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The Application of Secondary Deuterium Isotope Effects to Inorganic Reactions. The Mechanism of the Base Hydrolysis of *cis*-$[CoCl(en)_2py]^{2+}$

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The base hydrolysis of *cis*-$[CoCl(en)_2py]^{2+}$ (py = pyridine) is quite rapid. Initial measurements by Basolo and coworkers [1] gave a value of k_{OH} of *ca.* 1.6 × 10^3 M^{-1} s^{-1} at 25 °C and similar rate constants were obtained for complexes containing the 4-methyl-, 3-methyl- and 4-methoxy-pyridines. Tobe [2] has pointed out that the pyridine complexes "present something of a puzzle" as in aquation; ammonia, primary amines and heterocyclic amines have very similar labilising effects, but in basic solution the heterocyclic ligand labilises the leaving group some 10^2 to 10^3 times more effectively than the other amines. Thus for the complexes *cis*-$[CoCl(en)_2NH_2R]^{2+}$ (R = Me, Et, Pr^n or Bu^n) values of k_{OH} are 12.8 M^{-1} s^{-1} at 25 °C and 0.1 *M* ionic strength [3].

It has been suggested [2] that the heterocyclic nitrogen of pyridine can function as a π-electron pair donor by addition of hydroxide ion at the α-carbon, Fig. 1. Gillard and coworkers [4] have observed such pseudo-base formation in metal complexes of N-heterocyclic ligands. Some doubts have arisen concerning this mechanism as a result of more recent determinations of k_{OH}. Thus Tinner and Marty [5] report k_{OH} = 199 M^{-1} s^{-1} at *I* = 1.0 *M* ($NaClO_4$) and 25 °C and McKenzie and House [6] give k_{OH} = 332 M^{-1} s^{-1} at 25 °C and *I* = 0.1 *M* (NaCl). These rate constants are not markedly different from those of the imidazole [7] and benzimidazole [8] derivatives where k_{OH} = 29 M^{-1} s^{-1} and 220 M^{-1} s^{-1} respectively at 25 °C and *I* = 0.1 *M*. As a result, the prime reason for the initial suggestion of a special mechanism becomes questionable.

It is possible to make use of secondary deuterium isotope effects in an attempt to resolve this problem. The suggested mechanism involves a pre-equilibrium step which is presumed to be more rapid than loss of chloride ion. Thus the experimentally determined rate constant can be expressed as $k_{OH} = kK$ where K = k_1/k_{-1}. If perdeuteropyridine is employed as the heterocyclic ligand, a secondary deuterium kinetic isotope effect will be involved in the pre-equilibrium step, as a change of hybridisation from sp^2 to sp^3 occurs at C-2 of the pyridine ring on formation of the pseudo base. Such isotope effects largely reflect the change in frequency of the out of plane bending mode which accompanies rehybridisation of carbon from sp^2 to sp^3 [9–11]. The secondary deuterium isotope effect should be reflected in the relative k_{OH} values for the protio- and deuteriopyridine complexes. The observation of a secondary deuterium isotope effect would provide strong evidence for the occurrence of the pseudo-base mechanism. For this reason we have investigated the base hydrolysis of *cis*-$[CoCl(en)_2(py)]^{2+}$ and *cis*-$[CoCl(en)_2(d_5py)]^{2+}$.

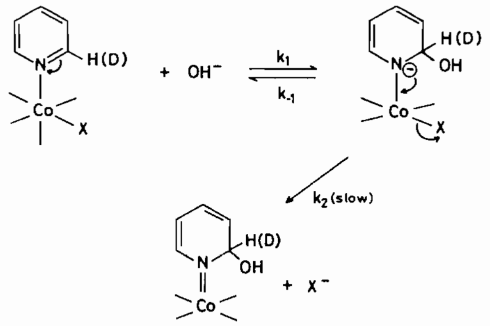


Fig. 1. Pseudo-base mechanism.

Experimental

The complex *cis*-$[CoCl(en)_2(py)](ClO_4)_2$ was prepared as previously described [6] and twice recrystallised from 0.1 *M* HCl by addition of $NaClO_4$. Perdeuteropyridine (d_5py) was purchased from Fluorochem Ltd. The deutero-complex was prepared as described for the protio-derivative. The ^{1}H NMR spectrum of *cis*-$[CoCl(en)_2(d_5py)](ClO_4)_2$ in DMF displayed no resonances attributable to pyridine protons.

