Anionopentaaminecobalt(III) Complexes with Polyamine Ligands.
17. Mercury(II)-assisted Aquation Rates of Chloropentaaminecobalt(III) Complexes.
Effect of High Ionic Strength

D. A. HOUSE

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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The second-order rate constants, k_{Hg}, for the Hg^{2+}-assisted aquation of $\Delta\Lambda$-cis-$CoCl(en)_2(imidazole)^{2+}$ have been obtained in HNO_3, $HClO_4$, H_2SO_4 and CF_3CO_2H over the ionic strength (I) range 0.1–3.0 M at 298.2 K. Empirical relationships relating the rate constant, $M^{-1} s^{-1}$, to the ionic strength are: $\log k_{Hg} = 0.261 - 1.56$ ($HClO_4$, I = 0.1–3.0 M); $10^3 k_{Hg} = 56.9I + 21(HNO_3$, I = 0.1–3.0 M); $10^3 k_{Hg} = 23.0$ (CF_3CO_2H, I = 0.3–3.0 M); $10^3 k_{Hg} = 63.6$ (H_2SO_4, I = 0.5–2.0 M). The effect of acidity ($HClO_4$, 0.01–1.0 M) and nitrate ion (0.04–1.0 M) in $HClO_4$ at I = 1.0 M has also been investigated. The rate is independent of $[H^+]$ in the range 0.3–1.0 M $HClO_4$ (I = 1.0, $NaClO_4$) and the effect of $[NO_3^-]$ can be expressed as $\log [NO_3^-] = 45 k_{Hg} - 3.49$.

Introduction

Brønsted's investigation of the rate of the Hg^{2+}-assisted aquation of $CoCl(NH_3)_5^{2+}$ is one of the classic studies on the influence of low ionic strength (I) on a reaction between ions of like charge [1, 2]. The second order rate constants so obtained have been reproduced in many text-books [3] as the well known Livingstone diagram [4] (plot of log k vs. $I^{1/2}$, I < 0.1 M). Since that time, there have been many other investigations of similar reactions [5]. The majority of these studies have been spectrophotometric determinations of the rate constant under pseudo-first-order conditions ($[Hg^{2+}] > 10$ [Co(III)]), often involving the use of high ionic strength (0.2–3.0 M) adjusted by the addition of acid. There is no apparent consensus as to either acid or ionic strength used (although I = 1.0 M, $HClO_4$ is common), and intercomparison of the literature data is difficult.

To facilitate such comparisons, we have measured the Hg^{2+}-assisted aquation rate of $\Delta\Lambda$-cis-$CoCl(en)_2$-(imidazole)$^{2+}$ in $HClO_4$, HNO_3, H_2SO_4 and CF_3-CO_2H over the ionic strength range 0.1–3.0 M at 298.2 K.
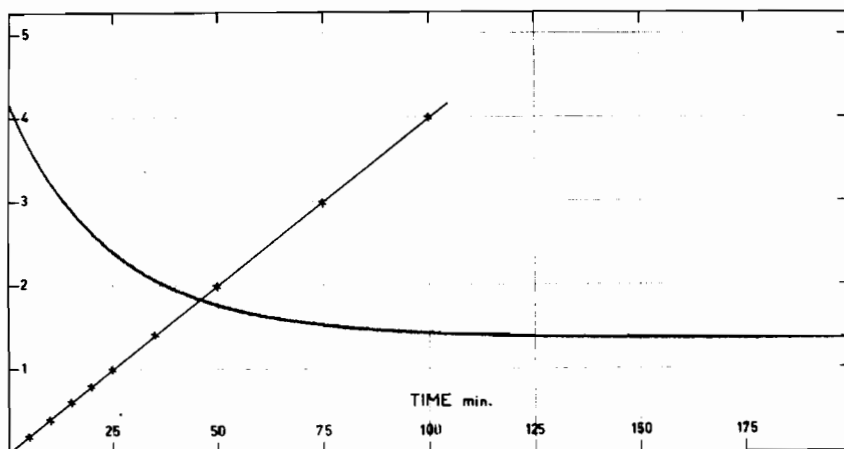

Fig. 1. Absorbance *vs.* time data for reaction (1) together with the $\ln[(A_0 - A_\infty)(A_t - A_\infty)^{-1}]$ *vs.* time plot. Reaction conditions are $[CF_3CO_2H] = 0.04 M$, $[Hg^{2+}]_i = 0.0199 M$, I = 0.10 M, T = 298.2 K, $\lambda = 550$ nm.

