The Kinetics of the First Stage of the Acid Hydrolysis of Some *trans*-$MBr_2(N_4)^+$ (M = Co, Cr) Complexes

D. A. HOUSE* and OTHMAN NOR

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

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The spectrophotometrically determined kinetic parameters for the rate of the first stage of the acid hydrolysis (μ = 1.0 M HNO_3) *of* trans-*RR,SS*-$CrBr_2$(*tnentn*)$^+$, trans-*R,S*-$CrBr_2$(*entnen*)$^+$, trans-*RSSR*-$CoBr_2$(*cyclam*)$^+$ *and* trans-*RSSR*-$CrBr_2$(*teta*)$^+$ *are* 10^5k_H (298.2) = 1.02, 4.27, 1.53, 170 s^{-1}; E_a = 94 ± 4, 100 ± 2, 115 ± 2, 74 ± 2 kJ mol^{-1}; *and* $\Delta S^{\#}_{298}$ = −35 ± 8, +1 ± 4, +41 ± 4, −58 ± 4 J K^{-1} mol^{-1}, *respectively. Dissociative mechanisms are proposed for both Cr(III) and Co(III) in these* trans-$MX_2(N_4)^+$ *systems.*

Introduction

We have, for some time, been interested in a comparison of kinetic parameters obtained for analogous halo amine complexes of Co(III) and Cr(III) [1, 2]. Despite dissimilar mechanisms proposed for the thermal aquation reaction for the two systems (dissociative for Co(III) [1, 3] and associative interchange for Cr(III) [1, 3]), there are considerable similarities in kinetic parameters and also some subtle differences [4].

One so far unexplained observation, based on only one or two measurements for Cr(III) is that the bromo/chloro aquation rate ratio for analogous complexes is about 4 for Co(III) [5] and about 15 for Cr(III) [2].

In this paper we report the kinetic parameters for the aquation of several *trans*-$MBr_2(N_4)^+$ (M = Co, Cr) complexes to extend the information available for Cr(III) systems*.

Experimental

The perchlorate salts of the *trans*-dibromocobalt(III) and chromium(III) complexes were prepared from the analogous dichloro compounds (see Table I for literature references).

Caution: Although we have had no difficulty with the perchlorate salts described here, these should be treated as potentially explosive compounds.

TABLE I. Analytical Data for Some *trans*-$[MBr_2(N_4)]ClO_4$ Complexes.

M	λ[a]	N_4	sec-NH Configuration	Empirical Formula	Calcd.			Found			Ref.[b]
					C	H	N	C	H	N	
Cr	570	tnentn	RR,SS	$CrC_8H_{22}N_4Br_2ClO_4$	19.79	4.57	11.54	20.05	5.17	11.17	c
Cr	610	entnen	R,S	$CrC_7H_{20}N_4Br_2ClO_4$	17.83	4.27	11.88	17.91	4.40	11.81	d,e
Co	635	cyclam	RSSR	$CoC_{10}H_{24}N_4Br_2ClO_4$	23.16	4.67	10.80	23.14	4.34	10.69	f
Cr		cyclam[i]	RSSR	$CrC_{10}H_{24}N_4Br_2ClO_4$	23.48	4.73	10.95	24.28	5.15	10.34	g
Cr	544	teta	RSSR	$CrC_{16}H_{36}N_4Br_2ClO_4$	32.26	6.09	9.40	32.22	5.82	9.66	h

[a] Wavelength used to monitor loss of first bromo ligand in acidic solution. [b] Reference to preparation of *trans*-$[MCl_2(N_4)]$-ClO_4. [c] Refs. 9, 11. [d] This research. [e] Ref. 7. [f] Ref. 18. [g] Ref. 8. [h] D. Yang and D. A. House, *Inorg. Chim. Acta Lett.*, *64*, L167 (1982). [i] Lack of solubility in any suitable aqueous acidic media prevented the measurement of kinetic data.

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*Author to whom correspondence should be addressed.

