < \alpha\text{-H}(\text{py})$. The observed downfield shifts are consistent with a coupling mechanism having contributions from both through-bond (contact) and through-space (dipolar or pseudo-contact) terms. It is clear that, on the NMR timescale and under our conditions, exchange of terminal pyridine ligands of $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{n+}$ is rapid for the mixed-valence

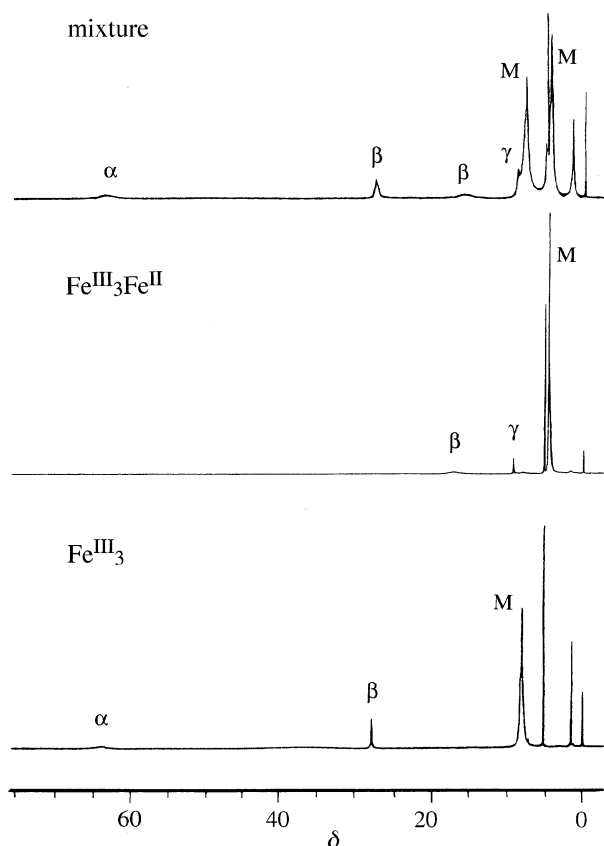


Fig. 2 ^1H NMR spectra of $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+$ (bottom), $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$ (middle) and a 1 : 1 mixture of the two complexes (top). In dichloromethane, 25 °C. $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{n+} = [\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3] = 9$ mM. α , β , γ = pyridine protons, M = methyl. Unmarked peaks are due to solvent, TMS and free pyridine.

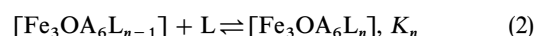
complex ($n = 0$) but slow for the oxidised complex ($n = 1$). Such a difference in ligand exchange rates is typical for high-spin iron(III) and iron(II) respectively.¹⁰ On addition of pyridine, the three sharp resonances of free pyridine were observed and no shifts or broadenings of any of the resonances could be detected.

For the reduced complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$, resonances were observed for the H(Me) and the γ -H(py); the chemical shift of the latter varied both with concentration of complex and with added pyridine, but the band widths did not. The other pyridine resonances were too broad to be observed with sufficient accuracy for kinetic work. The spectrum of a typical mixture shows all the above-mentioned resonances, broadened as discussed below.

3.2 Equilibria

Preliminary measurements easily showed that reaction (1) is in the ^1H NMR timescale at 270 MHz, in dichloromethane at room temperature, but first experiments with varying concentrations of oxidised and reduced complexes, respectively, gave inconsistent rate constants. This was traced to partial dissociation of the mixed-valence complex giving variable concentrations of free pyridine in the reaction mixtures. IR spectra confirmed the dissociation, showing distinct frequencies for coordinated and non-coordinated pyridine. The band at 1446 cm^{-1} is assigned to the 'X-sensitive' mode 19b of pyridine.¹¹ It was observed in the solid state [Fig. 3(a)] and in solution [Fig. 3(b)], but in solution a second band due to the corresponding vibration of free pyridine was observed at 1438 cm^{-1} . On addition of further pyridine to the solution both bands increased in intensity but the ratio of free to coordinated pyridine increased as expected. No dissociation was observed in the case of the oxidised complex, the peak at 1449 cm^{-1} being clear both in solid state and in solution [Fig. 3(c), 3(d)].

