Equilibria in Complexes of N-Heterocyclic Molecules. Part 25.† Kinetics of Pseudo-base Formation in Metal Complexes and Quaternized Organic Molecules derived from 5-Nitro-1,10-phenanthroline

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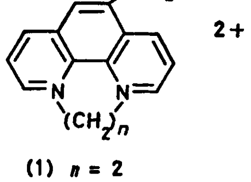
The kinetics of pseudo-base formation with $[OH]^-$ in various doubly charged quaternary cations and co-ordination compounds formed from 5-nitro-1,10-phenanthroline have been studied in detail. The groups bridging the 1,10-nitrogen atoms are Fe^{II}, Ru^{II}, $(CH_2)_2$, and $(CH_2)_3$. For the reaction $[Fe(5NO_2\text{-phen})_3]^{2+} + [OH]^- \rightleftharpoons [Fe(5NO_2\text{-phen})_2(5NO_2\text{-phen.OH})]^+$, values of the forward and reverse rate constants are respectively 2.24 $dm^3\ mol^{-1}\ s^{-1}$ and 0.014 s^{-1} at 291 K. The corresponding values for the ruthenium(II) analogue are 0.58 $dm^3\ mol^{-1}\ s^{-1}$ and 0.024 s^{-1} at 290 K. For the bridging group $(CH_2)_3$, the kinetics of the same reaction have been followed and the forward and reverse rate constants are respectively 5.35×10^3 $dm^3\ mol^{-1}\ s^{-1}$ and 0.34 s^{-1} at 273 K. For the ethylene-bridged compound, a second $[OH]^-$ group can be added to the molecule, *viz.*, $[5NO_2\text{-phen}(CH_2)_2{\cdot}OH]^+ + [OH]^- \rightleftharpoons [5NO_2\text{-phen}(CH_2)_2{\cdot}2OH]^0$. The equilibrium constant for this reaction is 95.4 $dm^3\ mol^{-1}$ at 273 K. The results obtained are compared with those for a wide variety of quaternized N-heterocyclic molecules and co-ordination complexes.

N-HETEROCYCLIC molecules such as 2,2′-bipyridyl and 1,10-phenanthroline ‡ can be quaternized by polymethylene groups, to form polycyclic structures.[1] The resulting ions form pseudo-bases [2,3] when treated with aqueous base. These reactions are quantitatively reversed on addition of acid.

Transition-metal complexes of these chelated N-heterocyclic ligands react similarly,[4] and we have therefore considered the organic quaternized ions as being analogous to metal complexes with respect to pseudo-base formation and attack by other nucleophiles. In continuing our studies of formation of pseudo-bases § by metal complexes,[5,6] we wished to compare as directly as possible the reactions of the metal and organic complexes. In particular, we sought to examine the incidence of covalent hydration in these complexes, since this is related, at least formally, by an acid–base equilibrium to pseudo-base formation. Covalent hydration is well established in purely organic systems,[7] and recent work has shown its occurrence in free 2,2′-bipyridyl [8] and in transition-metal complexes.[9]

In this paper we present detailed kinetic results for the reaction of $[M(5NO_2\text{-phen})_3]^{2+}$ with $[OH]^-$ to form pseudo-base species *via* attack at the ligand by the nucleophile with M = Ru^{II} and Fe^{II}. Additionally, we have investigated the analogous reactions with the organically quaternized molecules (1) and (2). It has been shown [10] that the phen analogues of these compounds form pseudo-bases in aqueous solution and we wished to compare the reactions of the various compounds in order to provide a basis for the understanding of the magnitudes of such effects in aqueous solution when related transition-metal complexes are involved. The results of our studies are presented below.



(1) $n = 2$
(2) $n = 3$

EXPERIMENTAL

Infrared spectra were recorded with a Perkin-Elmer 247 grating spectrometer and electronic spectra with a Beckman DK2A ratio-recording spectrophotometer. Hydrogen-1 n.m.r. spectra were obtained using a Perkin-Elmer R32 90 MHz spectrometer at 35 °C using internal standards. Thermogravimetric analyses were performed using a Stanton–Redcroft TG750 thermogravimetric balance.

