Notes

A Kinetic Investigation of the Base-catalysed Deuterium-exchange Reaction of Tris(2,2'-bipyridine)osmium(II) Ion in Dimethyl Sulphoxide Solution

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A complete deuterium exchange of the protons is observed in the complex ion $[Os(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridine) dissolved in $[D_6]$dimethyl sulphoxide containing NaOD and D_2O. The reaction rates of the different positions were found to decrease in the order: $3,3' \gg 5,5' > 6,6' > 4,4'$. The rate of exchange of the 3,3'-protons followed a simple second-order expression: rate = $k_2[Os(bipy)_3{}^{2+}][NaOD]$, indicating attack of OD^- on the protons in the rate-determining step.

During recent years, two new aspects of the chemistry of co-ordinated 2,2'-bipyridine (bipy) have emerged. First, a number of workers have independently demonstrated that a novel cyclometallated bonding mode exists in the complex $[Ir(bipy\text{-}N,N)_2(bipy\text{-}C,N)]^{3+}$, in which one of the bipy ligands is C-bonded to the iridium centre *via* the 3-carbon of one of its rings.[1–4] Secondly, it has been demonstrated that the 3,3'-hydrogens of $[Ru(bipy)_3]^{2+}$ are to some degree acidic, and will undergo deuterium exchange to form $[Ru([3,3'\text{-}D_2]bipy)_3]^{2+}$ when dissolved in dimethyl sulphoxide (dmso) containing $NaOCH_3$.[5] In a previous report,[6] it was noted that no exchange of protons occurs during the redox reaction between $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) and NaOD in D_2O but also observed[7] that when $[Os(bipy)_3]^{3+}$ is reduced by hydroxide in dmso, a slow deuterium exchange of the 3,3'-protons in the product, $[Os(bipy)_3]^{2+}$, follows the reduction process.

We have also observed this process when $[Os(bipy)_3]^{2+}$, prepared according to the normal procedure,[8] is treated with NaOD dissolved in a mixture of dmso and D_2O. This medium has been chosen since the solubility of NaOD in anhydrous dmso is too small and the real water concentration too poorly defined in 'dry' dmso.

Figure 1(*a*) shows the ^1H n.m.r. spectrum of $[Os(bipy)_3]^{2+}$ dissolved in dmso. This spectrum shows no immediate change upon addition of NaOD in D_2O, but a slow reaction gradually changes the spectrum to that shown in Figure 1(*b*). The observed spectra are similar to those reported for $[Ru(bipy)_3]^{2+}$ in dmso with $NaOCH_3$ added and show the same exchange of the 3,3'-protons in the bipy ligands of the complex.[5] Furthermore, it was confirmed that no significant dissociation takes place during the process, since no resonances due to free bipy were observed and the u.v.–visible absorption spectra of the solution remained unchanged. Also, under the same experimental conditions, no similar exchange can be seen in the n.m.r. spectrum of the free ligand.

The area of the 3,3'-proton peaks relative to the sum of the others shows a pseudo-first-order decay with time.

Table. Pseudo-first-order (k_1) and second-order rate constants (k_2) for the deuterium exchange in $[Os(bipy)_3][ClO_4]_2$ in dmso–water mixtures at 43.2 ± 0.3 °C

[Complex]/ mol dm^{-3}	x_{D_2O}	10^3[NaOD]/ mol dm^{-3}	10^4k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
0.0311	0.289	7.53	2.31	0.0189 ± 0.004
0.0243		18.5	2.24	
0.0243		24.9	3.85	
0.0311		57.4	9.92	
0.0311	0.307	5.71	0.81	0.0127 ± 0.002
0.0292		11.9	2.29	
0.0243		24.9	4.44	
0.0243		37.4	2.82	
0.0311		37.7	4.70	
0.0311		59.9	3.35	
0.0311	0.326	66.1	4.62	0.0080 ± 0.0011
0.0311		67.1	6.11	
0.0311	0.344	45.4	2.69	0.0060 ± 0.004

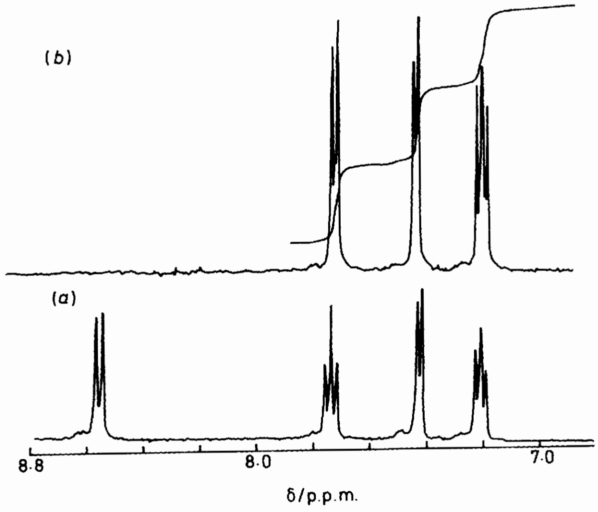

Figure 1. (*a*) ^1H N.m.r. spectrum of a solution of $[Os(bipy)_3][ClO_4]_2$ (0.027 mol dm^{-3}) in $[D_6]$dmso. (*b*) Spectrum of the same solution with the addition of NaOD in D_2O (5 µl, 10 mol dm^{-3}) after *ca.* 15 min at 43.2 °C

