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Hydrogen isotope exchange rates for polyamines bound to inert transition-metal complexes

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A. INTRODUCTION

The first observation of the NH → ND isotope exchange reaction in inert transition-metal amine complexes was made by Erlenmeyer and Gartner [1] at the University of Basel in 1934 using $[Co(NH_3)_6]^{3+}$ in H_2O partially enriched with D_2O. Initially, there was some debate with regard to the number of protons exchanged [2–4] but eventually it was concluded that the process went to completion. Nevertheless, the exchange rate was unexpectedly slow in D_2O when compared with the rapid exchange observed for the uncomplexed amine [5].

Subsequent investigations [6] showed that the rate of exchange was a function of the $[OD^-]$ concentration of the solution and a more detailed kinetic examination [7–10] revealed three potential exchange pathways with the overall rate law being:

$$-\frac{d[MNH]}{dt} = \{k_{ex}^{OD^-}[OD^-] + k_{ex}^{D_2O} + k_{ex}^{X^-}[X^-]\}[MNH] \qquad (1)$$

In this expression, $k_{ex}^{OD^-}$ is a base-assisted path, $k_{ex}^{H_2O}$ is a solvent-assisted path and $k_{ex}^{X^-}$ a path due to general base (anion) catalysis.

This short review will critically consider the rate data obtained for this type of

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reaction, and will endeavour to highlight the complexities that need to be considered in evaluating such parameters.

B. EXPERIMENTAL TECHNIQUES

An extraordinarily large range of techniques has been used to follow NH → ND exchange reactions. Obviously, the rate can be monitored in two directions:

$$\mathrm{NH + OD} \xrightarrow{k_{\mathrm{ex}}^{\mathrm{D_2O}}} \mathrm{ND + OH^-} \tag{2}$$

or

$$\mathrm{ND + OH^-} \xrightarrow{k_{\mathrm{ex}}^{\mathrm{H_2O}}} \mathrm{NH + OD^-} \tag{3}$$

and, although the rates for these two processes are not expected to be identical, only rarely has this expectation been tested experimentally [11,12]. Under almost identical conditions, the exchange rate for the *sec*-NH/D proton in $[\mathrm{Co(NH_3)_4(Meen)}]^{3+}$ has an isotope effect; $k_{\mathrm{ex}}^{\mathrm{D_2O}}/k_{\mathrm{ex}}^{\mathrm{H_2O}}$ of 1.93 [11]. It has also been shown [13], using $[\mathrm{Co(enD}_x\mathrm{H}_{4-x})_3]^{3+}$, that the sequence of removal rates is D by $\mathrm{OD^-}$ > H by $\mathrm{OD^-}$ > H by $\mathrm{OH^-}$ > D by $\mathrm{OH^-}$. In this case, the isotope effect, $k_{\mathrm{ex}}^{\mathrm{D_2O}}/k_{\mathrm{ex}}^{\mathrm{H_2O}}$, is about 1.7.

In the earliest investigations (1937–1960), the rate was followed using the isotopically enriched complex, exchanging ND for NH, in buffered $\mathrm{H_2O}$. To do this, samples of the reacting solution were taken from time to time and the dissolved complex was precipitated with a suitable anion and removed. The now partially deuterated solvent was distilled several times and the density measured by flotation [6,14]. Alternatively, the precipitated complex was collected and dried and the extent of deuteration monitored by IR spectroscopy [15]. This technique is relatively simple if there is only one type of ND proton reacting, e.g. $[t\text{-}\mathrm{CoCl_2(cyclamD_4)}]^+$ [16]. If there are several types (as in $\mathrm{M{-}(ND_3)}_x^{n+}$), the rate of formation of $\mathrm{M{-}(NH_3)}_x^{n+}$ is last in a sequence $\mathrm{ND_3 \rightarrow ND_2H \rightarrow NDH_2 \rightarrow NH_3}$ and a calibration curve of $\mathrm{M{-}(ND_3)}_x^{n+}$ at equilibrium in various $\mathrm{D_2O/H_2O}$ mixtures must be made [15] to establish the extent of protonation. Finally, proton NMR has been used to monitor ND → NH exchange in diamagnetic systems, although experimental details are sparse [11,17,18].

As pure $\mathrm{D_2O}$ (99.9%) has become less expensive, techniques have been developed whereby the extent of deuteration of the hydrogen complex, dissolved in buffered $\mathrm{D_2O}$, can be monitored without separation of the complex from solution.

The most popular of these, developed by Palmer in the late 1950s and early 1960s [19–23], was to use the formation of the –OH bending overtone in $\mathrm{D_2O}$ at 1650 nm (6000 $\mathrm{cm^{-1}}$) in the near IR [10,24–26]. In some cases, the rate process could be separated into two steps, e.g. for *cis*-$[\mathrm{Co(en)_2(NH_3)_2}]^{3+}$, but not in all situations where two processes were expected, e.g. for $[CoCl(NH_3)_5]^{2+}$, was this possible. The overtone technique is particularly useful for paramagnetic complexes.

About the same time, the proton NMR method was being developed [19] and the rapid advances in this form of spectroscopy has made the technique especially attractive for diamagnetic systems. Even the D NMR line broadening observed in paramagnetic systems can be utilised [27].

The most recent technique, which is quite metal-ion specific, is the use of ^{59}Co NMR spectroscopy [10,13,28–31] and the large deuterium isotope shift (5 ppm per D atom) allows, for example, all 13 isotopomers of $[Co(enH_xD_{x-4})_3]^{3+}$ to be detected [13].

At constant temperature, these time-dependent monitoring techniques give one or more pseudo-first order rate constant(s) (k_{obs}) for the exchange process if all the chemical variables in eqn. (1) are held constant.

(i) Interpretation of k_{obs}

For most inert transition metal polyamine complexes, the rate of the NH → ND exchange process is slow at pH <7 and becomes negligible at pH <3.

This observation gave impetus to reinitiate [32] the search for isomers involving coordinated *sec*-NH amine protons, e.g. (R)- and (S)-$[Co(sar)(NH_3)_4]^{2+}$ [33]. The successful outcome has swung the pendulum in the opposite direction and any observation relating to coordinated *sec*-NH proton inversion in acid solution [34] is sometimes regarded with surprise. This should not be so, as examination of eqn. (1) shows that the exchange can take place via a solvent-assisted or anion-assisted process as well as the "normal" base-assisted path. For example, the value of $k_{ex}^{D_2O}$ (34°C) $= 1.2 \times 10^{-4}\ s^{-1}$ for $[CoCl(trenen)]^{2+}$ [35] means that *sec*-NH proton exchange will take place in acid solution with a half-life of about 1.6 h.

Rather extensive measurements are required to evaluate all the constants in eqn. (1). If buffers are used, then a series of measurements of k_{obs} at constant pD, but different buffer concentrations will establish the presence or absence of a $k_{ex}^{X^-}$ path. If this is absent, a plot of k_{obs} vs. $[OD]^-$ should be linear and have a positive intercept (indicating the $k_{ex}^{D_2O}$ contribution), or pass through zero with $k_{ex}^{D_2O} \sim 0$. The slope of the line will be $k_{ex}^{OD^-}$. At this stage it is not possible to generalise as to the importance, or otherwise, of the $k_{ex}^{X^-}$ and $k_{ex}^{H_2O}$ paths for any particular system.