         D. A. House

TABLE I. Observed and Calculated Rate Constants for the Hg^{2+}-assisted Aquation of $\Delta\Lambda$-CoCl(en)$_2$(imid)$^{2+}$ in Various Media at 298.2 K.[a]

H^+ M	Hg^{2+}_{total} mM	I M	$10^4\,k_{obs}$ s^{-1}	$10^3\,k_{Hg}$ M^{-1} s^{-1}	$10^3\,k_{Hg}$ (calc.) M^{-1} s^{-1}
		HClO$_4$ (ionic strength variation)			
0.04	18.1	0.094	5.36 ± 0.07	29.6 ± 0.4	29.1[b]
0.27	19.0	0.33	6.21 ± 0.06	32.7 ± 0.3	33.5
0.47	19.4	0.53	6.85 ± 0.12	35.2 ± 0.6	37.8
0.94	20.8	1.00	10.6 ± 0.1	50.9 ± 0.5	50.1
1.81	19.6	1.87	16.6 ± 0.3	84.7 ± 1.5	84.4
2.80	20.0	2.86	31.3 ± 0.3	157 ± 1.5	153
		HNO$_3$ (ionic strength variation)			
0.04	21.0	0.103	5.78 ± 0.1	27.5 ± 0.5	26.9[c]
0.27	21.5	0.33	8.60 ± 0.1	40.0 ± 0.5	39.8
0.47	21.8	0.54	11.7 ± 0.2	53.7 ± 0.9	51.7
0.94	21.8	1.01	16.9 ± 0.3	77.5 ± 1.5	78.4
1.90	21.6	1.96	29.8 ± 0.3	138 ± 1.5	133
2.84	19.8	2.90	36.1 ± 0.5	182 ± 2.5	186
		CF$_3$CO$_2$H (ionic strength variation)			
0.04	19.9	0.10	6.63 ± 0.05	33.3 ± 0.3	
0.28	21.1	0.34	5.04 ± 0.02	23.8 ± 0.1	
0.47	19.5	0.53	4.47 ± 0.04	22.9 ± 0.2	
0.96	22.9	1.03	5.19 ± 0.06	22.7 ± 0.3	
1.89	24.3	1.96	5.33 ± 0.08	21.9 ± 0.3	
2.91	24.6	2.98	5.84 ± 0.08	23.7 ± 0.3	
		H$_2$SO$_4$ (ionic strength variation)			
0.165	21.6	0.56	13.5 ± 0.4	62.5 ± 1.8	
0.336	21.1	1.07	13.5 ± 0.2	64.0 ± 0.9	
0.74	20.7	2.28	13.3 ± 0.4	64.3 ± 1.9	
1.04	20.1	3.18	15.3 ± 0.3	76.1 ± 1.5	
		HClO$_4$ ([H$^+$] variation)			
0.01	20.9	1.0[d]	18.8 ± 0.3	90.0 ± 1.5	
0.12	18.7	1.0[d]	13.3 ± 0.3	71.6 ± 1.6	
0.31	23.8	1.0[d]	12.1 ± 0.1	50.8 ± 0.4	
0.50	19.0	1.0[d]	9.64 ± 0.12	50.7 ± 0.6	
0.94	20.8	1.00	10.6 ± 0.1	50.9 ± 0.5	
		HClO$_4$/HNO$_3$ ([NO$_3^-$] variation)[e]			
0.94	21.8	1.00	16.9 ± 0.3	77.5 ± 1.5	77.5[f]
0.96	25.6	1.04	19.5 ± 0.3	76.1 ± 1.5	75.5
1.00	25.9	1.08	19.0 ± 0.2	73.3 ± 0.8	73.1
1.00	27.0	1.08	19.4 ± 0.1	71.8 ± 0.4	71.5
0.97	26.9	1.05	18.4 ± 0.2	68.4 ± 0.7	68.9
0.97	28.2	1.05	17.5 ± 0.3	62.0 ± 1.1	62.8
0.94	20.8	1.00	10.6 ± 0.1	50.9 ± 0.5	50.4
		HClO$_4$[g] ([Hg^{2+}] variation)			
0.94	20.9	1.00	10.2 ± 0.1	49.2 ± 0.5	