The kinetics of base hydrolysis of the complexes were monitored using a Radiometer TTT1 automatic titrator with X10 scale expansion used as a pH-stat. The general experimental technique employed has been previously outlined [12]. A high alkalinity glass electrode type G202B was used as indicator electrode. The electrode system was standardised with NBS phosphate buffer (pH 6.86 at 25 °C) and borate buffer (pH 9.18 at 25 °C).

For each run, a solution of KNO_3 (100 cm^3, 0.1 *M*) was equilibrated at 25 °C and the pH adjusted to 8.70 by addition of 0.01 *M* NaOH. The powdered perchlorate salt (*ca.* 16 mg) was added (solution time *ca.* 10 s) and base consumption recorded, over two half lives. Infinity values (V_∞) were obtained after 10 half lives. The final base consumption data gave a

TABLE I. Hydroxide Ion Uptake at 25 °C and $I = 0.1$ M (KNO_3).

Time (s)	V_t (cm^3)	lnX[a]	10^3 k_{obs}[b] (s^{-1})	Time (s)	V_t (cm^3)	lnX[a]	10^3 k_{obs}[c] (s^{-1})
0	0	–	–	0	0	–	–
30	0.20	0.063	2.11	30	0.20	0.065	2.15
60	0.38	0.124	2.06	60	0.37	0.123	2.04
90	0.56	0.188	2.09	90	0.56	0.192	2.13
120	0.75	0.261	2.17	120	0.74	0.263	2.19
150	0.98	0.358	2.38	165	0.98	0.366	2.21
180	1.07	0.400	2.21	180	1.11	0.426	2.36
210	1.28	0.500	2.37	210	1.23	0.485	2.31
240	1.38	0.550	2.29	240	1.34	0.542	2.26
270	1.51	0.622	2.30	270	1.46	0.609	2.25
300	1.60	0.675	2.25	300	1.58	0.668	2.23
360	1.84	0.831	2.30	360	1.80	0.827	2.29
420	1.99	0.943	2.24	420	2.00	0.981	2.33
480	2.16	1.086	2.26	480	2.12	1.086	2.26
540	2.28	1.202	2.23	540	2.26	1.225	2.27
600	2.42	1.356	2.26	660	2.48	1.492	2.26
660	2.52	1.483	2.25	720	2.60	1.674	2.32
720	2.62	1.628	2.26	780	2.65	1.761	2.25
∞	3.26	–	–	840	2.72	1.897	2.26
				∞	3.20	–	–

[a] $X = (V_\infty - V_o)/(V_\infty - V_t)$. [b] For $[CoCl(en)_2(py)](ClO_4)_2$, mean $k_{obs} = (2.23 \pm 0.09) \times 10^{-3}$ s^{-1}, giving $k_{OH} = (2.23 \times 10^{-3})/(6.54 \times 10^{-6}) = (341 \pm 14)$ M^{-1} s^{-1}. [c] For $[CoCl(en)_2(d_5py)](ClO_4)_2$, mean $k_{obs} = (2.24 \pm 0.08) \times 10^{-3}$ s^{-1}, giving $k_{OH} = (2.24 \times 10^{-3})/(6.54 \times 10^{-6}) = (342 \pm 12)$ M^{-1} s^{-1}. Titrant base 0.01 M, complex concentration *ca.* 3.2×10^{-4} M.

molecular weight of (491 ± 16) for $[CoCl(en)_2(py)](ClO_4)_2$ (Calc. 493.5).

Hydroxide ion concentrations at $I = 0.1$ M were determined from the pH using $pK_w = 13.997$ and a value of 0.774 for the activity coefficient of the hydroxide ion. During each run the pH fluctuated by *ca.* ±0.05 unit from the set mean (pH 8.70) corresponding to a hydroxide ion concentration of $(6.54 \pm 0.7) \times 10^{-6}$ M.

Values of k_{obs}, the observed first order rate constant at constant pH were computed by three methods, (a) a 10–14 point by point calculation, Table I, using the expression $t\ k_{obs} = \ln[(V_\infty - V_o)/(V_\infty - V_t)]$, where V_o and V_t are the volumes of base at time zero and time t respectively, (b) the use of $t½$ and $t3/4$ times (interpolated from a plot of base consumption *vs.* time), using the expressions $k_{obs} = 0.693/t½$ and $k_{obs} = 0.693 \times 2/t3/4$, (c) the slope of a plot of $\ln[(V_\infty - V_o)/(V_\infty - V_t)]$ *vs.* time. In all cases the different methods gave identical rate constants within an assumed experimental error of 5%. The k_{OH} values listed in Table II are the mean values (±the standard deviation) computed by method (a). The second order rate constant $k_{OH} = k_{obs}/[OH^-]$ where $[OH^-] = 6.54 \times 10^{-6}$ M. The main source of error in the measurements is due to the lack of buffering by either solvent or coordinated water at pH 8.70 and this is reflected in the k_{OH} data.