In many cases, in the absence of critical data we have had to assume that $k_{ex}^{H_2O}$ and $k_{ex}^{X^-}$ are zero and have calculated $k_{ex}^{OD^-}$ using the expression $k_{obs} = k_{ex}^{OD^-}[OD^-]$ (Table 1).

(ii) The calculation of $[OD^-]$

We will first outline what we believe to be the most rigorous treatment and then proceed to more approximate methods. The problem is that most reactions

TABLE 1

Activation parameters for the base-assisted NH⇌ND exchange rates in transition-metal amine complexes[a]

Complex	T (°C)	I (M)	pD or pH	$pK_w^{solv.}$ [b]	k_{obs} (s^{-1})	k_{ex} [c] ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	Ref.
Octahedral									
$[Co(NH_3)_6]^{3+}$	90.0	1.0	0.1 M DCl	13.25	$\underline{1.23 \times 10^{-4}}$	2.2×10^{8}			10
	29.9	1.3	5.26[d]	14.82[e]		2.6×10^{6}			22
	29.9	0.7	5.26[d]	14.82[e]		2.5×10^{6}			
	25.0	0.7				1.6×10^{6}	59	+59	19,22,23
	25.0	0.1	5.61	14.751	6.67×10^{-4}	9.24×10^{5}			54
$[Co(ND_3)_6]^{3+}$	25.0	0.1	var.	13.996		1.17×10^{6}			15
		0.2	var.	13.996		1.32×10^{6}			
	25.0	var.				$\underline{5.76 \times 10^{6}}$	$\underline{54}$	$\underline{+47}$	14
	22.0	var.	4.81[f]	$\underline{13.867}$	3.92×10^{-4}	$\underline{4.57 \times 10^{6}}$			
	15.0	var.	4.81[f]	$\underline{14.132}$	1.26×10^{-4}	$\underline{2.61 \times 10^{5}}$			
	8.0	var.	4.81[f]	$\underline{14.421}$	3.59×10^{-5}	$\underline{1.45 \times 10^{5}}$			
	0.0	var.	4.81[f]	$\underline{14.737}$	8.25×10^{-6}	$\underline{7.12 \times 10^{4}}$			
$[Cr(NH_3)_6]^{3+}$	25.0[g]					2.6×10^{6}	50	+33	22
	25.0					2.5×10^{6}			27
$[Rh(NH_3)_6]^{3+}$	25.0[g]	1.0–2.5				2.1×10^{5}	63	+54	22
$[Ir(NH_3)_6]^{3+}$	25.0[g]					1.5×10^{4}	96	+142	22
	48.5					1.5×10^{6}			
$[Os(NH_3)_6]^{3+}$	25.0[g]					6×10^{6}			22
$[Ru(NH_3)_6]^{3+}$	25.0[g]					6×10^{8}			22
$[Co(en)_3]^{3+}$	33.0	0.5	3.74	14.553	5.6×10^{-7}	3.9×10^{6}			29
	33.0	0.6	0.1 M DCl	$\underline{14.531}$	1.7×10^{-7}	$\underline{5.9 \times 10^{6}}$			10
	25.0[g]					2.4×10^{6}			22,23
	25.0	var.	$\underline{5.15}$	$\underline{14.869}$	6.70×10^{-4}	$\underline{3.5 \times 10^{6}}$			24
	25.0[g]	0.9				2.5×10^{6}			19
$[Co(enD_4)_3]^{3+}$	33.0	0.5	6.02	13.744	2.2×10^{-2}	1.2×10^{6}			29
	25.0	var.				$\underline{5.21 \times 10^{5}}$	$\underline{53.5}$	$\underline{+44}$	14
	22.0	var.	4.81[f]	$\underline{13.867}$	3.50×10^{-4}	$\underline{3.99 \times 10^{5}}$			
	15.0	var.	4.81[f]	$\underline{14.132}$	1.13×10^{-4}	$\underline{2.53 \times 10^{5}}$			
	8.0	var.	4.81[f]	$\underline{14.421}$	3.24×10^{-5}	$\underline{1.32 \times 10^{5}}$			
	0.0	var.	4.81[f]	$\underline{14.737}$	7.7×10^{-6}	$\underline{6.52 \times 10^{4}}$			
$[Cr(en)_3]^{3+}$	25.0[g]					3.7×10^{6}			22
	25.0	var.	0.04 M NaOH			2.6×10^{6}	~48[i]		27

	48.0					3.7×10^{6}			
$[Ir(en)_3]^{3+}$	48.4		5.26^{d}	14.82^{e}		2×10^{6}			22
	$25.0^{g,h}$					2×10^{4}			22
$[Os(en)_3]^{3+}$	25.0^{i}					6×10^{6}			22
$[Rh(en)_3]^{3+}$	25.0^{g}					2.2×10^{5}			22
$[Co(tn)_3]^{3+}$	25.0^{g}	0.9				1.1×10^{7}			19
c-$[Co(en)_2(NH_3)_2]^{3+}$	25.0^{g}	0.9				2×10^{7}			19
$[Co(dien)_2]^{3+}$	$25.0^{g,i}$	0.6				1.4×10^{7}			19
t-$[Co(dien)_2]^{3+}$	25.0	2.0				4.7×10^{7} (NH)	56	+92	12
	34.9	2.0	0.03 M D^{+}	14.385		1.04×10^{8}			
	40.0					1.43×10^{8}			
	45.0					2.23×10^{8}			
	50.0					3.00×10^{8}			
t-$[Co(dienD_7)_2]^{3+}$	25.0	2.0				1.8×10^{7} (ND)	56	+84	12
	34.9	2.0	0.098 M H^{+}	13.676		3.5×10^{7}			
	40.0					7.1×10^{7}			
	45.0					8.0×10^{7}			
	50.0					1.1×10^{8}			
$[Co(pn)_3]^{3+}$	$25.0^{g,j}$	0.9				4.5×10^{6}			19
$[Co(rac\text{-}bn)_3]^{3+}$	$25.0^{g,j}$	0.12				5×10^{6}			19
$[Co(Meen)_3]^{3+}$	$25.0^{g,j}$	0.3	3.13	14.82	$\underline{6.1 \times 10^{-4}}$	3×10^{8} (NH?)			19
$[Co(en)(NH_3)_4]^{3+}$	30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	1.5×10^{-3}	$\underline{1.5 \times 10^{5}}$ (*c*-NH_3)			49
					6.5×10^{-3}	$\underline{6.5 \times 10^{5}}$ (*t*-NH_3)			
					3.2×10^{-3}	$\underline{3.2 \times 10^{5}}$ (en)			
$[Co(NH_3)_4(Meen)]^{3+}$	25.0			$\underline{14.689}$	$\underline{1.1 \times 10^{-4}}$				11,12
	34.4	1.0	3.29×10^{-2}		4.43×10^{-4}	2.97×10^{7} (NH)			
	45.0		1 M DCl		1.54×10^{-3}				
	50.0			$\underline{13.953}$	3.21×10^{-3}				
	55.0				6.60×10^{-3}				
$[Co(NH_3)_4(MeenD)]^{3+}$	25.0			$\underline{13.816}$	7.0×10^{-5}				13,47
	34.4	1.0	6.31×10^{-2}		3.21×10^{-4}	1.04×10^{7} (ND)			
	50.0		1 M HCl	$\underline{13.081}$	3.30×10^{-3}				
	55.0				6.66×10^{-3}				
$[Co(DMSO)(NH_3)_5]^{3+}$	29.0	0.6	0.1 M DCl	$\underline{14.679}$	7×10^{-5}	$\underline{3.3 \times 10^{9}}$ (*t*)			10
	6.8			$\underline{15.558}$	4×10^{-6}	$\underline{1.4 \times 10^{9}}$ (*t*)			
$[CoF(NH_3)_5]^{2+}$	25.0^{g}					1.1×10^{5} (*t*?)			23
	30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	5.58×10^{-5}	$\underline{5.8 \times 10^{3}}$ (*c*)			49
						v. fast (*t*)			
	34.0					3.2×10^{4} (*c*)			47
						1.5×10^{6} (*t*)			