TABLE I. *(continued)*

H^+ M	Hg^{2+}_{total} mM	$HClO_4^g$ ([Hg^{2+}] variation)			
		I M	$10^4 k_{obs}$ s^{-1}	$10^3 k_{Hg}$ $M^{-1} s^{-1}$	$10^3 k_{Hg}$ *(calc.)* $M^{-1} s^{-1}$
0.94	20.9	1.00	10.6 ± 0.2	50.7 ± 0.9	
0.94	20.8	1.00	10.6 ± 0.1	50.9 ± 0.5	
0.94	20.9	1.00	10.8 ± 0.1	51.6 ± 0.5	
0.88	44.7	1.01	22.4 ± 0.2	50.1 ± 0.4	
0.88	44.7	1.01	21.7 ± 0.2	48.5 ± 0.4	
0.88	44.7	1.01	23.7 ± 0.2	53.0 ± 0.4	
0.88	44.7	1.01	23.2 ± 0.2	51.9 ± 0.4	
0.82	64.5	1.01	33.3 ± 0.8	51.6 ± 0.12	

[a] Hg^{2+} added as $Hg(NO_3)_2 \cdot H_2O$. [b] Calculated using equation (2). [c] Calculated using equation (3). [d] Ionic strength adjusted with $NaClO_4 \cdot H_2O$. [e] [NO_3] are 1.0, 0.81, 0.63, 0.54, 0.41, 0.22 and 0.06 M respectively. [f] Calculated using equation (8). [g] Mean value $10^3 k_{Hg} = 50.8 \pm 1.4 M^{-1} s^{-1}$.

Experimental

$\Delta\Lambda$-*cis*-[CoCl(en)$_2$(midazole)] Cl$_2 \cdot \frac{1}{2}$H$_2$O was prepared as described previously [6, 7]. Hg(NO$_3$)$_2 \cdot$ H$_2$O (*ca.* 0.68 g) was dissolved in the appropriate volume of acid, and made up to 100 ml to give [Hg^{2+}]$_i$ *ca.* 0.02 M. The [Hg^{2+}]$_i$ was determined by titration with standard chloride ion using diphenylcarbazole indicator [8]. [H$^+$] was determined by titration with alkali and [NO$_3^-$] was determined spectrophotometrically, $\epsilon_{300nm} = 5.5 M^{-1}$ cm^{-1} [9]. The chloro to aqua conversion of the Co(III) complex was monitored at 550 nm using a Varian Superscan spectrophotometer operating in the fixed wavelength mode. Both sample and reference cells were maintained at 298.2 ± 0.05 K with circulating water. *Ca.* 5 mg of the solid complex was added directly to the 298.2 K acid solution in a 1.00 cm spectrophotometer cell. Solution time, mixing and transference to the spectrophotometer was less than 10 s. The reaction was monitored for 8—10 half-lives and pseudo-first-order rate constants, k_{obs}, were calculated from the expression

$$t k_{obs} = \ln[(A_o - A_\infty)(A_t - A_\infty)^{-1}],$$

where A_o, A_∞ and A_t are the absorbancies at time = 0, infinity and t respectively (Fig. 1). Second-order rate constants, k_{Hg}, were then calculated,

$$k_{Hg} = k_{obs}[Hg^{2+}]^{-1}$$

The mean of 7—12 point-by-point calculations over >3 half-lives was used to determine the cited k_{obs} in Table I.
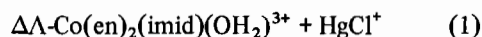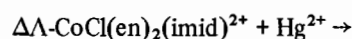
TABLE II. Normalising Factors (R) to Convert k_{Hg} (I = n, HClO$_4$) or k_{Hg} (I = n, HNO$_3$) to k_{Hg} (I = 1.0, HClO$_4$).[a]

I	0.1	0.2	0.3	0.5	1.0	2.0	3.0
R_{HClO_4}	1.71	1.61	1.52	1.35	1.00	0.55	0.30
R_{HNO_3}	1.88	1.55	1.32	1.01	0.65	0.37	0.26

[a] Valid for [Hg^{2+}]$_i$ < 10[H$^+$].