The quaternized species (1) and (2) were prepared as their dibromide salts using the method of Summers,[1] merely substituting $5NO_2$-phen for phen. The salts were recrystallized from aqueous ethanol. Elemental analyses were satisfactory. Compound (1) melts at >380 °C, (2) at 212 °C. Parameters from the electronic spectra in aqueous solution are: (1), $\lambda = 465$ ($\varepsilon = 1\,200$) and 305 nm ($\varepsilon = 1.45 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$); (2), $\lambda = 465$ ($\varepsilon = 545$) and 307 nm ($\varepsilon = 1.98 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$). In KBr disc, the most prominent absorptions in the i.r. region are: (1), 3 040, 3 020, 1 645, 1 600, 1 570, 1 535, 1 475, 1 435, 1 360, and 715 cm^{-1}; (2), 3 080, 2 980, 1 640, 1 600, 1 560, 1 535, 1 485, 1 455, 1 360, and 710 cm^{-1} (± 3 cm^{-1}), calibrated against polystyrene.

The complex $[Ru(5NO_2\text{-phen})_3]^{2+}$ was prepared as previously described [6] by refluxing $RuCl_3{\cdot}xH_2O$ (0.64 g) in an aqueous solution of sodium (+)-tartrate (2.44 g, 15 cm^3) until a deep green colour was obtained. The solution was filtered and then refluxed with an excess (1.73 g) of $5NO_2$-phen. Two purification procedures were adopted. In the first the aqueous solution of crude product was extracted with CH_2Cl_2 to remove the excess of ligand and any

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‡ bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, $5NO_2$-phen = 5-nitro-1,10-phenanthroline, tptz = 2,4,6-tris(2-pyridyl) 1,3,5-triazine.

§ We use the generic term 'pseudo-bases' to indicate the products of nucleophilic attack upon the N-heterocycles, whether by hydroxide ion (the original factor in pseudo-bases) or other nucleophiles.

[$Ru(5NO_2\text{-phen})_2Cl_2$] that may have formed, reduced in volume, and the complex precipitated as the perchlorate salt. This was washed with water and dried *in vacuo*. In the second the crude product in aqueous solution was run onto a Sephadex® C-25 cation-exchange column in the Na^+ form and any neutral species eluted with water. Further elution with 0.1 mol dm^{-3} Li[NO_3] released the complex, which was collected in fractions and examined for possible isomeric variation (meridional and facial) by electronic spectrophotometry. No variation could be detected and the combined fractions were evaporated until the complex crystallized as the nitrate salt. The material used in a previous study [5] was prepared by the same ion-exchange method and we are satisfied that there is no detectable isomeric difference between the material used in this study and that used previously.

The complex [$Fe(5NO_2\text{-phen})_3$]$^{2+}$ was prepared by treating a warm aqueous solution of AnalaR Mohr's salt (1.1 g) with $5NO_2$-phen (2.0 g). The solution was filtered and the complex precipitated as the perchlorate salt, which was washed thoroughly with water and dried *in vacuo*.

The electronic spectra are identical with those reported.[5,6] Water of crystallization in the complex perchlorate salts was determined thermogravimetrically. The stoicheiometries of the complexes are $Ru(5NO_2\text{-phen})_3(ClO_4)_2\cdot 2H_2O$ and $Fe(5NO_2\text{-phen})_3(ClO_4)_2\cdot 0.5H_2O$.

The reactions of [OH]$^-$ with all the complex species were too fast to follow using conventional techniques and so a stopped-flow spectrophotometric method was employed. Details of the instrumentation have been described elsewhere.[11] The reactions were followed at 390 nm at which wavelength an increase in absorbance is observed in each case. The reactions of the organic quaternized compounds (1) and (2) were monitored at 500 nm, increasing absorbance being also observed [(1), $\lambda_{max.}$ = 496; (2), $\lambda_{max.}$ = 496 nm].

The kinetics of the reaction with [OH]$^-$ were all followed using a large excess of nucleophile. Under these conditions linear first-order kinetics were invariably obeyed for at least 3 half-lives. Ionic strength was maintained at 0.2 mol dm^{-3} using Na[NO_3] for the reactions of the metal complexes and 0.01 mol dm^{-3} for the quaternized species, and [OH^-] varied between 5×10^{-4} and 2×10^{-2} mol dm^{-3}. Plots of log ($A_\infty - A$) against time, absorbances being assigned arbitrary units, were used to obtain individual values of $k_{obs.}$ at the chosen temperature.