The NMR spectra were used to estimate the extent of dissociation and to establish the conditions needed to suppress it. The equilibria were assumed to be



with $n = 1, 2, 3$, so that the Bjerrum formation number is given by

$$\langle n \rangle = \frac{\sum_{n=0}^3 n[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6\text{L}_n]}{\sum_{n=0}^3 [\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6\text{L}_n]} \quad (3)$$

Assuming the statistical relationship¹² $K_n = [(4 - n)/n]Q$, this reduces to

$$\langle n \rangle = 3Q[\text{L}]/(1 + Q[\text{L}]) \quad (4)$$

and the observed frequency of a given resonance is

$$\langle \nu \rangle = \nu_0 + (\nu_1 - \nu_0)[\text{L}]_b/[\text{L}]_T \quad (5)$$

where ν_0 , ν_1 are frequencies for bound and free ligand and $[\text{L}]_b$, $[\text{L}]_T$ are concentrations of bound and total ligand. As an estimate of ν_0 , the value observed in the solvent CDCl_3 was used.^{7b} Values of $\langle \nu \rangle$, for $\gamma\text{-H}(\text{py})$, were found to lie between $\nu_0 = 9.0$ and $\nu_1 = 7.68$ ppm. They increased with increasing complex concentration and decreased with added ligand concentration, and in the range of concentrations used in this work, the average value of $\langle n \rangle$ was found to be 1.5 when $[\text{L}] \approx 0.05$ M. Hence we estimate $Q \approx 10\text{ dm}^3\text{ mol}^{-1}$ and $K_3 \approx 20\text{ dm}^3\text{ mol}^{-1}$. Consistent with these estimates, the dissociation became insignificant with addition of 0.15 M excess pyridine.

3.3 Kinetics

As noted above, NMR spectra of mixtures of the two complexes showed a superposition of all the above bands, but also

a significant broadening of all of them, showing that self-exchange is in the slow limit of NMR kinetics (SUP 57363).[†] Data were fitted to the equations^{2b,c}

$$\pi \delta v_{1/2}^A[A] = \pi \delta v_{1/2}^B[B] = k[A][B] \quad (6)$$

where $\delta v_{1/2}^A$ is the increase in bandwidth of a resonance of species A, produced by a concentration [B] of species B, and *vice versa* (A, B = $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{+/0}$). For the oxidised complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+$, all three resonances showed the same increase in width with concentration of the reduced complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$. For the reduced complex, the one resonance which could be observed with the required precision, increased with concentration of oxidised complex. In the initial studies, rate constants k calculated from the slopes of these two plots did not agree, but when the measurements

