Inorganica Chimica Acta

LETTER

Activation volumes for the base hydrolysis of some chloro(diamine)-(triamine)chromium(III) complexes

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(Received April 22, 1991)

The mechanism of base hydrolysis of penta-aminehalochromium(III) complexes has proved to be difficult to establish in terms of the generally accepted SN_1CB mechanism operating for analogous Co(III) complexes [1–4].

Although the reaction is accelerated by base, rate constants for Cr(III) are generally much smaller than those for Co(III) and this has been interpreted in terms of either less acidic protons or a less reactive conjugate base for Cr(III) [5–7]. The recently measured rates of base hydrolysis at ambient pressure of an extensive series of $CrCl(diamine)(triamine)^{2+}$ complexes have been interpreted in terms of the conventional SN_1CB mechanism [8].

We now report the measurement of the activation volumes ($\Delta V^{\ddagger}$) for the base hydrolysis reaction as well as the partial molar volumes ($\bar{V}$) for the cations used. Interpretation of these data, when taken in conjugation with $\Delta V^{\ddagger}$ and $\bar{V}$ for $CrCl(NH_3)_5^{2+}$ and $CrCl(NH_2CH_3)_5^{2+}$ [9], requires some modification of the previous mechanistic proposal [8]. These modifications give a Cr(III) to Co(III) mechanistic comparison that rests more comfortably than the previous direct equivalence.

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Experimental†

Materials

Most of the compounds used were prepared by established procedures [10]. When zinc(II)-free solutions were required, the $ZnCl_4^{2-}$ salts were converted to $NO_3^- \cdot ClO_4^-$ or $(ClO_4^-)_2$ salts by metathesis. **Caution**: perchlorate salts are potentially explosive.

Chloro(diamine)(1,4,8-triazaoctane)chromium(III) tetrachlorozincate(II) salts, [CrCl(AA)(2,3-tri)]-$ZnCl_4$, AA = en, tn

Trichloro(1,4,8-triazaoctane)chromium(III), $[CrCl_3(2,3\text{-tri})]$ was prepared from $CrCl_3 \cdot 6H_2O$ (dehydrated in boiling DMF) and the free base (Aldrich) [11]. This material could not be purified by recrystallisation and was used directly to prepare $[CrCl(AA)(2,3\text{-tri})]ZnCl_4$ (AA = en, tn), following the procedure [10] described to prepare $[CrCl(AA)(dpt)]ZnCl_4$. *Anal.* Calc. for $[CrCl(tn)(2,3\text{-tri})]ZnCl_4 \cdot H_2O$: C, 19.07; H, 5.40; N, 13.90. Found: C, 19.04; H, 5.37; N, 13.87%. $[CrCl(ibn)(dpt)]ZnCl_4$ was similarly prepared from $CrCl_3(dpt)$ and the diamine. *Anal.* Calc. for $[CrCl(ibn)(dpt)]ZnCl_4$: C, 23.37; H, 5.69; N, 13.62. Found: C, 23.40; H, 5.70; N, 13.64%.

Chloro(diamine)(5-methyl-1,5,9-triazanonane)-chromium(III) tetrachlorozincate(II), [CrCl(AA)(Medpt)]$ZnCl_4$, AA = en, tn

Hydrated chromic chloride, $CrCl_3 \cdot 6H_2O$ (17 g) was heated (fumehood) in a stirred solution of DMSO (80 ml) until the temperature of the evolved vapour was 190 °C. The deep purple solution (*c.* 60 ml) was allowed to cool spontaneously to *c.* 170 °C and Medpt (10 ml) was slowly added. A small temperature rise occurred and the colour changed to dark green. Spontaneous cooling was continued and at *c.* 110 °C the diamine (5 ml) was added. A temperature of 110–120 °C was maintained for about 10 min and the colour changed to red–purple. After cooling to about 40 °C, the entire mixture was poured into a solution of $ZnCl_2$ (20 g) in 6 M HCl (300 ml) and left overnight at room temperature.

The crude purple–red product that deposited (5–7 g) was recrystallised from 0.1 M HCl at 60 °C (25 ml/g) by addition of $ZnCl_2$ (2 g/g) and an equal volume of 12 M HCl followed by ice cooling. Several

†Abbreviations used: en = $NH_2(CH_2)_2NH_2$, ibn = $NH_2C(CH_3)_2CH_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, Me_2tn = $NH_2CH_2C(Me)_2CH_2NH_2$, NMetn = $MeNH(CH_2)_3NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, Medpt = $NH_2(CH_2)_3N(Me)(CH_2)_3NH_2$, 2,3-tri = $NH_2(CH_2)_2NH(CH_2)_3NH_2$.