RESULTS AND DISCUSSION

(*a*) *The Metal Complexes*.—The kinetic results for the reaction of [OH]$^-$ with [$Fe(5NO_2\text{-phen})_3$]$^{2+}$ are given in Tables 1 and 2. Values of $k_{obs.}$ are the average of triplicate determinations with a reproducibility of ±5%. At each particular temperature a plot of $k_{obs.}$ against [OH^-] was linear with a non-zero intercept, indicating the general rate equation (1). This rate equation may be explained by the equilibrium process (2). The reaction, initially at least, is reversible upon addition of acid, quantitatively. In addition, extrapolation of stopped-flow results back to zero time gave absorbance values expected for the original complex [$Fe(5NO_2\text{-phen})_3$]$^{2+}$. A_∞ values did increase with increasing [OH^-], as expected for an equilibration. The values of A_∞ are not stable indefinitely. After a short time, dissociation of the ligands occurs, and this process (3) is not reversible on acidification. At temperatures greater

$$k_{obs.} = k_1[OH^-] + k_{-1} \qquad (1)$$

$$[Fe(5NO_2\text{-phen})_3]^{2+} + [OH]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(5NO_2\text{-phen})_2(5NO_2\text{-phen}\cdot OH)]^+ \qquad (2)$$

$$[Fe(5NO_2\text{-phen})_2(5NO_2\text{-phen}\cdot OH)]^+ \longrightarrow Fe^{2+} + 3(5NO_2\text{-phen}) + [OH]^- \qquad (3)$$

than 40 °C this process interferes with the observation of kinetics for the formation of the pseudo-base. In the temperature range studied, dissociation is negligible over the time period used to follow reaction (2). The kinetics of reaction (3) have not been followed in detail.

TABLE 1

Kinetic results for the reaction of [$Fe(5NO_2\text{-phen})_3$]$^{2+}$ with [OH]$^-$ at I = 0.2 mol dm^{-3}

[OH^-]/ mol dm^{-3}	T/K	$k_{obs.}$/s^{-1}	[OH^-]/ mol dm^{-3}	T/K	$k_{obs.}$/s^{-1}
0.005	291.2	0.026	0.02	300.5	0.154
0.01	291.2	0.036	0.025	300.5	0.186
0.015	291.2	0.046	0.005	305.2	0.117
0.02	291.2	0.056	0.01	305.2	0.153
0.025	291.2	0.072	0.015	305.2	0.202
0.005	295.4	0.040	0.02	305.2	0.250
0.01	295.4	0.053	0.025	305.2	0.303
0.015	295.4	0.068	0.005	310.2	0.222
0.02	295.4	0.088	0.01	310.2	0.277
0.025	295.4	0.120	0.015	310.2	0.341
0.005	300.5	0.073	0.02	310.2	0.412
0.01	300.5	0.095	0.025	310.2	0.530
0.015	300.5	0.121			

TABLE 2

Forward and reverse rate constants * and thermodynamic parameters for the reaction of [$Fe(5NO_2\text{-phen})_3$]$^{2+}$ with [OH]$^-$ at I = 0.2 mol dm^{-3}

T/K	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}
291.2	2.24 (0.09)	0.014 (0.002)
295.4	3.89 (0.29)	0.015 (0.005)
300.5	5.70 (0.18)	0.040 (0.003)
305.2	9.38 (0.23)	0.064 (0.004)
310.2	15.0 (0.90)	0.131 (0.015)

$\Delta H_1^{\ddagger}$ = 70.2 (2.0), $\Delta H_{-1}^{\ddagger}$ = 90.4 (6.2) kJ mol^{-1} at 298 K, $\Delta H^{\ominus}$ = −20.2 (8.2) kJ mol^{-1}, $\Delta S_1^{\ddagger}$ = 3.4 (0.4), $\Delta S_1^{\ddagger}$ = 28.9 (1.8) J K^{-1} mol^{-1}, $\Delta S^{\ominus}$ = −25.5 (2.2) J K^{-1} mol^{-1}.

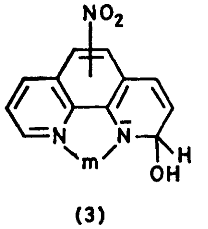
* For the reactions of this complex and of [$Ru(5NO_2\text{-phen})_3$]$^{2+}$ the present results disagree with some earlier ones. This disparity is attributed to an error of scale in the previous studies.[5]

Such dissociation does not occur in the case of [$Ru(5NO_2\text{-phen})_3$]$^{2+}$ and examination of this reaction affords a closer understanding of the mechanism of pseudo-base formation in this and similar types of coordination compounds containing N-heterocyclic ligands. The reaction initially follows that of the iron(II) complex and parallels that of pseudo-base formation [12] of [$Ru(5NO_2\text{-phen})_3$]$^{2+}$ with methoxide ion. The same general features observed in both of these reactions are again prominent and kinetic results for the reaction of [OH]$^-$ with [$Ru(5NO_2\text{-phen})_3$]$^{2+}$, obeying the general rate equation which applies in this case to reaction (4), are given in Tables 3 and 4.