Although a very limited range of initial concentrations could be used due to the low solubility of the complex, first-order plots were always linear for more than 80% of the reaction: equation (1). The values of the pseudo-first-order rate constants (k_1) at

$$-d[Os(bipy)_3{}^{2+}]/dt = k_1[Os(bipy)_3{}^{2+}] \qquad (1)$$

43.2 °C for a series of experiments at various concentrations of NaOD and D_2O are shown in the Table. A least-squares analysis of the pseudo-first-order rate constants and [NaOD] indicate that within the precision of the experiments the rates follow a simple second-order equation (2). This

$$d[Os(bipy)_3{}^{2+}]/dt = k_2[Os(bipy)_3{}^{2+}][NaOD] \qquad (2)$$

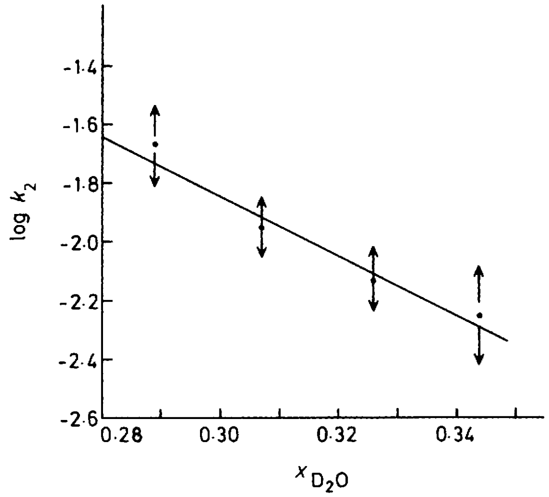

Figure 2. Plot of log k_2 *versus* molar fraction, x_{H_2O}, of water in dmso

expression is consistent with a mechanism involving an attack of OD^- on a 3,3′-proton in the rate-determining step.

From Figure 2 it is seen that the rate decreases when the water concentration is raised. The observed linear correlation between log k_2 and the molar fraction of water x_{D_2O} parallels the observations reported by earlier workers[9] and may be explained by solvation effects. Thus, using the rate expression given by the transition-state theory[10,11] the rate constant may be written as equation (3), where $\boldsymbol{k}$ = Boltzmann's constant, T = absolute temperature, $\boldsymbol{h}$ = Planck's constant, $K^{\ddagger}$ = equilibrium constant for the formation of the activated complex, and γ = activity coefficient of the indexed species.

$$k_2 = (\boldsymbol{k}T/\boldsymbol{h})K^{\ddagger}\{\gamma_{[Os(bipy)_3]^{2+}}\}(\gamma_{OH^-})/\gamma^{\ddagger} \qquad (3)$$

It is well known that in dmso–water mixtures γ_{OH^-} is particularly sensitive to the concentration of water because of a strong, specific solvation of OH^- by H_2O.[10] Quantitatively, this effect of x_{D_2O} on log $(\{\gamma_{[Os(bipy)_3]^{2+}}\}(\gamma_{OD^-})/\gamma^{\ddagger})$ in Figure 2 shows a slope of −5.0. In a study of the base hydrolysis of benzyl chloride in dmso–water Tommila and Pitkanen[9] observed a similar linear correlation with a slope of −4.5. This effect of specific solvation is also demonstrated in the solubility of NaOH and KOH in dmso–water[12] where, at $x_{H_2O} < 0.35$, the correlation between log $(\gamma_{Na^+})(\gamma_{OH^-})$ and x_{H_2O} is linear with a slope of −4.0. It therefore seems reasonable to conclude that in the data given in Figure 2 also the rate dependence on x_{D_2O} is an effect of the medium rather than a mechanistic effect.

When leaving the reaction mixture at 43.2 °C, a broadening of the remaining lines was sometimes observed. However, upon removing a small amount of a blue precipitate by filtration the spectrum was recovered. Consistent with recent reports[13] further deuterium exchange was observed; however, the rates at which these processes occurred were significantly lower than the rate of exchange at the 3,3′-positions. It was observed that the order of reactivity is 3,3′ ≫ 5,5′ > 6.6′ > 4.4′.

Proton exchange studies[14–16] on pyridine in water at 218 °C have shown that in basic solution a deuterium exchange takes place at all positions but the order of reactivity is, depending on the base strength, larger for either the 2,6-positions or for the 4-position. In a pyridine ring of the bipy complex both the adjacent pyridine ring and the metal ion act as electronegative substituents which may contribute to the acidity of the 3,3′-protons. It may, however, also be of importance that the 3,3′-hydrogens form a site of facile attack since the OH^- ion can enter into a structure where it forms hydrogen bonds to the 3,3′-protons of the ligands.

A consequence of these observations is that, for certain metal complexes containing the bipy ligand, base hydrolysis may proceed *via* an intermediate containing a deprotonated ligand, following the principles of the classical conjugate-base mechanism, which is the mechanism accepted for the base hydrolysis of a wide range of metal ammine complexes.[17] Thus, a base-catalysed mechanism operates for $[Cr(bipy)_3]^{3+}$ and the rate shows a complicated OH^- dependence.[18,19] It will be of obvious interest to examine the proton exchange in this and in other substitution reactions of highly charged bipy complexes, where the acidity of the ligand protons may be significant.

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