*Abbreviations used: entnen = 2,3,2-tet = $NH_2(CH)_2$-$NH(CH_2)_3NH(CH_2)_2NH_2$; tnentn = 3,2,3-tet = $NH_2(CH_2)_3$-$NH(CH_2)_2NH(CH_2)_3NH_2$; cyclam = 1,4,8,11-tetraazacyclotetradecane; te*ta* = C-*meso*-Me_6cyclam = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. Me_6-[14]-diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, en = $NH_2(CH_2)_2NH_2$, tn = NH_2-$(CH_2)_3NH_2$, DMF = dimethylformamide, DMSO = dimethylsulphoxide.

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trans-$[MCl_2(N_4)]ClO_4$ was suspended in water (10 mL/g) and an equal weight of solid NaOH was added. The solution was warmed to 60 °C and this temperature was maintained (10–15 min) until all the sparingly soluble starting material had dissolved and base hydrolysis was complete. An equal volume of 63% HBr was then added, followed by 60% $HClO_4$ (5 mL/g). Green or yellow-green crystals deposited from the 60° solution, which was then cooled in ice before collecting the product. Analytical data are presented in Table I. These dibromo perchlorate salts are almost insoluble in water but are much more soluble in DMF or DMSO.

Kinetics

The rate of loss of the first bromo ligand from these complexes was followed spectrophotometrically in 1.0 *M* HNO_3 solution. (0.5 *M* H_2SO_4 for *t*-$CoBr_2$-(cyclam)$^+$). A small amount (~20 mg) of the *trans*-dibromo perchlorate salt was placed in a dry 1.00 cm spectrophotometer cell and 4–5 drops of DMF (or 5:1 DMF:DMSO for the cyclam complex) were added to dissolve the solid. HNO_3 (1.0 *M*, 2–2.5 mL) at the desired temperature was then added, and, after mixing, the cell was transferred to a temperature controlled spectrophotometer cell holder. Initial spectral scan studies showed that, in most cases, two sets of isosbestic points developed with time, corresponding to the loss of one, and then two bromo ligands.

By suitable choice of wavelength (Table I), interference from the second slower step could be reduced to a minimum and all kinetic data reported are for the rate of the first spectrophotometric change.

Pseudo-first-order rate constants (k_{obs}) were calculated from the change in absorbance (A) at fixed wavelength with time (t) using the expression

$$t k_{obs} = \ln\left(\frac{A_0 - A_\infty}{A_0 - A_t}\right)$$

where A_0, A_∞ and A_t are the absorbances at t = 0, t = ∞ (6–7 half-lives) and at selected times, t, respectively.

Plots of this function were generally linear for 3–4 half-lives) and point-by-point calculations gave essentially constant (±3%) k_{obs} values over this time range. Reproducibility was of the order of ±5%.

Activation parameters were computer calculated from the variation of k_{obs} with temperature using the standard equations [6].

Control experiments showed that the rate of reaction was independent of the amount of DMF used in these experiments.

Results

Table II presents the spectrophotometrically determined pseudo-first-order rate constants (k_{obs}) for the rate of loss of the first bromo ligand from *trans*-RR,SS-$CrBr_2$(tnentn)$^+$, *trans*-RS-$CrBr_2$(entnen)$^+$, *trans*-RSSR-$CoBr_2$(cyclam)$^+$ and *trans*-RSSR-$CrBr_2$-(teta)$^+$ in 1.0 *M* HNO_3. The corresponding kinetic parameters obtained from the variation of k_{obs} with temperature, along with similar data obtained for analogous systems are presented in Tables III and IV.

Discussion

Several *trans*-$[MBr_2(N_4)]ClO_4$ complexes (Table I) have been prepared from the dichloro complexes by base hydrolysis, acidification and anation of the resulting diaqua with bromide ion in perchlorate ion media.

The entire synthetic procedure outlined in the Experimental Section was repeated, in each case replacing HBr with 12 *M* HCl, to reform the *trans*-$[MCl_2(N_4)]ClO_4$ salts. The infrared spectra of both parent and product were identical indicating that no proton inversion had taken place during the base hydrolysis reaction. Indeed, the close similarity of the i.r. spectra of *trans*-$[MX_2(N_4)]ClO_4$ (M = Co, Cr; X = Cl, Br), for each N_4 tetrad where measurements were made suggests an analogous sec-N–H configuration.

Although kinetic studies have been made [7, 8] using a number of the above *trans*-dichloro complexes, the isomeric configuration of the starting material has not always been established.