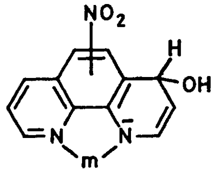
We have previously discussed[13] the possible sites of nucleophilic attack at co-ordinated phen and bipy. These are shown for 5NO$_2$-phen in structures (3)—(5).

$$[\mathrm{Ru(5NO_2\text{-}phen)_3}]^{2+} + [\mathrm{OH}]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ru(5NO_2\text{-}phen)_2(5NO_2\text{-}phen{\cdot}OH)}]^+ \quad (4)$$

It has been shown[14-16] that the 2- and 9-protons in tris complexes of this type are highly shielded by adjacent aromatic rings and that they consequently appear at higher field in ^{1}H n.m.r. spectra than either the 4-, 7-, or 6-protons. This feature indicates that in the case[12] of [OMe]$^-$ reacting with [Ru(5NO$_2$-phen)$_3$]$^{2+}$ the nucleophile attacks C(4) to produce as major species one akin to (4) and not to (3) as was initially thought. With [OH]$^-$ the position attacked is C(7) with the appearance of an upfield signal at 6.5 p.p.m. This is analogous to the signal produced with [OMe]$^-$ (6.48 p.p.m.) and with H$_2$O attack at [Ir(bipy)$_3$]$^{2+}$. In this latter case the upfield signal corresponding to the H atom attached to the newly created tetrahedral carbon atom is observed[13] at 6.77 p.p.m. After a short time a rearrangement takes place from (4) to (5), a similar reaction being observed in the case of the [OMe]$^-$ addition and in the final products of reaction[17] of unco-ordinated 5NO$_2$-phen with [OH]$^-$. In [Fe(5NO$_2$-phen)$_3$]$^{2+}$ no such rearrangement is observed due to the dissociation of the complex.



(3)



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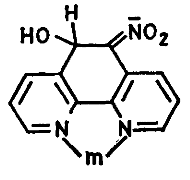


(5)

TABLE 3

Kinetic results for the reaction of [Ru(5NO$_2$-phen)$_3$]$^{2+}$ with [OH]$^-$ at I = 0.2 mol dm^{-3}

[OH$^-$]/ mol dm^{-3}	T/K	$k_{\mathrm{obs.}}$/s^{-1}	[OH$^-$]/ mol dm^{-3}	T/K	$k_{\mathrm{obs.}}$/s^{-1}
0.005	290.3	0.023	0.005	305.4	0.109
0.01	290.3	0.026	0.01	305.4	0.120
0.015	290.3	0.029	0.015	305.4	0.131
0.02	290.3	0.031	0.02	305.4	0.144
0.025	290.3	0.035	0.025	305.4	0.157
0.005	295.5	0.040	0.005	310.7	0.180
0.01	295.5	0.044	0.01	310.7	0.203
0.015	295.5	0.048	0.015	310.7	0.231
0.02	295.5	0.053	0.02	310.7	0.249
0.025	295.5	0.058	0.025	310.7	0.277
0.005	300.4	0.064	0.005	315.4	0.306
0.01	300.4	0.073	0.01	315.4	0.349
0.015	300.4	0.083	0.015	315.4	0.376
0.02	300.4	0.092	0.02	315.4	0.393
0.025	300.4	0.099	0.025	315.4	0.440

TABLE 4

Forward and reverse rate constants and thermodynamic parameters for the reaction of [Ru(5NO$_2$-phen)$_3$]$^{2+}$ with [OH]$^-$ at I = 0.2 mol dm^{-3}

T/K	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}
290.3	0.58 (0.02)	0.024 (0.001)
295.5	0.90 (0.02)	0.035 (0.001)
300.4	1.78 (0.05)	0.055 (0.001)
305.4	2.40 (0.05)	0.096 (0.001)
310.7	4.80 (0.13)	0.156 (0.002)
315.4	6.24 (0.37)	0.279 (0.006)

$\Delta H_1^\ddagger$ = 72.8 (3.1), $\Delta H_{-1}^\ddagger$ = 75.2 (9.3) kJ mol^{-1} at 298 K, $\Delta H^\ominus$ = −2.5 (12.4) kJ mol^{-1}, $\Delta S_1^\ddagger$ = 1.2 (0.8), $\Delta S_{-1}^\ddagger$ = −18.2 (0.9) J K^{-1} mol^{-1}, $\Delta S^\ominus$ = 19.4 (1.7) J K^{-1} mol^{-1}.