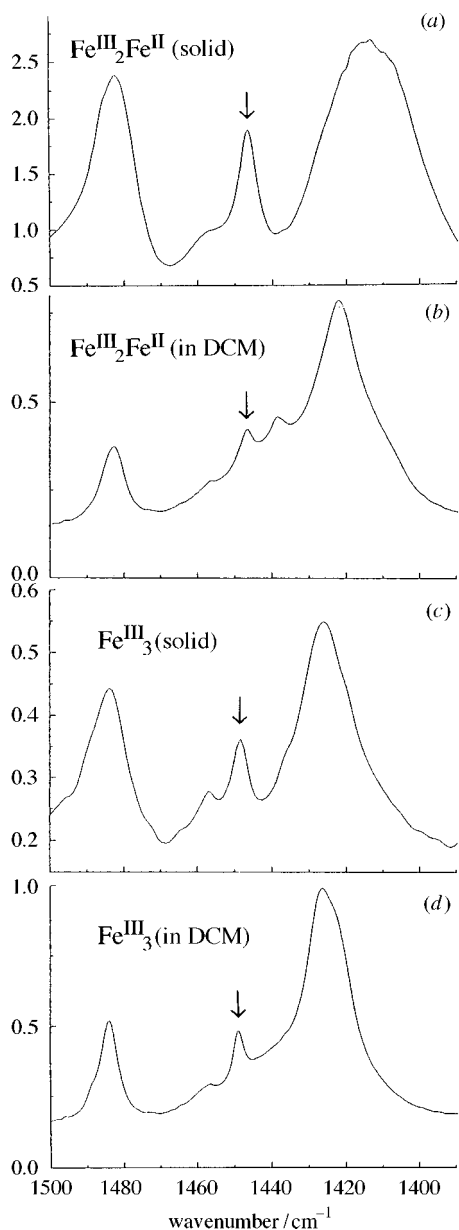


Fig. 3 IR spectra. Top to bottom: $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$ (a) in solid state (KBr disc); (b) in dichloromethane. $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]\text{ClO}_4 \cdot \text{py}$; (c) in solid state (KBr disc); (d) in dichloromethane. Bands marked with an arrow are assigned to coordinated pyridine.

[†] Supplementary material (SUP 57363, 3pp). Tables of concentrations and NMR linewidths are available from the British Library, for details contact the editorial office.

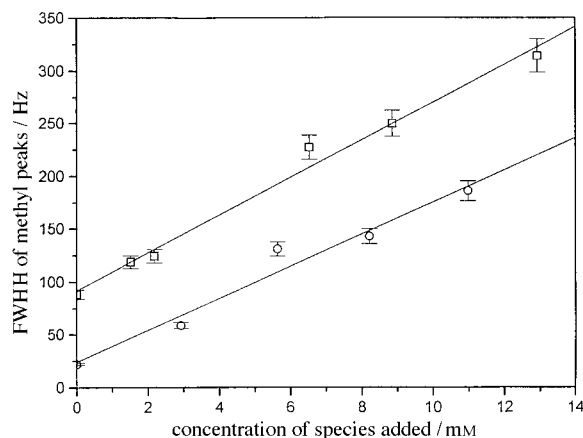


Fig. 4 Upper plot: FWHH of CH_3 band of the mixed valence complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$ vs. concentration of the oxidised complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+$. Lower plot: FWHH of CH_3 band of the oxidised complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^+$ vs. concentration of the mixed-valence complex $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]$. In dichloromethane, $T = 25^\circ\text{C}$; added pyridine concentration, 0.15 M.

were made in the presence of pyridine to suppress dissociation, satisfactory consistency was obtained as shown in Fig. 4. Experiments with added *tert-N*-butylammonium perchlorate (concentrations 0–10 mM) showed no significant dependence of rate constant on electrolyte concentration.

4 Conclusion

The rate constant of reaction (1) is $k = (3.7 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, in dichloromethane at 23°C . This value can be compared with results for two other analogous systems. Walsh *et al.* reported $k = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the self-exchange $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3]^{+/0}$, in dichloromethane at 24°C .¹³ In work currently in progress with trinuclear manganese complexes we have found no measurable line broadening in the system $[\text{Mn}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{py})_3]^{+/0}$ using similar resonances, and the same concentration ranges. The ruthenium(III, III, II) mixed-valence complex is generally assumed^{4,13} to be a strongly exchange-coupled and fully valence-delocalised metal cluster; the manganese complex, in the solid state, has been shown to be fully valence-localised with no evidence of internal electron transfer at room temperature.⁵ These three examples therefore support a conjecture, that rates of bimolecular self-exchange reactions between cluster complexes correlate with rates of unimolecular electron transfer within the clusters. This is expected if inner-sphere reorganisation energy contributes significantly to the energy barriers, for both types of reaction.

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