Isotope effects in complexed 2,2′-bipyridyl

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Rate constants for the base hydrolysis in water of the tris(2,2′-bipyridyl)iron(II) ion and its perdeuterioisotopomer differ, as do rate and equilibrium constants for the formation in water of 1:1 adducts of hydroxide with the bis(2,2′-bipyridyl)platinum(II) ion and its perdeuterioisotopomer.

Reactions in aqueous solutions of $[M(bipy)_n]^{m+}$ (bipy = 2,2′-bipyridyl) with nucleophiles, including hydroxide, have been exhaustively studied. The behaviour of such complex ions containing aromatic N-heterocyclic ligands is often unexpected. Rate equations in water for substitution by hydroxide or cyanide contain[1] dominant terms in $[M(bipy)_n{}^{m+}][OH^-]$ and $[M(bipy)_n{}^{m+}][CN^-]$. For M = Fe, $n = 3, m = 2$, the rate of base hydrolysis is given by eqn. (1):

$$\text{Rate} = [Fe(bipy)_3{}^{2+}]\,(k_0 + k_1\,[OH^-] + k_2\,[OH^-]^2 + \ldots) \qquad (1)$$

k_0 is small; depending on the conditions, the dominant terms may be first or even second order in $[OH^-]$. The stereochemical consequences[2] of such substitutions are unusual too. Likewise, with M = Pt or Pd, solutions of the bis(2,2′-bipyridyl) salts in water readily react[3] with hydroxide ions as in eqn. (2):

$$\underset{\mathbf{A}}{[Pt(bipy)_2]^{2+}} + OH^- \rightarrow \underset{\mathbf{B}}{[Pt\{bipy_2OH\}]^+} \qquad (2)$$

The origin of these facts, in molecular terms, has been a source of long-standing debate. We report here the effect of changing from the perprotio-bipy ($[^1H_8]$bipy) to perdeuterio-bipy ($[^2H_8]$bipy), for both systems, the six-coordinated d^6 spin-paired iron(II) of eqn. (1) and the four-coordinated d^8 platinum(II) of eqn. (2).

For reaction (1), in repeated experiments, the rate for the perprotio system is always greater than that for its isotopomer under the same conditions. We have found this for $[OH^-] = 0.0624$ mol dm^{-3} from 30 to 45 °C, and also, at 27 °C, for $0.0164 < [OH^-] < 0.2462$ mol dm^{-3}. For example, at 27 °C with $[OH^-] = 0.0329$ mol dm^{-3}, $k_H = (1.03 \pm 0.01) \times 10^{-3}$ s^{-1} and $k_D = (6.83 \pm 0.01) \times 10^{-4}$ s^{-1} (see Fig. 1). Where the k_1 term of eqn. (1) dominates, the isotope effect (k_H/k_D) is about 1.25.

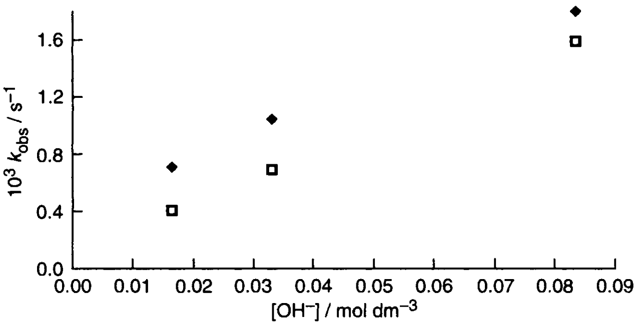
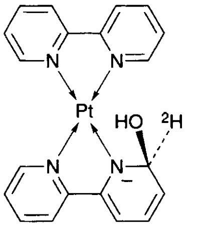


Fig. 1 Observed rate constants at 27 °C for reaction (1), with $[OH^-]$ up to 0.09 mol dm^{-3}; (◆) protio, (□) deuterioisomer

The formation of **B** from **A** in reaction (2) is quite fast so we used a stopped-flow method to show that $k_{H(2)} \approx 1.25\, k_{D(2)}$. Again, in many sets of experiments, the protio ligand always causes faster reaction than its isotopomer does. Typically at 10 °C, values of k_H and k_D (in dm^3 mol^{-1} s^{-1} $\times 10^{-2}$) are 8.2 ± 0.6 and 6.8 ± 0.2 respectively.

For the equilibrium constant, $K_H = [B]/[A][OH^-]$ of eqn. (2), our measured value from spectrophotometric titrations over a wide range of pH is $\log_{10}K_H = 4.49 \pm 0.03$ at 20.0 ± 0.5 °C. For the smaller equilibrium constant using the perdeuterioisotopomer, $\log_{10}K_D$ is 4.40 ± 0.03 at 20.0 ± 0.5 °C. Again, in many experiments, K_H is invariably greater than K_D.

The 1:1 stoichiometry of **B** in eqn.(2), a rather unreactive species, is settled but its structure has been debated. Some[3,5] have argued that coordination of the N-heterocycle is akin to quaternization, and consequently that **B** contains four-coordinated carbon with the nucleophile added at positions in the aromatic ring known to be activated in quaternization by electron withdrawal from the nitrogen, *i.e.* C^6 in 2,2′-bipyridyl as in **I** (or at C^4 in its isomers). Others[4,6] consider five-coordinated platinum(II) more likely in **B**.



I

The differences between k_H and k_D and between K_H and K_D suggest that reactions like (1) and (2) occur at a site involving C–H bonds. Addition of hydroxide to the aromatic ligand accounts for all the present and prior facts. Addition to the metal ion does not.

The effects of coordination and quaternization on the reactivity of N-heterocycles are related.

References

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