The values of k_1 and k_{-1} obtained by the usual least-squares methods for the reaction of [OH]$^-$ with the metal complexes were used to determine values of $\Delta H_1^\ddagger$ and $\Delta H_{-1}^\ddagger$ also *via* least-squares analyses. Values of $\Delta S_1^\ddagger$ and $\Delta S_{-1}^\ddagger$ were calculated using second- and first-order rate constants respectively. The standard enthalpy and entropy changes for reactions (2) and (4) were estimated from the relations $\Delta H^\ominus = \Delta H_1^\ddagger - \Delta H_{-1}^\ddagger$ and $\Delta S^\ominus = \Delta S_1^\ddagger - \Delta S_{-1}^\ddagger$.

The rapid addition of the [OH]$^-$ ion to the complexes is seen to arise from the relatively low values of $\Delta H^\ddagger$ (Tables 2 and 4).

(*b*) *The Quaternized Ligands*.—Kinetic results for the reaction of compound (2) with [OH]$^-$ are given in Table 5. In this case also increasing values of A_∞ were found with increasing [OH$^-$]. Reaction in Scheme 1 is

$$(2)^{2+} + [\mathrm{OH}]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(2)\text{–}\mathrm{OH}]^+$$

SCHEME 1

completely reversible upon addition of acid, the forward and reverse rate constants being k_1 and k_{-1} respectively. The general rate law (1) is again obeyed. Unfortunately, this reaction is very fast, even at 0 °C. For this reason a complete kinetic analysis has not been possible except at very low concentrations of [OH]$^-$. Least-squares analysis of $k_{\mathrm{obs.}}$ results has yielded values of k_1 and k_{-1} at 273.2 K, and, using $k_{\mathrm{obs.}}$ results for [OH$^-$] = 2.5 × 10^{-3} mol^{-1} dm^{-3}, values for $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$. The markedly enhanced rate of the reaction is seen to arise from the

TABLE 5

Kinetic results and thermodynamic parameters for the reaction of (2) with [OH]$^-$ at I = 0.01 mol dm^{-3}

[OH$^-$]/ mol dm^{-3}	T/K	$k_{\mathrm{obs.}}$/s^{-1}	[OH$^-$]/ mol dm^{-3}	T/K	$k_{\mathrm{obs.}}$/s^{-1}
0.0005	273.2	2.39	0.0025	276.4	13.5
0.0012	273.2	6.55	0.0025	278.6	15.3
0.0037	273.2	20.2	0.0025	283.0	20.3
0.005	273.2	28.9	0.0025	288.7	28.2
0.0075	273.2	41.3	0.0025	291.0	34.3
0.01	273.2	52.4	0.0025	295.5	42.2
0.0025	273.8	11.8			

k_1 = 5 340 (110) dm^3 mol^{-1} s^{-1}, k_{-1} = 0.34 (0.61) s^{-1} at 273.2 K, $\Delta H_1^\ddagger$ = 39.0 (1.0) kJ mol^{-1}, $\Delta S_1^\ddagger$ = −29.3 (0.8) J K^{-1} mol^{-1} at 298 K.

very much smaller value of $\Delta H_1^\ddagger$ with respect to that found for the metal complexes. The $\Delta S_1^\ddagger$ value of -29 J K^{-1} mol^{-1} is negative as expected for a process of addition.

A somewhat different pattern of reactivity emerges in the reaction of $[OH]^-$ with compound (1). At each temperature a plot of $k_{obs.}$ against $[OH^-]$ is not linear, but curves to approach a limiting value. However, a plot of $1/k_{obs.}$ against $1/[OH^-]$ *is* linear at each temperature and the reaction is reversible (at least initially) upon addition of acid. These results are in accordance with the general rate law (5) in which K_{eq} refers to the

$$k_{obs.} = k_2K_{eq}[OH^-]/(1 + K_{eq}[OH^-]) \qquad (5)$$

equilibrium constant for the formation of the pseudo-base and k_2 is the rate of a reaction of the pseudo-base initially formed (Scheme 2). Unlike the reaction involving compound (2), extrapolation of absorbance values back to zero time does not give the spectrum of the dipositive ion (1). In connection with this result, it is worth noting that addition of DCl to a solution of (1) in D_2O causes no change in the ^1H n.m.r. spectrum of the compound relative to that measured in D_2O alone. It is thus apparent that the reaction followed is the addition of a *second* $[OH]^-$ ion to a monopositive pseudo-base whose rate of formation is too fast to measure under the experimental conditions chosen, as in Scheme 3.

$$(1)^{2+} + [OH]^- \xrightleftharpoons{K_{eq}} [(1)-OH]^+$$

$$[(1)-OH]^+ \xrightarrow{k_2} \text{product}$$

SCHEME 2

$$(1)^{2+} + [OH]^- \xrightleftharpoons{\text{very fast}} [(1)-OH]^+$$

$$[(1)-OH]^+ + [OH]^- \xrightleftharpoons{K_{eq}} [(1)(OH)_2]^0$$

$$[(1)(OH)_2]^0 \xrightarrow{k_2} \text{product}$$

SCHEME 3

Kinetic results for the reaction are given in Tables 6 and 7. Values of K_{eq} and k_2 were derived from least-squares analyses of $k_{obs.}$ data in the appropriate form. Arrhenius plots of these quantities yielded the thermodynamic parameters of Table 7, also using the usual least-squares methods.