TABLE I (*continued*)

Complex	T (°C)	I (M)	pD or pH	$\mathrm{p}K_w^{\mathrm{solv.}\,b}$	k_{obs} ($\mathrm{s^{-1}}$)	$k_{\mathrm{ex}}{}^{c}$ ($\mathrm{M^{-1}\,s^{-1}}$)	$\Delta H^{\ddagger}$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta S^{\ddagger}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Ref.
$[\mathrm{CoCl(NH_3)_5}]^{2+}$	25.0^{e}	0.12				1.5×10^5 (*c*?)	63	+46	19,23
	34.0					$\sim 9 \times 10^5$ (*c*)			47
						1.9×10^4 (*t*)			
$[\mathrm{CoCl(ND_3)_5}]^{2+}$	25.0	0.2				5×10^4 (*c*)			48
						3×10^6 (*t*)			
$[\mathrm{CoBr(NH_3)_5}]^{2+}$	25.0					1.6×10^5 (*c*?)			23
$[\mathrm{Co(NCS)(NH_3)_5}]^{2+}$	34.0					2×10^6 (*c*)			47
						9.7×10^4 (*t*)			
$[\mathrm{Co(fumarato)(NH_3)_5}]^{2+}$	21.0					2.0×10^7 (*t*)			46
						3.5×10^5 (*c*)			
$[\mathrm{Co(NO_2)(NH_3)_5}]^{2+}$	25.0^{g}					3.8×10^5 (*c*?)	50	+21	23
	30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	1.8×10^{-4}	$\underline{1.8 \times 10^4}$ (*c*)			49
					1.7×10^{-5}	$\underline{1.7 \times 10^3}$ (*t*)			
	34.0					1.2×10^5 (*c*)			47
						1.2×10^5 (*t*)			
$[\mathrm{Co(CN)(NH_3)_5}]^{2+}$	30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	6×10^{-5}	$\underline{6 \times 10^3}$ (*c*)			49
					6.2×10^{-6}	$\underline{6.2 \times 10^2}$ (*t*)			
	34.0					4.9×10^3 (*c*)			47
						8.1×10^4 (*t*)			
$[\mathrm{Co(\mathit{O}CONH_2)(NH_3)_5}]^{2+}$	34.0					4×10^5 (*c*)			47
						2.6×10^4 (*t*)			
$[\mathrm{Co(\mathit{O}COCH_3)(NH_3)_5}]^{2+}$	34.0					3.5×10^5 (*c*)			47
						1.3×10^4 (*t*)			
$[\mathrm{CrCl(NH_3)_5}]^{2+}$	25.0		5.06	14.82	1.6×10^{-4}	9.5×10^3 (*t*?)			26
$[\mathrm{IrCl(NH_3)_5}]^{2+}$	25.0^{e}					2×10^3 (*c*?)	96^{i}		23
$[\mathrm{Cr(OH)(NH_3)_5}]^{2+}$	25.0		0.062 M NaOH			1.2×10^6			27
$[\mathrm{CoCl(NH_2CH_3)_5}]^{2+}$	25.0	0.2	$\underline{5.25}$	$\underline{14.65}$	6.5×10^{-5}	$\underline{1.6 \times 10^3}$ (*c*)			25
					$\geqslant 1 \times 10^{-3}$	$\gtrsim 2 \times 10^6$ (*t*)			
	25.0	0.8				1.4×10^7 (*t*)^{j}	$117^{j,k}$		17
	34.0	0.8	4.12	14.42	1.5×10^{-4}	3×10^7 (*t*)			17
c-$[\mathrm{CoCl(en)_2(NH_3)}]^{2+}$	25.0^{e}	1.1				1×10^6 ($\mathrm{NH_3}$)			19
						5×10^4 (en)			
c-$[\mathrm{CoCl(trien)(NH_3)}]^{2+}$	$25.0^{e,i}$	0.6	3.13	14.82		2×10^5 ($\mathrm{NH_3}$)			6
						5×10^7 (NH)			
t-$[\mathrm{CoCl(tren)(NH_3)}]^{2+}$	25.0	1.0	5.33	14.50	2.1×10^{-4}	3.3×10^5 ($\mathrm{NH_3}$)			55
						$\sim 5 \times 10^5$ (*c*)			

p-[CoCl(tren)(NH$_3$)]$^{2+}$		25.0	1.0	6.15	14.50	$\sim 6 \times 10^{-4}$	$\sim 4 \times 10^5$ (t-NH$_3$) $\sim 1 \times 10^5$ (NH$_3$) $\sim 1 \times 10^5$ (c) 3.5×10^5 (t-Cl)			55
[CoCl(trenen)]$^{2+}$		34.0	1.2	$\underline{1.44}$	14.42	6.9×10^{-4}	5.7×10^9 (NH)	117^k		12,35
		40.0	1.2	$\underline{1.44}$	$\underline{14.24}$	2.9×10^{-3}	$\underline{1.8 \times 10^{10}}$ (NH)	$\underline{54}$		
[Co(N$_3$)(trenen)]$^{2+}$		34.0	0.8	$\underline{2.37}$	14.42	1.2×10^{-3}	1.3×10^9 (NH)			12
α,β-syn-[CoCl(picdien)]$^{2+}$		22.2	0.43	var. D$^+$	13.807	var.	$\underline{4.3 \times 10^8}$ (c-NH)^n $\underline{5.6 \times 10^9}$ (t-NH)^n			51
[CoBr(picdien)]$^{2+}$		22.2	0.43	var. D$^+$	13.807	var.	$\underline{1.7 \times 10^9}$ (t-NH)^n			51
[Co(NO$_2$)(picdien)]$^{2+}$		22.2	0.43	var. D$^+$	13.807	var.	$\underline{4.6 \times 10^9}$ (t-NH)^n			51
[Co(ox)(NH$_3$)$_4$]$^+$		35.0^g					8×10^5			19
[Co(ox)(ND$_3$)$_4$]$^+$		25.0	0.1	var.	13.996		6.61×10^4			15
			0.2	var.			6.08×10^4			
[PtCl$_2$(en)(Meen)]$^{2+}$		34.3	3.5		14.42		2×10^{10}(NH?)			7
[Co(ox)(en)$_2$]$^+$		35.0^g	0.12				8×10^5			19
[Co(ox)(pn)$_2$]$^+$		35.0^{g,j}	0.12				1×10^6			19
[Co(ox)(i-bn)$_2$]$^+$		35.0^{g,j}	0.12				1×10^6			19
[Co(ox)(n-Pren)$_2$]$^+$		35.0^{g,j}	0.1	3.13^e	14.82^e		4×10^7 (NH?)			19
t-[CoCl$_2$(enD$_4$)$_2$]$^+$		0.0		10.0			$\sim 3 \times 10^3$			56
t-[Co(NO$_2$)$_2$(NH$_3$)$_4$]$^+$		25.0^g					1.5×10^5	50	+12	23
c-[Co(NO$_2$)$_2$(NH$_3$)$_4$]$^+$		25.0^g					1.2×10^5 (c) 4.5×10^5 (t)	44	+4	23
t-[Co(NO$_2$)$_2$(en)$_2$]$^+$		25.0^g					6.8×10^4			23
c-[Co(NO$_2$)$_2$(en)$_2$]$^+$		25.0	0.04	$\underline{6.69}$	$\underline{14.869}$	1.2×10^{-4}	$\underline{1.93 \times 10^4}$ (c)			24
		25.0^g					7.2×10^4 (c) $\underline{5.0 \times 10^5}$ (t)			23
t,t-[Co(NO$_2$)$_2$(Meen)$_2$]$^+$		34.3	1.0	6.35	14.42		9.3×10^4			18
t,t-[Co(NO$_2$)$_2$(MeenD)$_2$]$^+$		34.3	1.0	3.62	13.71	5×10^{-6}	6.1×10^4	66	+63^m	18,57
		45.0				2.6×10^{-5}				
		55.0				1.22×10^{-4}				
[Co(acac)$_2$(Meen)]$^+$	$\Lambda(S)\Delta(R)$	34.0		5.7–7.1			8.9×10^3 (NH)			58
[Co(CH$_3$acac)$_2$(Meen)]$^+$	$\Lambda(S)\Delta(R)$	34.0		7.7–9.2			7.0×10^2			59
	$\Lambda(R)\Delta(S)$						1.5×10^2			
[Co(Clacac)$_2$(Meen)]$^+$	$\Lambda(S)\Delta(R)$	34.0		4.8–6.2			9.1×10^4			
	$\Lambda(R)\Delta(S)$	34.0					1.7×10^4			
[Co(NO$_2$acac)$_2$(Meen)]$^+$	$\Lambda(S)\Delta(R)$	34.0		2.4–3.1			1.4×10^7			
	$\Lambda(R)\Delta(S)$	34.0					2.1×10^6			
[Co(acac)$_2$(Me$_3$en)]$^+$	$\Lambda(R)\Delta(S)$	34.0		5.7–7.1			2.4×10^3			60
	$\Lambda(S)\Delta(R)$						1.1×10^4			
[Co(acac)$_2$(Phen)]$^+$	$\Lambda(S)\Delta(R)$	34.0	0.2	1.2–3.1			4×10^7			58
	$\Lambda(R)\Delta(S)$						5×10^8			