A *trans*-MX_2(linear tetraamine)$^+$ can potentially exist in two sec-NH isomeric forms [10], the RR,SS-(N-racemic) and R,S(N-meso). The RR,SS-configuration has now been established for *trans*-CrX_2(tnentn)$^+$ (X = F [9], Cl [10, 11], Br [9]) by resolution and the RS-configuration for *trans*-$[CrX_2(entnen)]ClO_4$ (X = F [12], NCS [13]) by single crystal X-ray methods. Treating *trans*-RS-$[CrF_2(entnen)]ClO_4$ [14] with 12 *M* HCl produces a *trans*-$CrCl_2$(entnen)$^+$ isomer identical to that formed by direct synthesis [7], and thus the entnen complex used in this work and by Kutal and Adamson is believed to have the R,S-configuration. The RR,SS- and R,S-isomers of the corresponding dichloro(linear tetraamine)cobalt(III) complexes have also been distinguished [10, 15, 17].

Isomeric assignments for cyclam and teta (Me_6-cyclam) complexes are less well established. Although there is no direct single crystal X-ray evidence, the more kinetically inert *trans*-$CoCl_2$(cyclam)$^+$ isomer is believed to have the RSSR-configuration, while the kinetically labile form, the RRRR,SSSS-configuration [18]. The *trans*-$CoBr_2$(cyclam)$^+$ complex used in this work was obtained via the *trans*-RSSR-dichloro and the close similarity of the i.r. spectra of all four *trans*-$[MX_2$cyclam)$]ClO_4$ salts (M = Co, Cr; X = Cl, Br) suggests that this configuration is common throughout.

TABLE II. Spectrophotometrically Determined Pseudo-first-order Rate Constants (k_{obs}) for the Loss of the First Bromo Ligand from Some *trans*-$MBr_2(N_4)^+$ Complexes in 1.0 *M* HNO_3.

N_4	M	T		$10^4 k_{obs}$[a] (s^{-1})	$10^4 k_{calc}$[b] (s^{-1})
		°C	K		
R,S-entnen	Cr	40.7	313.9	3.18	3.26
		44.7	317.9	5.45	5.31
		49.1	322.3	9.28	8.93
		51.1	324.3	10.7	11.2
		53.2	326.4	14.9	14.3
		56.3	329.5	19.5	20.3
		58.5	331.7	26.1	25.9
		62.3	335.5	39.3	39.2
RR,SS-tnentn	Cr	50.6	323.8	1.88	2.00
				2.03	
		57.3	330.5	4.19	4.05
				4.08	
		61.7	334.9	6.40	6.34
				6.65	
		62.2	335.4	7.24	6.66
		65.3	338.5	7.62	9.06
				9.02	
RSSR-cyclam[c]	Co	45.2	318.4	3.00	2.94
		49.3	322.5	5.27	5.11
		50.1	323.3	5.57	5.69
		52.6	325.8	7.30	7.91
		55.2	328.4	11.5	11.1
		57.2	330.4	14.4	14.3
				15.2	
		59.6	332.8	17.3	19.4
				18.3	
		62.0	335.2	25.5	26.1
				26.1	
		62.4	335.6	29.0	27.4
				26.8	
		64.6	337.8	37.0	35.9
		64.9	338.1	39.5	37.2
RSSR-teta	Cr	29.8	303.0	28.7	27.2
		34.5	307.7	42.7	42.7
		37.8	311.0	53.5	58.0
		40.7	313.9	80.0	75.5
				77.0	
		43.5	316.7	96.3	97.0
				93.7	
		46.3	319.5	118	124
				114	
				123	
		50.3	323.5	179	175
				185	
				184	

[a] See experimental section for error estimates. [b] Calculated from the activation parameters cited in Tables III and IV. [c] 0.5 *M* H_2SO_4 ($\mu \sim 1.0$ *M*).

We note that in the recently determined crystal structure of *trans*-$Cr(OCONH_2)_2(cyclam)^+$, the cyclam also has the RSSR-configuration [24].

A single crystal X-ray structure [19] of *trans*-$[CrCl(teta)(OH_2)](NO_3)_2$ (an hydrolysis product of the *trans*-dichloro in water) shows this to have the RSSR sec-NH configuration and on this basis we assign the RSSR-configuration to the *trans*-$CrX_2(teta)^+$ (X = Cl, Br) isomers used in these kinetic studies. The assignment of the sec-NH configuration

TABLE III. Activation Parameters for the Acid Hydrolysis of Some *trans*-$CoX_2(N_4)^+$ Dichloro–Dibromo Pairs at 298.2 K.