Results

Observed and calculated rate constants for the reaction

$$\Delta\Lambda\text{-CoCl(en)}_2(\text{imid})^{2+} + Hg^{2+} \rightarrow$$

$$\Delta\Lambda\text{-Co(en)}_2(\text{imid})(OH_2)^{3+} + HgCl^+ \quad (1)$$

at 298.2 K in the presence of a variety of acids at variable ionic strength are listed in Table I. The rate law $-d[CoCl(N_5)^{2+}]/dt = k_{Hg}[CoCl(N_5)^{2+}]$-[Hg^{2+}] was verified over a three-fold variation in [Hg^{2+}] at I = 1.0 M, HClO$_4$. The rate is independent of [H$^+$] for 10[H$^+$] > [Hg^{2+}] at constant ionic strength, but at lower [H$^+$] the rate increases with decreasing [H$^+$]. The variation of rate with ionic strength is markedly dependent on the anion of the acid used to provide the [H$^+$]. Empirical relationships relating k_{Hg} to the ionic strength are:

HClO$_4$ (I = 0.1–3.0 M)	$\log k_{Hg} = 0.26I - 1.56$	(2)
HNO$_3$ (I = 0.1–3.0 M)	$10^3 k_{Hg} = 56.9I + 21$	(3)

TABLE III. Thermal and Hg^{2+}-assisted Rate Constants for the Aquation of Some $CoCl(N_5)^{2+}$ Systems at 298.2 K.

No.	Complex	k_{Hg}[a] $M^{-1} s^{-1}$	k_H s^{-1}	Reference[b]
1	$CoCl(NH_3)_5^{2+}$	1.22×10^{-1}	1.77×10^{-6}	20:24
2	$cis\text{-}CoCl(en)_2(NH_3)^{2+}$	1.45×10^{-2}	4.2×10^{-7}	19:25
3	$trans\text{-}CoCl(en)_2(NH_3)^{2+}$	4.64×10^{-3}	2.9×10^{-7}	19:26
4	$cis\text{-}CoCl(en)_2(MeNH_2)^{2+}$	$\underline{2.42 \times 10^{-2}}$	1.6×10^{-7}	18:25
5	$cis\text{-}CoCl(en)_2(EtNH_2)^{2+}$	$\underline{1.45 \times 10^{-2}}$	2.1×10^{-7}	18:25
6	$cis\text{-}CoCl(en)_2(nPrNH_2)^{2+}$	$\underline{1.70 \times 10^{-2}}$	3.1×10^{-7}	18:25
7	$cis\text{-}CoCl(en)_2(iPrNH_2)^{2+}$	$\underline{8.88 \times 10^{-2}}$	1.23×10^{-6}	18:25
8	$cis\text{-}CoCl(en)_2(nBuNH_2)^{2+}$	$\underline{1.98 \times 10^{-2}}$	4.7×10^{-7}	27:25
9	$cis\text{-}CoCl(en)_2(iBuNH_2)^{2+}$	$\underline{1.96 \times 10^{-2}}$	4.5×10^{-7}	27:25
10	$cis\text{-}CoCl(en)_2(sBuNH_2)^{2+}$	$\underline{1.0 \times 10^{-1}}$	4.1×10^{-6}	27:25
11	$cis\text{-}CoCl(tn)_2(NH_3)^{2+}$	1.22×10^{-1}	6.5×10^{-6}	28:28
12	$cis\text{-}CoCl(tn)_2(Me(NH_2))^{2+}$	1.70	4.35×10^{-5}	28:28
13	$cis\text{-}CoCl(tn)_2(EtNH_2)^{2+}$	2.09	4.43×10^{-5}	28:28
14	$cis\text{-}CoCl(tn)_2(nPrNH_2)^{2+}$	2.13	3.67×10^{-5}	28:28
15	$cis\text{-}CoCl(tn)_2(nBuNH_2)^{2+}$	2.06	4.28×10^{-5}	28:28
16	$cis\text{-}CoCl(tn)_2(iBuNH_2)^{2+}$	1.98	3.90×10^{-5}	28:28
17	$cis\text{-}CoCl(tn)_2(BzNH_2)^{2+}$	7.4×10^{-1}	2.90×10^{-5}	28:28
18	$cis\text{-}CoCl(en)_2(py)^{2+}$	1.54×10^{-2}	2.6×10^{-7}	19:25
19	$cis\text{-}CoCl(en)_2(NH_2CH_2CN)^{2+}$	5.39×10^{-4}	5.4×10^{-8}	30:25
20	$cis\text{-}CoCl(en)_2(4Mepy)^{2+}$	$\underline{1.95 \times 10^{-2}}$	2.4×10^{-6}	29:25
21	$cis\text{-}CoCl(en)_2(3Mepy)^{2+}$	$\underline{1.65 \times 10^{-2}}$	1.6×10^{-6}	29:25
22	$cis\text{-}CoCl(en)_2(3,5Me_2py)^{2+}$	$\underline{2.7 \times 10^{-2}}$	7.44×10^{-7}	29:25
23	$cis\text{-}CoCl(en)_2(imid)^{2+}$	$\underline{5.09 \times 10^{-2}}$	5.7×10^{-7}	31:25
24	$sfc\text{-}CoCl(dien)(NH_3)^{2+}$	2.88×10^{-2}	3.16×10^{-7}	22:22
25	$sfc\text{-}CoCl(dien)(en)^{2+}$	4.95×10^{-3}	9.4×10^{-8}	15:32
26	$sfc\text{-}CoCl(dien)(tn)^{2+}$	4.74×10^{-2}	2.16×10^{-7}	21:32
27	$sfc\text{-}CoCl(en)(tri)^{2+}$	$\underline{3.17 \times 10^{-1}}$	3.06×10^{-6}	30:26
28	$mer\text{-}CoCl(dien)(en)^{2+}$	$\underline{5.21 \times 10^{-3}}$	1.78×10^{-7}	15:32
29	$mer\text{-}CoCl(dien)(tn)^{2+}$	2.5×10^{-1}	5.65×10^{-6}	34:32
30	$usf\text{-}CoCl(dien)(NH_3)_2^{2+}$	7.76×10^{-2}	1.92×10^{-6}	22:22
31	$usf\text{-}CoCl(dien)(en)^{2+}$	1.49×10^{-2}	2.56×10^{-7}	15:22
32	$usf\text{-}CoCl(dien)(tn)^{2+}$	1.0×10^{-1}	4.3×10^{-6}	22:32
33	$cis\text{-}CoCl(en)_2(enol)^{2+}$	3.54×10^{-2}	1.7×10^{-6}	35:25
34	$cis\text{-}CoCl(en)_2(pnol)^{2+}$	2.92×10^{-3}	1.0×10^{-6}	36:36