TABLE 1 (*continued*)

Complex		T (°C)	I (M)	pD or pH	$pK_w^{solv.\ b}$	k_{obs} (s^{-1})	$k_{ex}{}^c$ ($M^{-1}\ s^{-1}$)	$\Delta H^\#$ (kJ mol^{-1})	$\Delta S^\#$ (J K^{-1} mol^{-1})	Ref.
t-$[CoF_2(en)_2]^+$		25.0^g					1×10^3			23
c-$[Co(CN)_2(en)_2]^+$		30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	6.8×10^{-4}	$\underline{6.8 \times 10^4}$ (t-N)			49
						3.1×10^{-4}	3.1×10^4 (t-C)			
t-(RR,SS)-$[CrF_2(3,2,3\text{-tet})]^+$		25.0	0.5	$\underline{8.5}$	$\underline{14.869}$	1.3×10^{-4}	$\underline{3 \times 10^2}$ (NH)			61
t-(RR,SS)-$[CrCl_2(2,3,2\text{-tet})]^+$		25.0	1.0	$\underline{7.5}$	$\underline{14.869}$	1.3×10^{-4}	$\underline{3 \times 10^3}$ (NH)			61
t-(RSSR)-$[CrCl_2(teta)]^+$		25.0	1.0	$\underline{7.5}$	$\underline{14.869}$	4.4×10^{-5}	$\underline{1.3 \times 10^3}$ (NH)			61
t-(RR,SS)-$[CoCl_2(3,2,3\text{-tet})]^+$		25.0	0.02	~ 5.0	$\underline{14.869}$	$\sim 1 \times 10^{-4}$	$\underline{\sim 1 \times 10^5}$ (NH)			61
t-(R,S)-$[CoCl_2(2,3,2\text{-tetD}_6)]^+$		25.0		6.19			$\sim 1 \times 10^5$ (NH)			56
c-(RRRR,SSSS)-$[CoCl_2(cyclamD_4)]^+$		0.0	0.1	5.18			3.2×10^6 (NH)			16,43
t-(RSSR)-$[CoCl_2(cyclam)]^+$		25.0	0.1	6.54						43
		0.0	0.1	7.80						
$[Co(sar)(NH_3)_4]^+$		33.0	1.0	3.13×10^{-2}	14.82^e	5.7×10^{-6}	1.1×10^8	58	+88	11,33
		40.0		1 M DCl		1.3×10^{-5}	2.6×10^8			
		50.0				4.7×10^{-5}	9.6×10^8			
c-$[Co(CO_3)(NH_3)_4]^+$		30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	1.3×10^{-3}	$\underline{1.3 \times 10^5}$ (t-N)			49
						2.2×10^{-3}	$\underline{2.2 \times 10^5}$ (t-O)			
c-$[Co(AcO)_2(NH_3)_4]^+$		30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	1.4×10^{-4}	$\underline{1.4 \times 10^4}$ (t-N)			49
						6.8×10^{-4}	$\underline{6.8 \times 10^4}$ (t-O)			
c-$[Co(CN)_2(NH_3)_4]^+$		30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	3.9×10^{-4}	$\underline{3.9 \times 10^4}$ (t-N)			49
						6.2×10^{-5}	$\underline{6.2 \times 10^3}$ (t-C)			
c-$[Co(SO_3)_2(NH_3)_4]^-$		30.0		$\underline{\sim 6.7}$	$\underline{14.699}$	4.9×10^{-4}	$\underline{4.9 \times 10^4}$ (t-S)			49
$[Co(ox)_2(Meen)]^-$	Λ(R)Δ(S)	34.0		5.7–7.1			2.2×10^4			60
	Λ(S)Δ(R)						1.8×10^5			
$[Co(ox)(Me_3en)]^-$	Λ(R)Δ(S)	34.0		4.3–6.5			1.2×10^5			60
	Λ(S)Δ(R)						8.1×10^5			
t-$[Cr(NCS)_4(NH_3)_2]^-$		25.0		0.5 M NaOH			3.0×10^4			27
		25.0		$\underline{8.51}$	$\underline{14.869}$	1.03×10^{-3}	$\underline{2.2 \times 10^4}$			62
Square planar										
$[Pt(NH_3)_4]^{2+}$		25.0^g					4.8×10^5	44	+8	22
$[Pt(ND_3)_4]^{2+}$		25.0	var.				$\underline{1.06 \times 10^5}$	$\underline{48}$	$\underline{+2}$	6
		20.0	var.	5.61	$\underline{13.867}$	1.35×10^{-3}	$\underline{7.63 \times 10^4}$			
		14.0	var.	5.61	$\underline{14.132}$	7.87×10^{-4}	$\underline{5.07 \times 10^4}$			
		7.0	var.	5.61	$\underline{14.421}$	4.68×10^{-4}	$\underline{3.08 \times 10^4}$			
		0.0	var.	5.61	$\underline{14.737}$	3.04×10^{-4}	$\underline{1.82 \times 10^4}$			