TABLE 6

Kinetic results for the reaction of (1) with $[OH]^-$ at $I = 0.01$ mol dm^{-3}

$[OH^-]$/ mol dm^{-3}	T/K	$k_{obs.}$/s^{-1}	$[OH^-]$/ mol dm^{-3}	T/K	$k_{obs.}$/s^{-1}
0.0005	273.2	1.22	0.005	283.5	21.6
0.0011	273.2	2.60	0.0075	283.5	26.7
0.0025	273.2	5.81	0.01	283.5	37.6
0.0037	273.2	7.76	0.0005	288.3	3.03
0.005	273.2	9.63	0.001	288.3	7.16
0.0075	273.2	12.3	0.0025	288.3	16.3
0.01	273.2	14.8	0.0037	288.3	25.2
0.0085	278.8	1.78	0.005	288.3	31.6
0.001	278.8	3.90	0.0075	288.3	42.3
0.0025	278.8	8.67	0.01	288.3	49.3
0.0037	278.8	12.0	0.0005	293.3	3.61
0.005	278.8	15.4	0.001	293.3	9.69
0.0075	278.8	18.9	0.0025	293.3	22.7
0.01	278.8	22.5	0.0037	293.3	29.7
0.0005	283.5	2.62	0.005	293.3	43.2
0.001	283.5	5.48	0.0075	293.3	60.8
0.0025	283.5	11.5	0.01	293.3	88.6
0.0037	283.5	17.7			

TABLE 7

Rate and equilibrium constants together with thermodynamic parameters for the reaction of (1) with $[OH]^-$ at $I = 0.01$ mol dm^{-3}

T/K	K_{eq}/dm^3 mol^{-1}	k_2/s^{-1}
273.2	95.4 (1.8)	29.8 (0.6)
278.8	84.9 (2.3)	49.9 (3.2)
283.5	76.7 (5.0)	77.1 (5.0)
288.3	43.1 (3.7)	172.8 (14.8)
293.3	32.9 (9.9)	302.6 (90.9)

$\Delta H_{eq} = -37.3$ (4.5) kJ mol^{-1}, $\Delta S_{eq} = -97.5$ (15.9) J K^{-1} mol^{-1}, $\Delta H_2^\ddagger = 75.9$ (3.6) kJ mol^{-1} at 298 K, $\Delta S_2^\ddagger = 61.2$ (1.0) J K^{-1} mol^{-1}.

One other possible explanation for the reaction observed is that the first fast reaction is the formation of or the deprotonation of an initially formed covalent hydrate (Scheme 4). However, neither of these interpretations are borne out by the n.m.r. studies below, in that neither (1) nor (2) displays an ^1H n.m.r. spectrum in D_2O which could be interpreted in any way other than that belonging to the unreacted dipositive ion.

$$(1)^{2+} + H_2O \xrightleftharpoons{\text{fast}} [(1)-H_2O]^{2+}$$

$$[(1)-H_2O]^{2+} \xrightleftharpoons[\text{fast}]{[OH]^-} [(1)-OH]^+$$

SCHEME 4

The difference between the results obtained for pseudo-base formation with (1) and (2) is somewhat difficult to explain. One possible reason for the differences in kinetic behaviour is that even though the molecules are chemically almost identical the site of nucleophilic attack may be different in each case. Hydrogen-1 n.m.r. studies were not possible for the organically quaternized compounds using $[OH]^-$ as the nucleophile because of the insolubility of the species formed. A study by ^1H n.m.r. of the reaction with $[N_3]^-$ as the nucleophile was however possible, with more favourable solubility characteristics in D_2O solution, and we discuss this *faute de mieux*, since the analogy with the $[OH]^-$ nucleophile is not too remote.