[a]Underlined values have been normalised to I = 1.0 M, $HClO_4$ using the R values in Table II. [b]First reference for k_{Hg}: second reference for k_H.

CF_3CO_2H (I = 0.3–3.0 M) $10^3 k_{Hg} = 23.0$ (4)

H_2SO_4 (I = 0.3–2.0 M) $10^3 k_{Hg} = 63.6$ (5)

These relationships have been used to calculate k_{Hg} (calc.) in Table I.

Most data in the literature for reactions of type (9) have been obtained at I = 1.0 M, $HClO_4$ and we will assume this as our 'standard state'. To convert literature data at other ionic strengths ($HClO_4$) or in other media (HNO_3) we have used the normalising ratios $R_{HClO_4} = k_{Hg}$ (I = 1.0, $HClO_4$)/k_{Hg} (I = n, $HClO_4$)

and $R_{HNO_3} = k_{Hg}$ (I = 1.0, $HClO_4$)/k_{Hg} (I = n, HNO_3) which can be derived from eqns. (2) and (3).

$$\log R_{HClO_4} = 0.26 (1 - I) \qquad (6)$$

$$R_{HNO_3} = [0.42 + 1.13 I]^{-1} \qquad (7)$$

Table II lists the appropriate R values for some selected ionic strengths.

Using HNO_3 plus $HClO_4$ mixtures at constant ionic strength (I = 1.0 M), the effect of [NO_3^-] on the rate can be represented as

$$\log[NO_3^-] = 45k_{Hg} - 3.49 \qquad (8)$$

Perlmutter–Hayman has excellently summarised the present state of the art for primary salt effects in aqueous solution [10]. For reactions between ions of unlike sign, the salt effect is governed by the principle of ionic strength *i.e.*, by some form of the Debye–Huckel–Brønsted–Davies equation [11]. However, reactions between ions of like sign *i.e.*, eqns. (1), (9), do not appear to obey such a relationship. In these cases, the rate is determined by the concentration of the supporting ion of opposite sign and specific salt effects are often apparent. These are precisely the situations observed in the present study. Perchlorate and nitrate show different types of positive salt effects, whereas the effects of trifluoroacetate and sulphate are more in line with a neutral molecule–ion reaction.