0020-1693/91/$3.50

smaller crops of the crude $ZnCl_4^{2-}$ salt were obtained from the HCl/DMSO mother liquor, but the total yield was never more than 20%. *Anal.* Calc. for [CrCl(en)(Medpt)]$ZnCl_4$: C, 21.62; H, 5.44; N, 14.01. Found: C, 21.31; H, 5.32; N, 13.82%. Calc. for [CrCl(tn)(Medpt)]$ZnCl_4$: C, 23.37; H, 5.69; N, 13.62. Found: C, 23.11; H, 5.57; N, 13.44%.

Instrumentation

Kinetic measurements at ambient pressure were performed in the thermostatted cell compartment of a Varian DMS-100 spectrophotometer [10], a Shimadzu UV-250 spectrophotometer or on a Durrum D110 stopped-flow instrument. Measurements at elevated pressure were performed on a modified Zeiss PMQ II spectrophotometer equipped with a thermostatted high pressure cell [12] or on a home-made high pressure stopped-flow unit [13]. The temperature control on all instruments was ± 0.1 °C and an on-line data acquisition system was employed to analyse the absorbance–time traces [14]. Density measurements were performed by using an Anton Paar DMA02 digital density meter thermostatted at 25 (± 0.003) °C. Triply distilled water and specially cleaned glassware were employed. Densities were measured at a range of concentrations of the complexes, and apparent molar volumes were calculated in the usual way [15].

Results and discussion

The structure of *mer*-CrCl(en)$(dpt)^{2+}$ has been determined by X-ray crystallography [10] to be the conformer shown in Fig. 1. This has the *sec*-NH proton pointing away from the leaving group (Cl^-) and we will assume that this is the configuration adopted for all the *mer*-CrCl(diamine)$(triamine)^{2+}$ complexes described here.

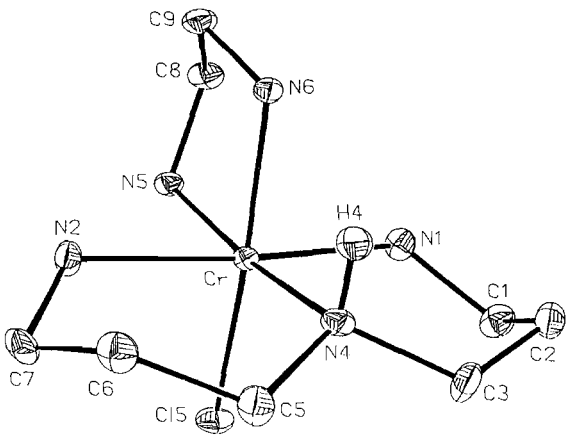


Fig. 1. The configuration of the *mer*-CrCl(en)$(dpt)^{2+}$ cation [10].

Table 1 presents the rate constants for the base hydrolysis kinetics at ambient and elevated pressures for several CrCl(diamine)$(triamine)^{2+}$ complexes. The kinetic parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$) obtained from the variation of k_{OH} with temperature or pressure are given in Table 2.

In general, the rate of base hydrolysis of pentaaminechlorochromium(III) complexes is remarkably insensitive to the nature of the non-replaced ligands, when compared to the Co(III) analogs. A spread of about 4×10^2 for Cr(III) relative to $\sim 10^7$ for Co(III) [16, 17] is observed.

An important feature in the base hydrolysis of pentaaminechlorocobalt(III) complexes is the 'flat *sec*-NH proton' effect [1, 2, 18] where an acceleratory effect of $\sim 10^3$ is observed in the rate when this structural feature is present [18].

The present series contains a system where the effect of this structural feature can be observed for Cr(III). A base hydrolysis rate decrease of about 5 is observed when dpt is replaced by Medpt, indicating only a very small contribution from this influence.

Thus, the direct application of the generally accepted SN_1CB mechanism for Co(III) systems, to the analogous Cr(III) systems requires some imaginative modification [8]. The measurement of the activation volume ($\Delta V^{\ddagger}$) for the base hydrolysis of several of these pentaaminechlorochromium(III) complexes now suggests that the SN_1CB mechanism is not directly applicable to Cr(III) systems.