$[Pt(en)_2]^{2+}$	25.0^g					1.6×10^5			22,23
$[Pt(NH_3)_3(Meen)]^{2+}$	25.0	0.3		14.87		6.6×10^4	60	+41	9
	37.5					1.9×10^5			
	50.0			14.10		4.3×10^5			
$[Pt(en)(Meen)]^{2+}$	34.0	1.0		14.42		1.9×10^5			7
$[Pt(bipy)(Meen)]^{2+}$	25.0	0.2		14.87		3.9×10^7			9
	37.5					1.34×10^8			
	30.0	1.0		13.83		2.7×10^6			63
$[Pt(bipy)(Me_2en)]^{2+}$	30.0	1.0		13.83		1.02×10^7			63
	?					1.3×10^7			64
$[Pt(bipy)(Me_3en)]^{2+}$	30.0	1.0		13.83		8.7×10^7			63
$[Pt(NH_3)_2(Me_2en)]^{2+}$	?					4.2×10^4			64
$[Pt(NH_3)_3(sar)]^+$	39.0	1.0				3.5×10^3			44
$[PtCl(dien)]^+$	25.0^g					1.5×10^5			23
$[PtBr(dien)]^+$	25.0^g					2.5×10^5 (NH_2)			23
						6×10^6 (NH)			
$[PtI(dien)]^+$	25.0^g					2×10^6 (NH_2)			23
						2×10^8 (NH)			
$[Pt(NO_2)(dien)]^+$	25.0^g					1.4×10^6 (NH_2)			23
						1×10^8 (NH)			
$[Pt(NCS)(dien)]^+$	$25.0^{g,j}$					3×10^6 (NH_2)			23
						6×10^8 (NH)			
c-$[PtCl_2(NH_3)_2]$	25.0	0.11	4.80	14.751	1.57×10^{-4}	1.35×10^6	24.9	−44	54
	32.0		5.03	14.517	5.57×10^{-4}	1.74×10^6			
	40.0		5.05	14.262	1.40×10^{-3}	2.29×10^6			
$[PtCl_2(en)]$	25.0	0.11	5.07	14.751	1.06×10^{-4}	5.14×10^5	21.7	−64	54
	32.0		5.09	14.517	2.43×10^{-4}	6.40×10^5			
	40.0		5.11	14.262	5.68×10^{-4}	8.12×10^5			
$[PtCl_2(tn)]$	25.0	0.11	6.35	14.751	1.41×10^{-4}	3.64×10^4	50.3	+10	54
	32.0		6.25	14.517	2.98×10^{-4}	5.92×10^4			
	40.0		5.59	14.262	2.10×10^{-3}	1.01×10^5			
$[Pt(NH_3)(edda)]$	39.0	1.0				2.8×10^5			44
$[PtCl_2(sar)]^-$	33.5	1.0				1.1×10^6 (NH)			8
$[PtCl_2(gly)]^-$	33.5	1.0				9×10^6 (NH_2)			8
$[Pd(ND_3)_4]^{2+}$	0.0	0.16	7.17	$\underline{14.737}$	2.44×10^{-4}	$\underline{9.04 \times 10^3}$			6
	10.0^l		5.59		2.08×10^{-4}				
	20.0^l		5.59		9.79×10^{-4}				
$[Pd(NH_3)_4]^{2+}$	25.0^g					$<1 \times 10^8$			22
$[Pd(en)_2]^{2+}$	25.0^g					1.5×10^7			22,23
rac-$[Pd(en)(Me_2en)]^{2+}$	27.0	1.0				1×10^5			65

TABLE 1 (*continued*)

Complex	T (°C)	I (M)	pD or pH	$\mathrm{p}K_w^{\mathrm{solv.}}$ [b]	k_{obs} ($\mathrm{s^{-1}}$)	k_{ex} [c] ($\mathrm{M^{-1}\,s^{-1}}$)	$\Delta H^{\#}$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta S^{\#}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Ref.
meso-$[\mathrm{Pd(en)(Me_2en)}]^{2+}$	27.0	1.0				5.3×10^4			65
rac-$[\mathrm{Pd(NH_3)_2(Me_2en)}]^{2+}$	27.0	1.0				1.1×10^5			65
meso-$[\mathrm{Pd(NH_3)_2(Me_2en)}]^{2+}$	27.0	1.0				1.4×10^5			65
$[\mathrm{Pd(pn)(Me_2en)}]^{2+}$	27.0[j]	1.0				2.8×10^4			65
$[\mathrm{Pd(bipy)(Me_2en)}]^{2+}$	27.0	1.0				1.3×10^7			65
$[\mathrm{PdBr(dien)}]^{+}$	25.0[g]					4×10^8			23
$[\mathrm{Pd(NO_2)(dien)}]^{+}$	25.0[g]					6×10^8			23
$[\mathrm{Pd(sar)(en)}]^{+}$	27.0	1.0				5.2×10^5			65
$[\mathrm{Pd(Meala)(en)}]^{+}$	27.0	1.0				2.1×10^5			65
$[\mathrm{Pd(Mephe)(en)}]^{+}$	27.0	1.0				6.5×10^4			65
rac-$[\mathrm{Pd(gly)(Me_2en)}]^{+}$	27.0	1.0				1.6×10^6			65
meso-$[\mathrm{Pd(gly)(Me_2en)}]^{+}$	27.0	1.0				8.5×10^5			65
rac-$[\mathrm{Pd(glygly)(Me_2en)}]^{0}$	27.0	1.0				5.2×10^3			65
meso-$[\mathrm{Pd(glygly)(Me_2en)}]^{0}$	27.0	1.0				5.5×10^3			65

[a] Underlined values have been recalculated or estimated from the data in the original literature.

[b] $\mathrm{p[OD^-]} = \mathrm{p}K_w^{\mathrm{solv.}} - \mathrm{pD}$ (measured) or $\mathrm{p[OH^-]} = \mathrm{p}K_w^{\mathrm{solv.}} - \mathrm{pH}$ (measured).

[c] $k_{\mathrm{ex}} = k_{\mathrm{obs}}[\mathrm{OD^-}]^{-1}$ or $k_{\mathrm{ex}} = k_{\mathrm{obs}}[\mathrm{OH^-}]^{-1}$.

[d] ±0.2 as an unspecified correction factor for the change in pH on dissolving an equivalent amount of the complex in buffered H_2O.

[e] Values at 25°C.

[f] Corrected for ionic strength effects.

[g] Same conditions as for footnote d [22].

[h] Extrapolated from high-temperature measurements.

[i] Extrapolated.

[j] Unknown geometric configuration.

[k] Based on the variation of k_{obs} vs. T at constant $[\mathrm{D^+}]$. A value of $\sim 54\ \mathrm{kJ\,mol^{-1}}$ would be a better estimate for k_{ex}.

[l] Complicated by synchronous $\mathrm{Pd{-}NH_3}$ dissociation.

[m] These $\Delta S^{\#}$ values are apparently associated with k_{obs}.

[n] Recalculated from plots of k_{obs} vs. $[\mathrm{OD^-}]$.

have been studied using buffer systems in D_2O and the "pH" has been measured using a glass electrode calibrated with a (different) buffer in H_2O. Also, the use of NMR techniques has, until recently, required rather high concentrations of complex ion (>0.1 M) and a 0.33 M solution of a $Co(III)^{3+}$ complex has $I = 2.0$ M without any added electrolyte.