Discussion

The control of ionic strength for reactions in solution between charged ions is a well established procedure. In many studies, a series of measurements have been made at low ionic strength, and the data extrapolated to zero ionic concentration. Alternatively, the ionic strength can be kept constant at some large value which does not change during the course of the reaction. This latter method is quite widely used, but for reactions where the rate constant varies with ionic strength, a comparison of data in different media is often difficult.

The kinetics of Hg^{2+}-assisted aquation for many inert halogenopentaamine and tetraamine transition metal complexes have been investigated [5]. The relatively simple stoichiometry

$$MX(N_5)^{2+} + Hg^{2+} \rightarrow M(N_5)(OH_2)^{3+} + HgX^+ \qquad (9)$$
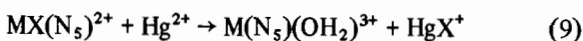
disguises a particularly complex situation [2]. Nevertheless, this reaction has been used in the classical kinetic literature to illustrate 'salt effects' on reaction rates [1, 12].

Among the problems associated with this reaction at low ionic strengths are:

(a) Possible hydrolysis of the Hg^{2+} ion to give $Hg(OH)^+$ at low acidity. This work shows that $[H^+] > 10[Hg^{2+}]$ are necessary to prevent this hydrolysis from affecting the reaction rate.

(b) Possible reaction of HgX_n^{2-n} (X = halide ion, n = 1–4) with the complex. Low concentrations of these species cannot be avoided as they are a product of the reaction. However, the use of halide salts of the complex can only worsen the situation especially when subtle salt effects are being investigated [12]. It has been shown previously that $HgCl^+$ is a better 'catalyst' than Hg^{2+} by a factor of about 2 [13–15].
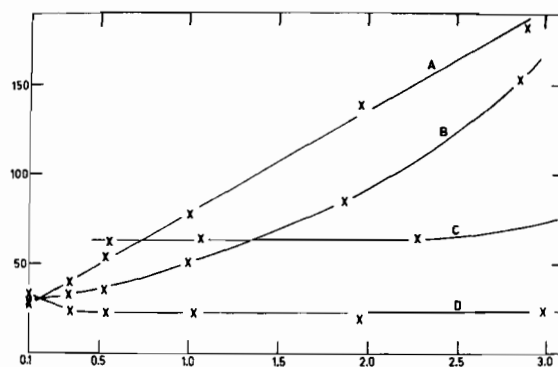

Fig. 2. Plot of $10^3 k_{Hg}$ (up) *vs.* I (across) for reaction (1) in various media. A = HNO_3, B = $HClO_4$, C = H_2SO_4, D = CF_3CO_2H.

At high ionic strength, either controlled by excess acid or added electrolytes, there is the problem of ion pairing with the Co(III) species or complex formation with Hg^{2+}. The current controversy in the literature [16, 17] over the interpretation of product ratios from competition studies involving reaction (9) may well have its origin in these effects.

Our aim in this work has been to establish empirical relationships between the rate of Hg^{2+}-assisted aquation of a chloropentaaminecobalt(III) complex and the ionic strength in various media, in order that intercomparisons of the literature data may be made for structure–reactivity relationships. We assume, for this purpose, and perhaps with some justification (see Table IV), that all $CoCl(N_5)^{2+}$ systems will show similar behaviour in the various media.

$\Delta\Lambda$-*cis*-[CoCl(en)$_2$(imidazole)]Cl$_2 \cdot \frac{1}{2}$H$_2$O was chosen as the Co(III) complex for personal reasons, as well as for several desirable chemical properties:

(a) rapid solubility (<3 s) in all media used,

(b) excellent 'shelf-life' in the solid state,

(c) reasonable absorbance difference at 550 nm between the chloro parent and aqua product,

(d) at 298.2 K and $[Hg^{2+}]_i$ *ca.* 0.02 M, half-lives varied from 3–20 min,

(e) a kinetically 'well-behaved' system.

The data in Table III summarise the literature data for some thirty four $CoCl(N_5)^{2+}$ systems where both the thermal and Hg^{2+}-assisted aquation rates have been determined. In this table, k_{Hg} values have been normalised to I = 1.0 M, $HClO_4$ as the 'standard state' using the R factors in Table II or eqns. (6), (7). Thermal aquation rate constants (k_H) are, fortunately, not particularly sensitive to changes in ionic strength.

