Solvation Effects on Reactivity in Nucleophilic Attack at Iron(II)–Di-imine Complexes

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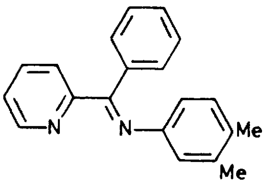
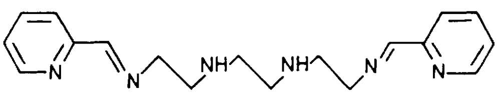
Comparison of transfer chemical potential trends for iron(II)–di-imine complexes with activation volumes for their reaction with hydroxide, in aqueous methanol, permits a detailed assessment of the role of solvation.

Several years ago it was found that bimolecular reactions of the tris-2,2′-bipyridyl- and tris-1,10-phenanthroline-iron(II) cations, $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$, with hydroxide or cyanide in aqueous solution had activation volumes of *ca.* $+20$ cm^3 mol^{-1}.[1] Such values are very different from the value of *ca.* -10 cm^3 mol^{-1} characteristic of bimolecular reactions in the gas phase or in inert solvents.[2] Subsequent determinations of $\Delta V^{\ddagger} = +4$ and -9 cm^3 mol^{-1} for reaction of the closely related d^6 complex $Mo(CO)_4(bipy)$ with cyanide in methanol and in dimethyl sulphoxide suggested that desolvation of the strongly hydrophilic hydroxide or cyanide nucleophiles dominated the determined activation volumes.[3] However, initial state–transition state analyses of reactivity trends for reaction of iron(II) di-imine complexes with



(1)



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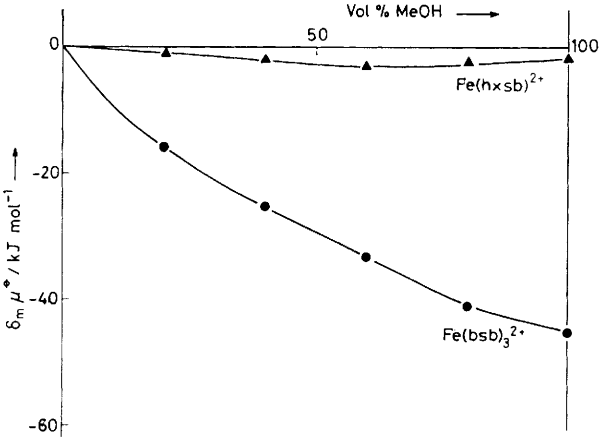

Figure 1. Transfer chemical potentials ($\delta_m\mu^\ominus$) for the $Fe(bsb)_3^{2+}$ and $Fe(hxsb)^{2+}$ cations, from water into aqueous methanol at 298.2 K, molar scale.

hydroxide or cyanide in water-rich binary solvent mixtures showed that solvation of the iron(II) complex cation played a major role in such media.[4] Now we show, from transfer chemical potentials and activation volume data for two very different Schiff base–iron(II) complexes, how desolvation (both water and methanol) of both the complex and the nucleophile can be important. Indeed taken in combination, desolvation effects can result in activation volumes as high as +29 cm^3 mol^{-1} for an intrinsically bimolecular process.

Transfer chemical potentials ($\delta_m\mu^\ominus$) for the Schiff base complexes $Fe(bsb)_3^{2+}$ and $Fe(hxsb)^{2+}$, where the ligands bsb = (**1**) and hxsb = (**2**), were derived from solubilities of their perchlorate salts. These were measured at 298.2 K, with concentrations monitored spectrophotometrically; $Fe(bsb)_3^{2+}$ has ν_{max} 17 240 (ϵ 13 000),[5] $Fe(hxsb)^{2+}$ has ν_{max} 16 890 cm^{-1} (ϵ 6 140 mol^{-1} dm^3 cm^{-1}).[6] Transfer chemical potentials for perchlorate[7] were converted into the single ion assumption $\delta_m\mu^\ominus(AsPh_4^+) = \delta_m\mu^\ominus(BPh_4^-)$ using the data of Tissier.[8] Transfer chemical potentials for the two Schiff base complexes are shown in Figure 1. There are large differences between the trends for the two complexes. The more striking plot is that for the $Fe(hxsb)^{2+}$ cation which, surprisingly, suggests no preferential solvation by methanol, in other words that hydrophilic and hydrophobic tendencies are in balance. On the other hand, the $Fe(bsb)_3^{2+}$ cation is greatly stabilised on transfer from water into methanol–water mixtures, especially as the proportion of methanol rises. This cation is large and has a wholly hydrophobic periphery, so the observed trend is understandable.

This marked contrast between the solvation characteristics enables us to rationalise the unexpected differences in activation volume trends[9] depicted in Figure 2 (uncertainties are between ±0.6 and ±1.9 cm^3 mol^{-1}). In water, $\Delta V^\ddagger$ values for hydroxide attack at the two complexes are almost equal, and are modestly positive. This can be understood in terms of the established bimolecular mechanism[10] by invoking a large positive contribution to $\Delta V^\ddagger$ from desolvation of the heavily hydrated hydroxide ion.[3] The small variation in $\Delta V^\ddagger$ for hydroxide attack at the $Fe(hxsb)^{2+}$ cation can be attributed to the continuing importance of this hydroxide desolvation on forming the transition state (hydroxide is strongly preferentially solvated by water in methanol–water mixtures), with no marked changes in solvation at the cation. The marked *increase* in $\Delta V^\ddagger$ for hydroxide attack at the $Fe(bsb)_3^{2+}$ cation as the proportion of methanol rises, to give the unusually large value of +29 cm^3 mol^{-1} in 85% methanol, can be attributed to an increasingly large contribution from desolvation (solvating methanol) of the iron(II) complex as its ground-state solvation by methanol increases (*cf.* Figure 1).

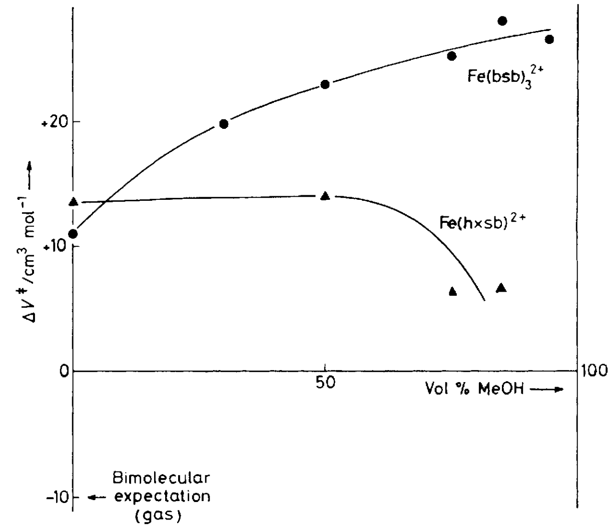

Figure 2. Activation volumes ($\Delta V^\ddagger$) for reaction of the $Fe(bsb)_3^{2+}$ and $Fe(hxsb)^{2+}$ cations with hydroxide in methanol–water mixtures, at 298.2 K.

The results in this communication emphasise the importance of desolvation in controlling $\Delta V^\ddagger$ values and their trends. Such solvation effects can be of importance both for water and for a polar organic solvent. Our system provides a good example of the value of complementary information from thermodynamic measures of solvation and from pressure effects on reactivity.[11]

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