In D_2O solution the 2- and 9-protons of (1) are furthest downfield (numbering system for 5NO$_2$-phen used) at 10.11 and 9.91 p.p.m. The H(9) proton signal is partly overlapped by either the H(4) or H(7) signals, the second of these two doublets appearing at 9.78 p.p.m. H(6) is found as a sharp singlet at 9.70 p.p.m. and the ethane bridge hydrogen atoms at 5.8 p.p.m. The two CH_2 groups are not resolved; asymmetric nitro-substitution has no apparent effect on the chemical shifts of the CH_2 hydrogen atoms. Upon addition of $[N_3]^-$ ion a fast spectral change occurs, the signal from the ethylene bridge splitting into two poorly resolved triplets at 5.92 and 6.22 p.p.m. The sharp singlet of H(6) is preserved at 9.00 p.p.m., but most of the downfield signals are broadened and a new doublet is evident upfield at 7.30

TABLE 8

Equilibrium constants together with forward and reverse rate constants for the formation of N-heterocyclic pseudo-bases with $[OH]^-$

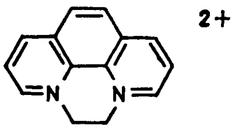
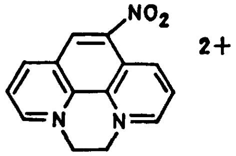
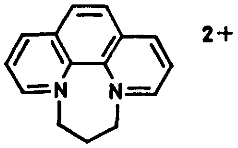
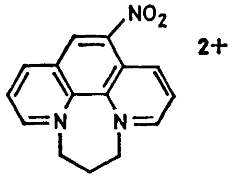
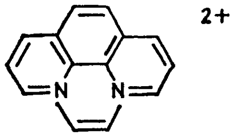
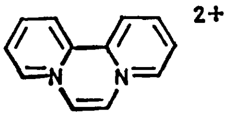
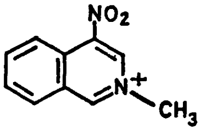
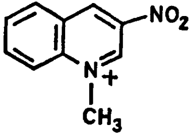
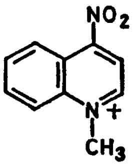
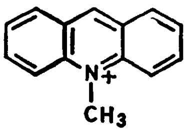
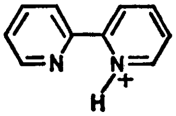
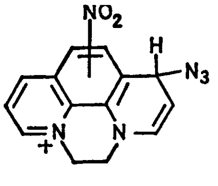
Compound	T/K	I/mol dm^{-3}	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}	K_{eq}/dm^3 mol^{-1}	Ref.
$[Fe(5NO_2\text{-phen})_3]^{2+}$	298.2	0.2	5.70	0.04	142.5	This work
$[Ru(5NO_2\text{-phen})_3]^{2+}$	298.2	0.2	1.78	0.054	33.0	This work
	298.2	0.2	5.5×10^5	25	2.2×10^4	10
	298.2	0.01			30 [a]	This work
	298.2	0.2	9.4×10^5	14	6.7×10^4	10
	273.2	0.01	5 340	0.34	1.6×10^4	This work
	298.2	0.2	1.5×10^6	0.032	4.7×10^7	10
	298.2	0.2	1.3×10^4	1.45	9×10^3	3
	298.2	0.1	8.8×10^6	1.1×10^{-2}	8×10^8	2
	298.2	0.1	1.3×10^5	7.1×10^{-3}	1.8×10^7	*b*
	298.2		Too fast to measure at pH 9.5			*c*
	298.2	0.1	5.5×10^2	5.8×10^{-2}	9.5×10^3	2
	298 (?)				*ca.* 0.03 [d]	8

TABLE 8 (*Continued*)

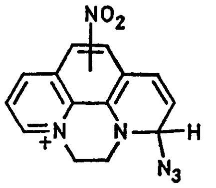
Compound	T/K	I/mol dm^{-3}	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}	K_{eq}/dm^3 mol^{-1}	Ref.
$[Ru(tptz)_2]^{2+}$	273.2	1.0	34.0	0.68	58.9	*e*
$[Co(tptz)_2]^{2+}$	273.2	1.0	36.9	0.85	44.7	*e*
$[Ni(tptz)_2]^{2+}$	273.2	1.0	200	4	50	*e*
$[Pt(bipy)_2]^{2+}$	298.2				10^5	17
$[Pt(5,5'Me_2\text{-}bipy)_2]^{2+}$ [f]	298.2				3.2×10^4	17
$[Pd(5,5'Me_2\text{-}bipy)_2]^{2+}$	298.2				6.7×10^4	17

[a] Value for the addition of the second $[OH]^-$ ion. [b] J. W. Bunting and W. G. Meathrel, *Canad. J. Chem.*, 1974, **52**, 303. [c] J. Bunting and W. G. Meathrel, *Canad. J. Chem.*, 1974, **52**, 951. [d] For the expression $K_{eq} = [bipy{\cdot}H_2O]/[bipy]$. [e] P. A. Williams, *Transition Metal Chem.*, 1979, **4**, 24. [f] $5,5'Me_2$-bipy = 5,5'-Dimethyl-2,2'-bipyridyl.

p.p.m. These spectral changes are consistent with nucleophilic attack at either the 4,7 (6) or 2,9 (7) positions. Of these two choices, the latter appears more likely given the spectral changes relating to the hydrogen atoms of the bridging ethane group.