N	X	k_H (s^{-1})	E_a kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	Ref.
$(en)_2$	Cl	3.2×10^{-5}	110	+59	a
		3.2×10^{-5}	112 ± 2.6	+44 ± 8	b
	Br	1.39×10^{-4}	107	+31	a
		1.50×10^{-4}	98 ± 1.9	+11 ± 6	b
$(tn)_2$	Cl	5.33×10^{-3}	89	+29	c
	Br	9.49×10^{-3}	76	−9	c
R,S-entnen	Cl	1.2×10^{-5}	111 ± 1.5	+39 ± 5	b
		1.5×10^{-5}	102	+4	d
	Br	1.14×10^{-4}	98.6 ± 2.8	+11 ± 9	b
RR,SS-tnentn	Cl	5.44×10^{-5}	105 ± 2	+18 ± 4	e
		5.6×10^{-5}	106 ± 3.1	+29 ± 10	b
	Br	5.41×10^{-4}	98.4 ± 1.6	+23 ± 5	b
RSSR-cyclam	Cl	1.36×10^{-6}	103 ± 2	−20 ± 4	g
	Br	1.53×10^{-5}	115 ± 2	+41 ± 4	f
RSSR(?)-te*ta*	Cl	2.65×10^{-4}	115	+71	h
	Br	3.85×10^{-2}	92	+32	h
(RS)(?)-Me_6-[14]-diene	Cl	3.62×10^{-2}	97	+51	h
	Br	5.10×10^{-2}	98	+57	h

[a] J. A. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta, 11,* 47 (1974), Table IV. [b] Ref. 25. [c] I. R. Jonassan, R. S. Murray, R. D. Stranks and Y. K. Yandell, *Proc. Int. Conf. Coord. Chem., 12,* 32 (1966). [d] Ref. 16. [e] H. G. Hamilton and M. D. Alexander, *Inorg. Chem., 8,* 2131 (1969), data recalculated. [f] This research (1.0 *M* HNO_3). [g] Ref. 18, data recalculated. [h] Ref. 20.

TABLE IV. Activation Parameters for the Acid Hydrolysis of Some *trans*-$CrX_2(N_4)^+$ Dichloro–Dibromo Pairs at 298.2 K.

N	X	k_H (s^{-1})	E_a kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta S^{\#}_{calc}$ [a]	Ref.
$(en)_2$	Cl	2.25×10^{-5}	97	−17	−24	b
	Br	3.26×10^{-4}	94	−4	−5	b
$(tn)_2$	Cl	2.08×10^{-5}	103	+1	−4	c
	Br	3.62×10^{-4}	96	+2	−2	c
RS-entnen	Cl	3.23×10^{-6}	107	0	+5(−18)	d
	Br	4.27×10^{-5}	100 ± 2	+1 ± 4	−8	e
RR,SS-tnentn	Cl	1.06×10^{-6}	95	−50	−11(−15)	f
	Br	1.02×10^{-5}	94 ± 4	−35 ± 8	−13	e
RSSR-cyclam	Cl	2×10^{-8}	116	−8	+2	g
	Br				−18	e
RSSR-te*ta*	Cl	1.26×10^{-5}	93	−37	−23	h
	Br	1.70×10^{-3}	74 ± 2	−58 ± 4	−16	e

[a] Calculated from the relationship: $-\Delta S^{\#}(Cr) = 0.33\Delta S^{\#}(Co) - 5$. Numbers in parenthesis related to the different $\Delta S^{\#}(Co)$ data from Table III. [b] Ref. 2, Table 23. [c] Ref. 4. [d] Ref. 7. [e] This research. [f] Ref. 11. [g] Ref. 8. [h] Table I, footnote h.

in the *trans*-CoX_2(te*ta*)$^+$ isomer used in previous kinetic studies [20, 21] was not made, and the variation in kinetic parameters reported in these two investigations may be due to the use of different isomers.

Although no sec-NH isomeric pairs were used in this research, it is known that the sec-NH configuration is kinetically important in Co(III) complexes of cyclam [18] and entnen [16].