Kineticists routinely use high ionic strength backgrounds (typically $I = 1.0$ M) as "standard states" and this normally satisfactory procedure makes the precise estimate of $[OD^-]$ from "pH" measurement rather difficult. We define $K_w^{D_2O}$ as the ionic product of deturium oxide, and tables of these ionic products on both the molar and molal scales at different temperatures (see later) are available and widely used [36,37]. What is not generally stated is that these values have been extrapolated to zero ionic strength [36,38]. Consequently, for any reaction with $I > 0$, values of $K_w^{D_2O}$ must be corrected by the appropriate activity–activity coefficient factor.

Thus:

$$K_w^{D_2O} = [D^+][OD^-] \qquad (I = 0) \tag{4}$$

$$= [D^+][OD^-]\left\{\frac{\gamma_{D^+} \cdot \gamma_{OD^-}}{a_{D_2O}}\right\} \qquad (I > 0) \tag{5}$$

and

$$pK_w^{D_2O} - \left\{\log \frac{a_{D_2O}}{\gamma_{D^+} \cdot \gamma_{OD^-}}\right\} = p[D^+] + p[OD^-] \tag{6}$$

It is usually assumed that the values of the activity–activity coefficient factors for γ_{D^+}, γ_{OD^-} and a_{D_2O} in D_2O are the same as for γ_{H^+}, γ_{OH^-} and a_{H_2O} in H_2O at 25°C, i.e. $(\gamma_{D^+} \cdot \gamma_{OD^-})/a_{D_2O} = 0.607$ at $I = 0.1$ M NaCl [39] and

$$p[D^+] + p[OD^-] = 14.869 - 0.217 \tag{7}$$

$$= 14.652 \tag{8}$$

The other factor in eqn. (7), $p[D^+]$, is estimated from the measured "pH". The glass electrode is normally calibrated using a standard buffer in H_2O with a known $[H^+]$ (relative to zero ionic strength) and an established temperature coefficient. This calibrated electrode is then used to measure the "pH" of the D_2O solution containing the dissolved complex at the appropriate ionic strength.

An empirical relationship [40] between the "pH" measured this way, and $p[D^+]$ has been established as

$$p[D^+] = pH_{meas.} + 0.40 \tag{9}$$

but this must now be corrected for the activity of D^+. In 0.1 M D_2O ionic media, we again assume that this is the same as the activity coefficient of H^+ in 0.1 M H_2O ionic media, i.e. $\gamma_\pm = 0.7964$ [41] at 25°C, $I = 0.1$ M, for HCl.

Thus

$$\mathrm{p[OD^-]} = 14.652 - \log \gamma_{\pm} - (\mathrm{pH_{meas.}} + 0.40) \tag{10}$$

$$= 14.751 - (\mathrm{pH_{meas.}} + 0.40) \tag{11}$$

$$= \mathrm{p}K_{\mathrm{w}}^{\mathrm{solv.}} - (\mathrm{pH_{meas.}} + 0.40) \tag{12}$$

For $I = 1.0$ M (NaCl) the corresponding equation (25°C) is:

$$\mathrm{p[OD^-]} = 14.869 - 0.272 + 0.092 - (\mathrm{pH_{meas.}} + 0.40)$$

$$= 14.689 - (\mathrm{pH_{meas.}} + 0.40) \tag{13}$$

but at these high ionic strengths and high pH, $\mathrm{Na^+}$ ions can compete with $\mathrm{H^+}$ ions for sites on the glass electrode, and "sodium ion corrections" [42] may be required.

A common standard state media would remove the need for these corrections and a set of relative $k_{\mathrm{ex}}^{\mathrm{OD^-}}$ would be obtained. Unfortunately, with such a wide variety of techniques available for monitoring the reaction, it is difficult to set a media that is applicable to all situations.

The corrections are important as a change in ionic strength from 0.1 to 1.0 M for pD = 5.40 changes the $\mathrm{[OD^-]}$ from 4.45 to 5.14×10^{-10} M and hence, with $k_{\mathrm{obs}} = 2 \times 10^{-4}\ \mathrm{s^{-1}}$, $k_{\mathrm{ex}}^{\mathrm{OD^-}}$ values are 4.49 and $3.89 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$, respectively. If the zero ionic strength relationship (25°C)

$$\mathrm{p[OD^-]} = \mathrm{p}K_{\mathrm{w}}^{\mathrm{D_2O}} - \mathrm{p[D^+]} \tag{14}$$

is used, then $k_{\mathrm{ex}}^{\mathrm{OD^-}} = 5.89 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ for the above situation, an increase by a factor of 1.5 relative to $I = 1.0$ M.

One technique that has been used to cope with the $\mathrm{p[D^+]}$ activity coefficient correction is to "calibrate" the glass electrode with a standard buffer made in the appropriate ionic media [43]. The assumption is that the resulting difference from zero ionic strength will be the same for both the standard buffer and the test solution. Ionic strength corrections to $\mathrm{p}K_{\mathrm{w}}^{\mathrm{D_2O}}$ for the appropriate electrolyte are, however, still required. A more empirical approach can be taken [12,38,44] by using the relationship

$$K_{\mathrm{w}}^{\mathrm{solv.D_2O}} = F \times K_{\mathrm{w}}^{\mathrm{solv.H_2O}} \tag{15}$$

as complete ionic strength and temperature variation data are known for $K_{\mathrm{w}}^{\mathrm{solv.H_2O}}$ [39]. Modern data [36,37] would give the constant, F, as 0.134 (Table 2), although 0.195 was used in earlier work [12].

Using $F = 0.134$, $\mathrm{p}K_{\mathrm{w}}^{\mathrm{solv.D_2O}}$ in 0.1 M NaCl at 25°C would be $13.996 - 0.217 - \log(0.134) = 14.651$ compared with 14.652 from the previous assumptions. The agreement is not quite so good at other temperatures (Table 2).

A survey of the literature shows that the conversion from pD to $\mathrm{[OD^-]}$ leaves much to be desired. If both k_{obs} and $k_{\mathrm{ex}}^{\mathrm{OD^-}}$ are cited, then the appropriate $\mathrm{p}K_{\mathrm{w}}^{\mathrm{solv.}}$ that has been used in the investigation can be calculated and this has been done in the

TABLE 2

Selected values of $pK_w^{solv.}$ for various temperatures and ionic strengths (NaCl)

I	0.1	0.5	1.0	2.0
10.0°C, $pK_w^{H_2O} = 14.5346$, $pK_w^{D_2O} = 15.439$				
$\gamma_{H^+}\cdot\gamma_{OH^-}/a_{H_2O}$	0.613	0.520	0.542	0.699
(log)	(−0.213)	(−0.284)	(−0.266)	(−0.156)
$\gamma_\pm$ (HCl)	0.8016	0.7694	0.8295	1.053
(log)	(−0.096)	(−0.114)	(−0.081)	(+0.022)
$pK_w^{solv.H_2O}$ [a]	14.418	14.365	14.350	14.357
$pK_w^{solv.D_2O}$ [a]	15.322	15.269	15.254	15.261
$pK_w^{solv.D_2O}$ [b]	15.291	15.238	15.223	15.230
25.0°C, $pK_w^{H_2O} = 13.9965$, $pK_w^{D_2O} = 14.869$				
$\gamma_{H^+}\cdot\gamma_{OH^-}/a_{H_2O}$	0.607	0.514	0.535	0.696
(log)	(−0.217)	(−0.289)	(−0.272)	(−0.157)
$\gamma_\pm$ (HCl)	0.7964	0.7571	0.8090	1.009
(log)	(−0.099)	(−0.121)	(−0.092)	(+0.004)
$pK_w^{solv.H_2O}$ [a]	13.878	13.828	13.816	13.835
$pK_w^{solv.D_2O}$ [a]	14.751	14.701	14.689	14.708
$pK_w^{solv.D_2O}$ [b]	14.751	14.701	14.689	14.708
50.0°C, $pK_w^{H_2O} = 13.2617$, $pK_w^{D_2O} = 14.103$				
$\gamma_{H^+}\cdot\gamma_{OH^-}/a_{H_2O}$	0.589	0.497	0.507	0.629
(log)	(−0.230)	(−0.304)	(−0.295)	(−0.201)
$\gamma_\pm$ (HCl)	0.7850	0.7508	0.7697	0.9327
(log)	(−0.105)	(−0.124)	(−0.114)	(−0.030)
$pK_w^{solv.H_2O}$ [a]	13.137	13.082	13.081	13.091
$pK_w^{solv.D_2O}$ [a]	13.978	13.923	13.922	13.932
$pK_w^{solv.D_2O}$ [b]	14.001	13.955	13.953	13.964