There is substantial evidence in the literature in support of an associative mechanism for the aquation and photochemical substitution reactions of Cr(III) amine complexes [19]. Volumes of activation for the aquation of a series of complexes of the type $Cr(NH_3)_5L^{3+}$ have an average value of *c.* -6 cm^3 mol^{-1}, which is significantly more negative than the corresponding value of *c.* $+2$ cm^3 mol^{-1} for a similar series of Co(III) complexes and demonstrates the operation of an I_a compared to I_d mechanism [15, 20]. On increasing the steric congestion on the amine ligand, $\Delta V^{\ddagger}$ for the aquation of $Cr(NH_2Me)_5Cl^{2+}$ is $+0.5$ cm^3 mol^{-1} and significantly more positive than the value of -10.6 cm^3 mol^{-1} for the aquation of $Cr(NH_3)_5Cl^{2+}$ [21]. This demonstrates that steric effects may force the aquation mechanism to change from I_a to I_d in such systems. Even in the case of photo-induced aquation reactions of pentaammine complexes of Cr(III), pressure dependence studies have suggested the operation of an I_a mechanism [22–24].

If we consider a general conjugate base hydrolysis scheme, then $\Delta V^{\ddagger}$ can be considered as the sum of two components

TABLE 1. Observed and calculated rate constants for the base hydrolysis of some $CrCl(N_5)^{2+}$ complexes as a function of temperature and pressure

N_5	$[OH^-]$ (M)	μ (M)	T (°C)	P (MPa)	$10^3 \times k_{obs}$ (s^{-1})	$10^2 \times k_{OH}$ [a] ($M^{-1}\ s^{-1}$)	$10^2 \times k_{OH}$(calc.)[b] ($M^{-1}\ s^{-1}$)
(en)(dien)	0.035	0.05	25.0	5	0.866 ± 0.012	2.47 ± 0.03	
				25	0.653 ± 0.036	1.87 ± 0.10	
				50	0.563 ± 0.014	0.61 ± 0.04	
				75	0.466 ± 0.041	1.33 ± 0.12	
				100	0.335 ± 0.016	0.957 ± 0.05	
(en)(Medpt)	0.01	0.05	25.0	0.1	0.215 ± 0.019	2.15 ± 0.19	
	0.02				0.445 ± 0.020	2.23 ± 0.10	
	0.04				0.792 ± 0.030	1.98 ± 0.07	
	0.05				1.13 ± 0.043	2.26 ± 0.09	
	0.05		12.0	0.1	0.185 ± 0.009	0.370 ± 0.02	0.365
			20.0		0.568 ± 0.015	1.14 ± 0.03	1.13
			25.0		1.14 ± 0.004	2.28 ± 0.01	2.21
			30.0		2.33 ± 0.012	4.66 ± 0.02	4.24
	0.1	0.1	13.8	0.1	0.366 ± 0.02	0.336 ± 0.02	0.366
	0.1		19.0		0.951 ± 0.06	0.951 ± 0.06	0.817
	0.04		24.8		0.666 ± 0.05	1.67 ± 0.12	1.94
	0.06		25.2		1.20 ± 0.04	2.00 ± 0.07	2.06
	0.1		26.3		2.85 ± 0.04	2.85 ± 0.04	2.41
	0.04		30.6		1.68 ± 0.01	4.20 ± 0.03	4.45
	0.05	0.05	25.0	5	1.21 ± 0.046	2.42 ± 0.09	
				25	0.870 ± 0.062	1.74 ± 0.12	
				50	0.634 ± 0.025	1.27 ± 0.09	
				75	0.476 ± 0.026	0.952 ± 0.05	
				100	0.375 ± 0.033	0.750 ± 0.07	
(en)(dpt)	0.5	0.5	25.0	5	48.0 ± 3	9.6 ± 0.6	
				25	38.0 ± 5	7.6 ± 1.0	
				50	32.0 ± 4	6.4 ± 0.8	
				75	22.0 ± 4	4.4 ± 0.2	
				100	19.0 ± 0.5	3.8 ± 0.1	
(ibn)(dpt)	0.1	0.5	25.0	0.1	49.0 ± 3	49.0 ± 3	
	0.2				104 ± 12	52.0 ± 6	
	0.3				154 ± 18	51.3 ± 6	
	0.4				202 ± 14	50.5 ± 4	
	0.5				273 ± 23	54.6 ± 5	
	0.5	0.5	10.6	0.1	35 ± 4	7.0 ± 0.8	6.7
			20.0		145 ± 5	29.0 ± 1	26.7
			25.0		272 ± 23	54.4 ± 5	53.7
			30.0		511 ± 20	102 ± 4	106
			36.5		1380 ± 90	276 ± 18	247
	0.5	0.5	25.0	5	273 ± 10	54.6 ± 2.0	
				25	229 ± 10	45.8 ± 2.0	
				50	196 ± 9	39.2 ± 1.8	
				75	134 ± 7	26.8 ± 1.4	
				100	112 ± 7	22.4 ± 1.4	
(tn)(dpt)	0.5	0.5	25.0	5	265 ± 13	53.0 ± 2.6	
				25	226 ± 10	45.2 ± 2.0	
				50	166 ± 4	33.2 ± 0.8	
				75	136 ± 9	27.2 ± 1.8	
				100	99 ± 5	19.8 ± 1.0	
(tn)(Medpt)	0.04	0.1	13.8	0.1	3.15 ± 0.12	7.89 ± 0.3	