(6)



(7)

The spectrum shows further (and slower) changes with time. After a few hours the ethane hydrogen signals are again seen as a singlet and the singlet corresponding to H(6) has shifted upfield with the H(3) and H(8) signals at 8.4 p.p.m. Migration of the azide to C(6) has undoubtedly occurred. Similar migrations have often been found [18] in pseudo-bases and covalent hydrates of other N-heterocyclic molecules, and the reaction observed between $[OH]^-$ and (1) undoubtedly involves an analogous shift of substitution.

Different spectral changes are evident in the corresponding reaction with the propane-bridged analogue (2). The CH_2 protons α and β to the nitrogen atoms in the parent compound, occurring at 5.23 (triplet) and 3.48 (quintet) p.p.m. respectively, are both unsplit upon addition of $[N_3]^-$. After the initial addition, the H(6) signal has moved only to 9.51 p.p.m. (9.55 p.p.m. in the parent molecule). Again the initial reaction does not involve C(6) and retention of the signals of the propane bridge lead us to the conclusion that the 4- and 7-carbon atoms are those which are involved in the nucleophilic addition in this case. After some time, changes like those found in the ethane-bridged compound are observed indicating again final attack at C(6).

The differences observed in the ^1H n.m.r. spectra of the two compounds with $[N_3]^-$ do show that the pattern of substitution by nucleophiles at the aromatic ring is dependent upon subtle electronic and steric effects. On the basis of charge it might be expected that the equilibrium constant for the addition of a second nucleophile to the complex ion would be smaller than that for the first addition. K_{eq} for the first addition to (2) is 1.6×10^4 dm^3 mol^{-1} ($= k_1/k_{-1}$) at 273 K. For the second addition at (1), $K_{eq} = 30$ dm^3 mol^{-1} at 298 K. We are not yet however in a position to explain why only the addition of the first molecule of $[OH]^-$ to (1) should be so much faster than the corresponding addition to (2).

Equilibrium constants and forward and reverse rate constants for the formation of the pseudo-base species studied in this work, together with several others for comparison, are collected in Table 8. Examination of the rates of formation of the pseudo-bases from organically quaternized N-heterocycles suggests that charge has little effect. The rates of the forward reaction vary from 10^2 to 10^7 dm^3 mol^{-1} s^{-1}, some of the fastest reactions belonging to the monopositive ions. The rates of the reverse reaction do however appear to be fastest for the dipositive complex ions. The value of K_{eq} for the addition of the first $[OH]^-$ to (2) is comparable to values found for related ions. From our studies with (1) it appears that the addition of the second $[OH]^-$ ion is much less favourable. Similar results have been obtained [19] for pseudo-base formation with $[CN]^-$ ion in metal complexes of $5NO_2$-phen.

For the metal complexes, arguing from the effect of charge, we could predict that equilibrium constants for analogous systems would fall in the orders shown below,

$$\begin{array}{ccccc} Fe^{II} & < & Co^{III} & < & Ni^{IV} \\ \vee & & \vee & & \vee \\ Ru^{II} & < & Rh^{III} & < & Pd^{IV} \\ \vee & & \vee & & \vee \\ Os^{II} & < & Ir^{III} & < & Pt^{IV} \end{array}$$

the vertical ordering arising from a secondary size effect. The equilibrium constants for $[M(5NO_2\text{-phen})_3]^{2+}$ ($M = Fe^{II}$ or Ru^{II}) and for $[M(5,5'Me_2\text{-bipy})_2]^{2+}$ ($M = Pd^{II}$ or Pt^{II}) certainly appear to follow this predicted trend. For a series of bivalent metal complexes of tptz, little variation is observed, the order being $Ru^{II} > Ni^{II} > Co^{II}$. Again we emphasize the fact that kinetic and thermodynamic behaviour in these systems are affected by small and subtle changes in electronic and steric properties. Further studies may help to elucidate the detailed differences in such systems, and to explain the fact that the phenomena of covalent hydrate and pseudo-base formation are easily observable in certain systems, but that in closely related complexes the values of the equilibrium constants are very small.

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