[a] Calculated using the expression: $pK_w^{solv.} = pK_w + \log\left(\frac{\gamma_{H^-}\cdot\gamma_{OH^-}}{a_{H_2O}}\right) - \log\gamma_\pm$.

[b] Calculated using the expression: $K_w^{H_2O} = 0.134 K_w^{D_2O}$.

data compilation. Unfortunately, for quite a number of complexes studied, this information is not available and it is not possible to assess the validity of the procedure.

(iii) The estimation of activation parameters

Until recently, temperature control in NMR spectrometers was one of mankind's less sophisticated technological achievements and was certainly not satisfactory for accurate kinetics (probably not better than ±1°C). Even the use of external water bath temperature control results in temperature changes during data acquisition. Nevertheless, attempts using NMR, and other techniques, have been made to determine the influence of temperature on the exchange rate.

Although data for the temperature variation of $K_w^{D_2O}$ were available in 1936 [38], this information was not used directly by the early investigators. They preferred to measure k_{obs} at fixed pD (using a buffer with a small temperature coefficient) and to calculate the apparent activation energy from the variation of k_{obs} with temperature. This apparent activation energy was then corrected for the heat of ionisation of D_2O (60.3 kJ mol^{-1} [38]).

$$E_a^{app} - 60.3 = E_a^{ex} \tag{16}$$

This calculation is only satisfactory if the temperature variation of the reaction rate is identical with the temperature variation of $K_w^{D_2O}$. Nevertheless, this procedure persisted until the mid-1960s. Subsequently, data for the temperature variation of $K_w^{D_2O}$ have become more widely disseminated [36,37]. These early investigators also cited $\Delta S^{\ddagger}$ (entropy of activation) values. It is not clear if these relate to the ln k_{obs} vs. $1/T$ K plot or have been recalculated from k_{ex} and E_a^{ex} data. For at least one study, the cited $\Delta S^{\ddagger}$ value certainly relates to the former and, as such, has no relevance to the k_{ex} reaction.

Clearly, what should be done in these systems is that, after each temperature change, the glass electrode should be recalibrated at that temperature. The "pH" of the D_2O/buffer/complex solution at that temperature and known ionic strength should be measured, and the appropriate $pK_w^{solv.}(T)$ should be calculated using activity coefficients at the appropriate temperature. Once $k_{obs}(T)$ has been obtained, then

$$k_{ex}^{OD^-}(T) = k_{obs}(T)\{[\text{antilog}[pK_w^{solv.}(T) - pH_{meas.}(T) - 0.40]\}^{-1} \tag{17}$$

and the variation of $k_{ex}^{OD^-}$ with temperature will give E_a, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the normal way [42].

Unfortunately, in many instances, it is not possible to recalculate activation parameters because the appropriate data are not given. Consequently, a number of entries in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ columns [12] may not relate to $k_{ex}^{OD^-}$ at all.

(iv) $k_{ex}^{OD^-}$ *values*

Table 1 lists the $k_{ex}^{OD^-}$ (or $k_{ex}^{OH^-}$) values reported in the literature, or recalculated from literature data. No attempt has been made to recalculate all the values corrected for ionic strength, but the value of $pK_w^{solv.}$ used by the investigator has been cited (or calculated) wherever possible. In a number of instances, the ionic strength of the medium is poorly described, and under these circumstances we have no option but to use the zero ionic strength relationship (14). There seem to be many instances where data are accumulated in the 30–35°C range (the accepted operating temperature of an NMR spectrometer), but $K_w^{D_2O}$ (25°C) has been used in the calculation of $[\mathrm{OD}^-]$. We have not attempted to recalculate these data, but have signalled the problem when it has been suspected.

For many of the complexes cited in Table 1 there are several types of NH proton, e.g. $-\mathrm{NH_3}$, $\mathrm{R{-}NH_2}$, *sec*-NH, and NH protons in different environments. In $[\mathrm{CrCl(NH_3)_5}]^{2+}$, there are four $\mathrm{NH_3}$ groups adjacent (*cis*) to the chloro ligand and one $\mathrm{NH_3}$ remote (*trans*). These give rise to more or less easily detected sequential rates.

The $[\mathrm{CoX(NH_3)_5}]^{n+}$ system is particularly interesting as there is considerable debate as to which set of $\mathrm{NH_3}$ ligands has the most acidic proton, and is therefore the most likely to participate in the $\mathrm{S_N1CB}$ base hydrolysis mechanism [45]. Actually, the question that should be asked is, which deprotonated species gives the most reactive conjugate base and the relative acidities may not be relevant. Nevertheless, two exchange rate processes for $[\mathrm{CoX(NH_3)_5}]^{n+}$ can be detected [10,46–49], but which corresponds to the *cis*-$\mathrm{NH_3}$ and which to the unique *trans*-$\mathrm{NH_3}$ is still subject to some uncertainty.

In summary (Table 3), it appears that when $\mathrm{X = CN^-}$ or $\mathrm{NO_2^-}$, the rate of *trans*-$\mathrm{NH_3}$ exchange is less than that of the *cis* groups, but for $\mathrm{X = H_2O}$, $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{N_3^-}$, $\mathit{O}\mathrm{CONH_2^-}$, fumerate, $\mathrm{CH_3NH_2}$ and DMSO the rate of *trans*-$\mathrm{NH_3}$ exchange is faster.

Returning to the topic of differences between $-\mathrm{NH}$, $-\mathrm{NH_2}$ and $-\mathrm{NH_3}$ protons, the apparent exchange rate order is $-\mathrm{NH} \gg -\mathrm{NH_2} \sim -\mathrm{NH_3}$ for all metals. It is known that a chloropentaamine Co(III) polyamine complex with a planar *sec*-NH functional group has a base hydrolysis rate much greater than the isomeric system where the *sec*-NH group is folded [50]. At the moment, there are insufficient NH → ND data available on isomeric Co(III) systems to see if this lability is reflected in the exchange rate [51].

