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Rates of Intermediate Pseudobase Formation between HO^- and Tris-(5-nitro-1,10-phenanthroline)-M(II) Ions, M = Co, Ni, Cu*

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In an attempt to evaluate the differences in magnitude and rate of pseudobase formation in transition metal complexes of N-heterocyclic ligands, we have adopted two approaches. In the first, the effects of ligand substitution have been studied [1, 2]. Here we report variations in kinetics of attack of HO^- at the ligand in a series of *tris-* complexes of 5-nitro-1,10-phenanthroline, (5-NO_2phen).

Solutions of $M(5\text{-}NO_2phen)_3^{2+}$ (M = Co, Ni, Cu) were prepared by dissolving their perchlorate salts in H_2O to give $M(5\text{-}NO_2phen)_3^{2+} \approx 10^{-3}$ mol dm^{-3}. An excess of ligand was maintained in order to enforce *tris*-coordination. In all cases the *final* products of reaction are the aquated metal ions (which ultimately precipitate as their hydroxides) and free ligand. However, prior to this reaction, an equilibrium step can be followed which is ascribed to pseudobase formation (1), and which has been observed [1, 2] in a wide variety of similar reactions.

$$M(5\text{-}NO_2phen)_3^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(5\text{-}NO_2phen)_2(5\text{-}NO_2phen\cdot OH)^+ \quad (1)$$

The reactions are *all* reversible, provided that reacidification is carried out quickly after HO^- is added, and can be followed by stopped-flow spectrophotometric techniques which have been previously described in detail [3].

In these reactions, unlike others [2], the values of the reverse rate constant k_{-1} are very close to zero and the magnitude of the equilibrium constants (k_1/k_{-1}) are large. Such behaviour has been observed with other systems related to these and with pseudobase formation with CN^- ion [1, 2]. Ionic strength for all reactions was maintained at 1.0 mol dm^{-3} ($NaNO_3$). Values of the forward rate constants (k_1) were obtained *via* least-squares analyses of k_{obs} *versus* [HO^-] plots. Activation parameters were obtained from the usual Arrhenius plots using least-squares techniques.** The results are summarised in Table I, with those of related reactions for comparison.

Considerable variation in $\Delta H_1^{\ddagger}$ is apparent, but it is seen that this parameter is not dominant in terms of rate. Coupled with the variation is a compensating change in $\Delta S_1^{\ddagger}$ which gives rise to similar rates of reaction for all the complexes. One order of magnitude is almost enough to embrace the rates of all complexes at 298 K. It thus appears that variation of the metal in isostructural† complexes has little effect on rates of reaction. Solvation effects do appear to be important as is evidenced by the widely varying $\Delta S_1^{\ddagger}$ values. In most cases, $\Delta S_1^{\ddagger}$ is negative as expected for an addition of the type involved. For the Fe(II) and Ru(II) complexes, $\Delta S_1^{\ddagger}$ is only slightly positive. One difference in the series is that with these two complexes appreciable rates for the reverse dissociative step have been measured [4]. This is not the case with the analogous Co(II), Ni(II) and Cu(II) complexes where plots of

TABLE I. Rate Constants and Thermodynamic Parameters for Pseudobase Formation at 298 K and I = 1.0 mol dm^{-3}.

Complex	k_1/dm^3 mol^{-1} s^{-1}	$\Delta H_1^{\ddagger}$/kJ mol^{-1}	$\Delta S_1^{\ddagger}$/J K^{-1} mol^{-1}
$Co(5\text{-}NO_2phen)_3^{2+}$	0.23 (1)	41.2 (2)	−125.6 (4)
$Ni(5\text{-}NO_2phen)_3^{2+}$	0.75 (2)	67.1 (47)	−27.1(10)
$Cu(5\text{-}NO_2phen)_3^{2+}$	1.03 (1)	62.5 (47)	−45.1 (5)
$Fe(5\text{-}NO_2phen)_3^{2+\,a}$	4.25	70.2 (20)	3.4 (4)
$Ru(5\text{-}NO_2phen)_3^{2+\,a}$	1.18	72.8 (31)	1.2 (8)

^{a}Values from ref. 4.

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*Part 28 in the seriys Equilibria in Complexes of N-Heterocyclic Molecules. Part 28 is ref. 1.

**Full lists of k_{obs} results are available from the authors on request.

†Although we have not attempted to clarify the isomeric ratios *fac:mer*, which may vary from metal to metal. Indeed this point has been overlooked or neglected in McBride's Scholarly Compendium [5], since clearly K_2 and K_3 values will be isomer-sensitive.

k_{obs} *versus* $[HO^-]$ have negligible intercepts and thus small values of k_{-2}.

We have previously shown [1] that statistical effects are evident in the rates of reaction of related complexes where 2,2′-bipyridyl is substituted for 5-NO_2 phen. While some patterns of reaction have then emerged from our studies in this series of closely related compounds, marked variations are found for similar complexes where either the metal is changed or the ligand substitution is altered. More detailed studies will be required before the diversity of this class of reactions is fully understood.

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