The increased rate of chloride release for CoCl-$(N_5)^{2+}$ systems in the presence of Hg^{2+} is believed to be due to the formation of N$_5$CoClHg, with ClHg as a more facile leaving group [18]. As both the

TABLE IV. Comparison of Observed and Calculated Rate Constants, k_{Hg}, for Some $CoCl(N_5)^{2+}$ Systems at 298.2 K.

$CoCl(N_5)^{2+}$	Medium	I M	k_{Hg} (reported) $(M^{-1} s^{-1})$	k_{Hg} (calc.)[a] $(M^{-1} s^{-1})$	Ref.
$CoCl(NH_3)_5^{2+}$	$HClO_4$	0.3	5.7×10^{-2}	8.7×10^{-2}	37
	$HClO_4$	1.0	12.2×10^{-2}		20
cis-$CoCl(en)_2(py)^{2+}$	$HNO_3/NaNO_3$	0.2	0.9×10^{-2}	1.4×10^{-2}	29
	$HClO_4$	1.0	1.5×10^{-2}		19
cis-$CoCl(en)_2(NH_3)^{2+}$	$HClO_4/NaClO_4$	0.2	5.7×10^{-3}	9.2×10^{-3}	18
	$HClO_4$	1.0	14.5×10^{-3}		19
$unsym$-fac-cis-$CoCl(en)(dien)^{2+}$	HNO_3	1.0	3.01×10^{-2}	1.96×10^{-2}	34
	$HClO_4$	1.0	1.49×10^{-2}		15
cis-$CoCl(en)_2(nBuNH_2)^{2+}$	$HClO_4/NaClO_4$	0.2	1.2×10^{-2}	1.9×10^{-2}	27
	$HClO_4/NaClO_4$	0.66	1.8×10^{-2}	2.2×10^{-2}	38

[a]Normalised to I = 1.0 M, $HClO_4$ using equations (7) or (8).

thermal and Hg^{2+}-assisted aquation reactions are thought to proceed via a dissociative mechanism, a common five-coordinate species could be produced. Bifano and Linck [19] have shown for a limited number of systems, that a plot of log k_{Hg} vs. log k_H is linear with a slope of 0.6. Figure 2 shows a similar plot for the entries in Table III. These data give a least-squares slope of 0.96, much closer to the value of 1.0 that is expected if similar five-coordinate species are produced in the two reactions. In fact, the two rate constants are related by the expression

$$\log k_{Hg} = 0.96 \log k_H + 4.36 \ (T = 298.2 \ K) \qquad (10)$$

which can be used to obtain a crude estimate of either one, knowing the other.

Conclusion

This work has shown that for reactions of the type illustrate by eqn. (9), there is probably no back-ground electrolyte in the concentration range 0.1–3.0 M that is free from specific interactions with the reactants. Most of the previous data has been obtained in our presently assumed 'standard conditions' (I = 1.0 M, $HClO_4$) and it is desirable that this should continue. If for solubility limitations [29] or for other reasons, the standard conditions cannot be used then I = 1.0 M, HNO_3 is probably the 'next best' choice. The use of the normalising ratios in Table II gives reasonable (within 30%) agreement for literature data on systems where different ionic strengths or media have been used (Table IV). For studies at low ionic strength it seems desirable to use a total perchlorate medium i.e., $[CoCl(N_5)](ClO_4)_2$, $Hg(ClO_4)_2$, $HClO_4$, but in 1.0
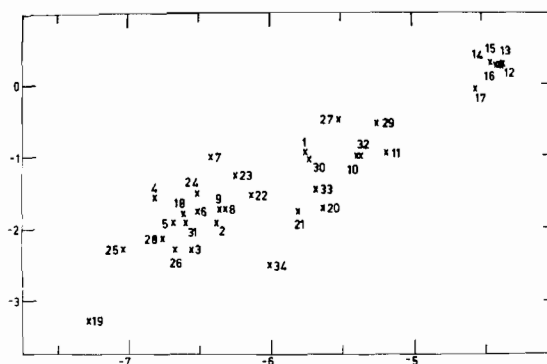
Fig. 3. Plot of log k_{Hg} (up) vs. log k_H (across) for the entries in Table III.

M $HClO_4$, the use of $Hg(NO_3)_2$ and Cl^-, NO_3^- or $ZnCl_4^{2-}$ salts of the complex does not appear to have a marked effect on k_{Hg} (see however, reference 15). In both situations, $[H^+]$ should, if possible, be greater than $10[Hg^{2+}]$ to avoid hydrolysis of the Hg^{2+} ion.

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