When comparing Br:Cl reactivity trends in analogous Co(III) and Cr(III) complexes, the following patterns emerge:

(i) In every case, the bromo complex aquates more rapidly than the chloro analog.

(ii) With one exception (see below) the activation energy for the dibromo is less than that for the dichloro.

(iii) For Co(III) complexes, $\Delta S^{\#}_{298}$ is more negative (less favourable) for dibromo's than for dichloro's.

(iv) For Cr(III) complexes, $\Delta S^{\#}_{298}$ is more positive (more favourable) for dibromo's than for dichloro's, except for te*ta*.

(v) The dibromo/dichloro rate ratio at 298.2 °K lies between 1.4 and 15 for Co(III) complexes, whereas the corresponding rate ratio lies between 10 and 17 for Cr(III) with te*ta* being an exception in both cases.

One or two of these trends require further comment.

The upper limit of 15 for the dibromo/dichloro rate ratio in the Co(III) systems may be too high as kinetic data for both the *trans*-RR,SS-$CoCl_2$(tnentn)$^+$ and *trans*-RSSR-$CoCl_2$(cyclam)$^+$ systems were obtained at pH = 2 ($\mu = 0.01$ *M*), whereas the data for the dibromo systems were obtained at $\mu = 1.0$ *M*. The effects of such ionic strength changes are difficult to estimate but we would expect a slight negative salt effect [22] which would tend to lower the rate ratio.

The kinetic parameters for the *trans*-RSSR-CoX_2(cyclam)$^+$ (X = Cl, Br) pair do not follow trends (ii) and (iii) and the dichloro is the only Co(III) system cited with a negative entropy of activation. It is possible that the aquation rate parameters may contain some contribution from the base hydrolysis path, because even at pH = 2, k_{obs}(298.2) for this path will be only 16 times slower than the measured "aquation". The corresponding factor at pH = 2, for *trans*-RR,SS-$CoCl_2$(tnentn)$^+$ is 550, which would not be detectable.

Overall, the kinetic parameters for the Co(III) and Cr(III) systems do show different patterns, with both E_a and $\Delta S^{\#}$ being more favourable for the Cr–Br systems, but only E_a being more favourable for the Co–Br cases, and thus a smaller M–Br/M–Cl rate ratio for Co(III).

In terms of mechanism, it is generally accepted that a large positive $\Delta S^{\#}$ is indicative of a dissociative mechanism, but this simplistic picture is often complicated by less well understood factors related to the particular system. A dissociative mechanism is proposed for the thermal aquation of both $CoCl_2(N_4)^+$ and $CoCl(N_5)^{2+}$ systems, but for $CrCl(N_5)^{2+}$ at least, a more associative mechanism is postulated [3, 23]. However, there are suggestions [24] that in some *trans*-$CrCl_2(N_4)^+$ systems, steric crowding would inhibit an associative process and that a dissociative pathway is operating. Support for this suggestion comes from a consideration of $\Delta S^{\#}$(Cr) vs $\Delta S^{\#}$(Co) plots for $MX(N_5)^{2+}$ and *trans*-$MX_2(N_4)^+$ systems (X = singly charged anion). While there is considerable scatter in the data, there appears to be an approximately linear relation for the *trans*-$MX_2(N_4)^+$ series with $-\Delta S^{\#}(Cr) = 0.33\ \Delta S^{\#}(Co) - 5$ (Table IV) and a line of opposite slope $\Delta S^{\#}(Cr) = 1.2\ \Delta S^{\#}(Co)$ for $MX(NH_3)_5^{2+}$ (X = Cl, Br, I, NO_3, NCS) systems. The steric acceleration and parallel Br/Cl rate ratios, observed in the aquation of *trans*-RSSR-MX_2(te*ta*)$^+$ relative to *trans*-RSSR-MX_2(cyclam)$^+$ for both Co(III) and Cr(III) also supports a parallel dissociative mechanism.

Thus we would suggest that for the aquation of *trans*-$MX_2(N_4)^+$ systems (M = Co, Cr), a dissociative mechanism is operating and the major difference between the two metal centers is a more fully developed trigonal bipyramid transition state for Co(III) [11] accounting for the stereochemical changes observed in some of the Co(III) systems [16, 18].

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