[a] $k_{OH} = k_{obs}[OH^-]^{-1}$. [b] Calculated from the activation parameters cited in Table 2.

TABLE 2. Activation parameters for the base hydrolysis of some $CrCl(L_5)^{2+}$ complexes at 298 K[a]

L_5	$10^3 \times k_{OH}$ (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})	Reference
$(NH_3)_5$	1.85[j]	106 ± 0.3	+57 ± 1	+17.0 ± 0.9[g]	b, c
cis-$(en)_2$(DMSO)	5.0	122	+121 ± 4		d
sfac-(en)(dien)	15.6	102	+61 ± 4	+23.3 ± 1.9[h]	d, f
	7.33[g]	104	+60		e
sfac-(dien)$(DMSO)_2$	20.6	100	+58 ± 2		d
mer-(en)(Medpt)	22.1[h]	95.5 ± 3	+76 ± 6	+30.3 ± 1.6	f
	19.9	105 ± 8	+44 ± 16		f
cis-$(tn)_2$(DMSO)	75.3	102	+84 ± 2		d
mer-(pn)(dpt)	96.4	96	+56 ± 4		d
mer-(en)(dpt)	105	97	+48 ± 10	+25.3 ± 1.0[i]	d, f
ufac-(NMetn)(dien)	221	106	+101 ± 2		d
$(MeNH_2)_5$	421[i]	101 ± 0.4	+85 ± 1	+34.8 ± 1.7[g]	b, c
mer-(tn)(Medpt)	~460				f
mer-(ibn)(dpt)	537[i]	102 ± 3	+83 ± 6	+24.0 ± 1.9	f
mer-(Me_2tn)(dpt)	586	82	+26 ± 8		d
mer-(tn)(dpt)	606	106	+105 ± 6	+25.5 ± 1.0[i]	f
mer-(en)(2,3-tri)	735	108	+113 ± 4		d

[a]$\mu = 0.1$ M unless otherwise stated. [b]Ref. 4. [c]Ref. 9. [d]Ref. 8. [e]Ref. 5. [f]This research. [g]$\mu = 1.0$ M. [h]$\mu = 0.05$ M. [i]$\mu = 0.5$ M. [j]$\mu = 0.2$ M.

$$\Delta V^{\ddagger} = \Delta \bar{V}(K) + \Delta V^{\ddagger}(k)$$

$$ML_4(NHR_2)X^{n+} + OH^- \overset{K}{\rightleftharpoons} ML_4(NR_2)X^{(n-1)+} + H_2O$$

$$\downarrow k$$

$$ML_4(NHR_2)(OH)^{(n+m-1)+} \xleftarrow[\text{fast}]{H_2O} ML_4(NR_2)^{(n+m-1)+} + X^{m-}$$

We would not expect $\Delta \bar{V}(K)$ to depend on either the nature of the non-leaving ligand nor the metal center, but mainly on the charge of the complex. For a series of Co(III) complexes [25], it has been shown that $\Delta V^{\ddagger}$ has an average value of +30 cm^3 mol^{-1} for 16 complexes with a 2+ charge. This resulted in a $\Delta V^{\ddagger}(k)$ value of +8 cm^3 mol^{-1} ($\Delta \bar{V}(K) = +22$ cm^3 mol^{-1} [25–27] which is in line with the operation of a dissociative mechanism, i.e. a D(CB) mechanism.