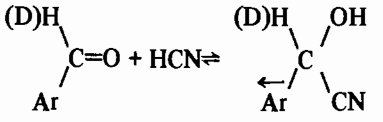
TABLE II. Values of k_{OH} for *cis*-$[CoCl(en)_2(py)]^{2+}$ and *cis*-$[CoCl(en)_2(d_5py)]^{2+}$ at 25 °C and $I = 0.1$ M (KNO_3).[a]

cis-$[CoCl(en)_2(py)]^{2+}$	*cis*-$[CoCl(en)_2(d_5py)]^{2+}$
341 ± 14	342 ± 12
321 ± 6	310 ± 14
329 ± 13	315 ± 16
351 ± 15	345 ± 17
310 ± 14	362 ± 14
347 ± 17	337 ± 17
Mean 333 ± 7	Mean 335 ± 8

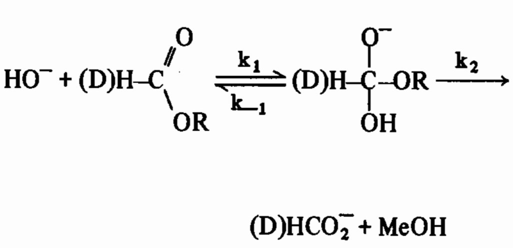
[a] Rate constants evaluated as shown in Table I.

Results and Discussion

The values of k_{OH} determined for the pyridine and deuteropyridine complexes are summarized in Table II. The rate constants are identical within experimental error with $k_{OH} = (334 \pm 8)$ M^{-1} s^{-1} at 25 °C and $I = 0.1$ M (KNO_3). The lack of any observable secondary deuterium isotope effect is consistent with either an S_N1 (CB) mechanism or a pseudo-base mechanism. The isotope effect for the latter occurs in a pre-equilibrium step and as a result could be quite small. For the pseudo-base mechanism (Fig. 1) it can be readily shown that $k_{OH} = k_1k_2/(k_{-1} + k_2)$, so that if $k_2 << k_{-1}$ then $k_{OH} = k_1k_2/k_{-1} = Kk_2$. In the addition of CN^- ion to substituted benzaldehydes (1), values of k_D/k_H varied from 1.15 to 1.20, only slightly lower than the calculated maximal value of 1.21 [13], while k_D/k_H = 1.23 at 25 °C for the hydrolysis and hydrazinolysis of formate esters (2).

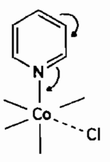


$$\mathrm{(D)H(Ar)C{=}O + HCN \rightleftharpoons (D)H(Ar)C(OH)(CN)} \qquad (1)$$



$$\mathrm{HO^- + (D)H{-}C(=O)OR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (D)H{-}C(O^-)(OH){-}OR \xrightarrow{k_2} (D)HCO_2^- + MeOH} \qquad (2)$$

The present results do not completely exclude the pseudo-base mechanism, but in addition do not provide any positive evidence in its favour. It therefore appears appropriate to consider that the normal $S_N1(CB)$ pathway applies. For chloro-pentamine complexes of the type *cis*-$[CoCl(en)_2NH_2R]^{2+}$ where R = Me, Et, Pr^n, Bu^n the rate constant k_{OH} = 12.8 M^{-1} s^{-1} at 25 °C and I = 0.1 M [3]. Unsaturated heterocyclic amines such as pyridine, imidazole and benzimidazole give values of k_{OH} which can be *ca.* 25 times greater. It is probable that this effect arises due to additional stabilisation of the transition state for halide loss due to electron delocalisation from the aromatic ring as shown in (I).



(I)

This conclusion is supported by the observation of a somewhat lower value of $\Delta H^{\ddagger}$ for the pyridine complex compared with the aliphatic amine complexes [6]. In addition, heterocycles such as imidazole and benzimidazole are susceptible to electrophilic attack [14] rather than nucleophilic attack as occurs with pyridine. For the former heterocycles a pseudo-base mechanism cannot be invoked.

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