TABLE 3

NH → ND labilisation for $[\mathrm{CoX(NH_3)_5}]^{n+}$ in order of decreasing rate

trans-$\mathrm{NH_3}$	*cis*-$\mathrm{NH_3}$
DMSO[a]	$\mathrm{NH_3}$[a]
$\mathrm{Cl^-}$	$\mathit{N}\mathrm{CS^-}$
$\mathrm{F^-}$	$\mathrm{NH_2CO}\mathit{O}^-$
$\mathrm{NH_2}\mathit{COO}^-$	$\mathrm{CH_3CO}\mathit{O}^-$
$\mathrm{CH_3CO}\mathit{O}^-$	$\mathrm{Br^-}$
$\mathit{C}\mathrm{N^-}$	$\mathit{N}\mathrm{O_2^-}$
	$\mathrm{Cl^-}$
	$\mathit{C}\mathrm{N^-}$
	$\mathrm{F^-}$

[a] There are 3+ cations, whereas the remainder are 2+.

Considerable discussion in the early literature concentrated on the differences between $[M(NH_3)_6]^{3+}$ and $[M(en)_3]^{3+}$ exchange rates. Unfortunately, this was complicated by a misinterpretation of the work of Anderson et al. [6] who found that $[Co(NH_3)_6]^{3+}$ exchanged more rapidly than $[Co(en)_3]^{3+}$. The reverse was cited in later literature [19,22]. A comparison of all $M(N_6)^{3+}$ systems ($N_6 = NH_3$ or en) indicates little difference in exchange rates.

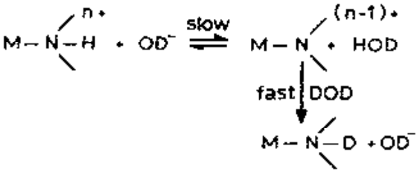
(v) Charge effects

These are difficult to evaluate and trends can be dominated by specific ligand effects. In the series $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)(NH_3)_5]^{2+}$, *trans*-$[Co(NO_2)_2(NH_3)_4]^{+}$, the exchange rate order is $3+ > 2+ > 1+$, but there is only a factor of 10 separating the fastest from the slowest. Similarly, in the square planar series, charge appears to have little influence on exchange rate or, for that matter, substitution rate [52].

C. THE REACTION MECHANISM

(i) Octahedral systems

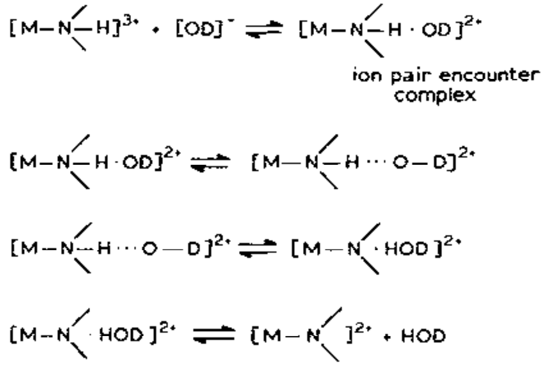
The general consensus [14] is that the reaction proceeds via direct attack of the proton attached to the nitrogen while bound to the central metal:



(18)

followed by rapid N—D bond formation from D_2O and the deprotonated complex.

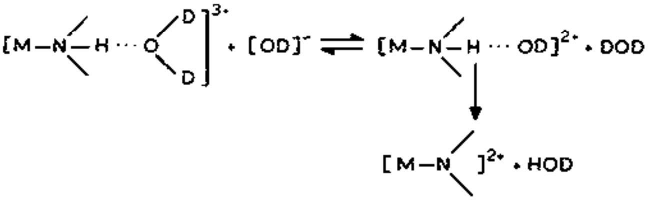
Thus the transition region species probably involves H-bond formation after the initial ion pair encounter complex is established:



(19)

The solvent-assisted and general anion-assisted processes are imagined to involve D_2O or X^- in place of OD^-.

Of course, this scheme is indistinguishable from one where the deprotonation takes place on a D_2O molecule in a solvation sphere, hydrogen bonded to the M–N–H group:



(20)

and in some ways may be preferred in view of the rather small ionic charge influence on the reaction rate.

The solvated, deprotonated species probably has some very short life-time as it can adjust to a planar configuration prior to solvent attack. If this were not so, racemisation or *sec*-NH isomerisation reactions would not take place. However, NH → ND exchange process do not even require this adjustment and consequently are often several orders of magnitude faster than racemisation [11]*. Nevertheless, there are some base-assisted substitution reactions where every act of deprotonation results in product formation and $k_{ex} \approx k_{substitution}$ [53].

(ii) Square planar systems

The NH → ND exchange process in octahedral systems may well involve hydrogen-bonded solvent molecules in the second coordination sphere about the central metal. For square planar systems, such solvent molecules can interact directly with the metal centre via transient metal–oxygen bonding and consequently form more ordered intramolecular hydrogen bonding (eqn. (21)).

This model was proposed in the early 1960s [22] and has been revived from time to time [54].

Such a process should have a much lower entropy of activation than in the octahedral case, and this seems to be observed experimentally [54].

D. CONCLUSIONS

There are a number of interesting reactions of transition metal polyamine complexes that are subsequent to NH deprotonation. These include inversion, race-

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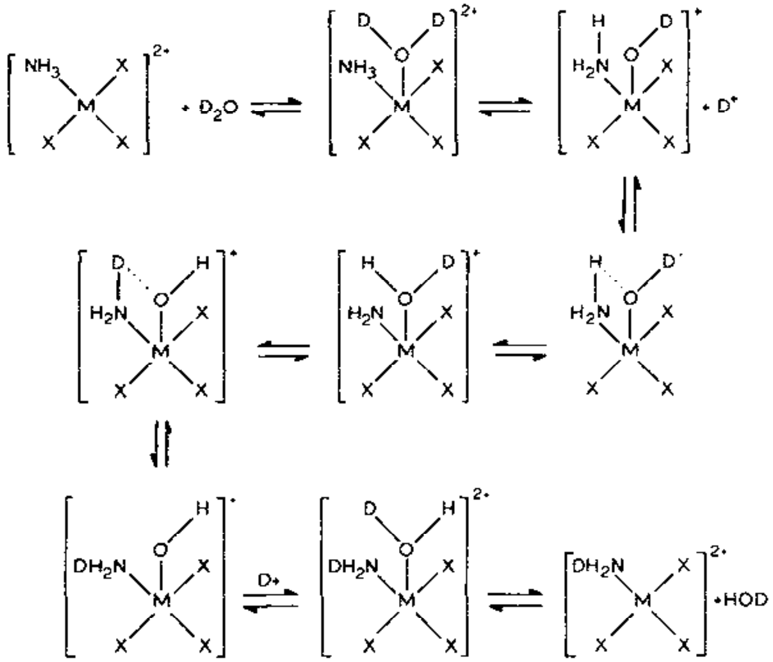
* A referee has suggested that the slower rates of racemisation relative to NH → ND exchange may be due to the incorporation of the N-atom in a ring system. This proposal has yet to be tested using a coordinated *sec*-monoamine system, e.g. $M—NHR_1R_2$.



(21)

misation, and base-assisted substitution [53]. All these reactions, with rates depending on the OH^- concentration, should be considered under the same framework as NH exchange, and the same difficulties in estimating $[OH^-]$ from pH measurements or buffers apply.

Indeed, they all owe their unique characteristics to the fact that the rate of NH exchange can be "tuned" by varying the $[OH^-]$, which in turn can vary over many orders of magnitude. There are some of the above processes that occur so rapidly that even an $[OH^-]$ of 10^{-12} M (pH = 3) is sufficient to provide an effective pathway [51].

Finally, we would urge all those involved in measuring such rate processes to cite the specific parameters used to calculate the appropriate rate constants so that these may be used in meaningful comparisons.

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