However, in the case of a limited number of pentaammine Cr(III) complexes [9], $\Delta V^{\ddagger}$ was significantly smaller (11–18 cm^3 mol^{-1} less positive) giving negative to small values for $\Delta V^{\ddagger}(k)$ which raised doubt on the nature of the rate determining step. Only in the case of the pentakis(methylamine) complex did the increase in steric hindrance result in a very similar $\Delta V^{\ddagger}(k)$ value for the Cr(III) complex as for the Co(III) complex, indicating the operation of a D(CB) mechanism.

The results of this present study exhibit the same trends as those observed before [9]. The $\Delta V^{\ddagger}$ data for the now studied complexes seem to nicely span the scale between the values for $CrCl(NH_3)_5^{2+}$ and $CrCl(NH_2Me)_5^{2+}$. There is a definite trend in $\Delta V^{\ddagger}$ to more positive values as we increase the steric hindrance/substitution on the chelating ligands, which reflects in a gradual increase in $\Delta V^{\ddagger}$ with increasing $\bar{V}$. If we assume that $\Delta \bar{V}(k)$ for the formation of the conjugate base species remains rather constant for the series of complexes, based on our previous results for many different systems [25–27], then there is a gradual increase in $\Delta V^{\ddagger}(k)$ from −5 to +13 cm^3 mol^{-1} (Table 3). This trend clearly demonstrates a mechanistic changeover from more associative (I_a) to more dissociative (I_d or D) for substitution on the conjugate base species. A type of interchange mechanism (ICB) would be appropriate to account

TABLE 3. Activation volume contributions (cm^3 mol^{-1}) in the base hydrolysis of $CrCl(N_5)^{2+}$ systems

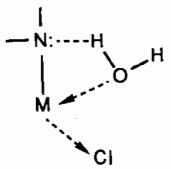
N_5	$\Delta V^{\ddagger}_{obs}$	$\bar{V}^a$	$\Delta V^{\ddagger}(k)^b$
$(NH_3)_5$	+17.0	87.5	−5.0
(en)(dien)	+23.3	152.8	+1.3
(en)(dpt)	+25.3	186.8	+3.3
(ibn)(dpt)	+24.0	206.9	+3.5
(tn)(dpt)	+25.5	233.4	+1.9
(en)(Medpt)	+30.3	239.7	+8.3
$(NH_2CH_3)_5$	+34.8	168.8	+12.8

[a]Calculated from density measurements on the basis that $\bar{V}(ClO_4^-) = 48.6$ cm^3 mol^{-1}. [b]$\Delta V^{\ddagger}(k) = \Delta V^{\ddagger}_{obs} - \Delta \bar{V}(K)$ where $\Delta \bar{V}(K) = +22.0$.

for all the data presently available for base hydrolysis reactions of Cr(III) amine complexes.

The results in Table 3 indicate that the competition between Cr–Cl bond breakage on the conjugate base species and the addition of a solvent molecule is controlled by the nature of the non-leaving ligand. An increase in steric hindrance promotes a dissociative mechanism, making the Cr(III) center very similar to the Co(III) center in the extreme case. This is also seen in the almost two orders of magnitude increase in k_{OH} on going from $CrCl(NH_3)_5^{2+}$ to $CrCl(NH_2Me)_5^{2+}$. In the pentakis(methylamine) complex we are dealing with a very compact coordination sphere (compare $\bar{V}$ for this complex with the others quoted in Table 3) which indicates that the free rotation of the five methyl groups causes steric congestion and induces a dissociative substitution mode. In comparison the (en)(dien) complex has a very similar partial molar volume, but due to its open structure can undergo substitution according to an interchange process.

Finally we would like to comment on the nature of the conjugate species and its reactivity in the case of Co(III) and Cr(III) complexes. It has been suggested that the lone pair of electrons on the amido ligand can form an additional bond with the Co(III) center to cause the dissociation of the leaving group, i.e. Cl^- in the present system [28]. The results of this study suggest that there may be a very specific interaction between the lone pair of electrons and the entering solvent molecule, presumably via hydrogen bonding [29]. This interaction will bring the solvent molecule in the immediate vicinity of the metal center, and depending on the nature of the metal center and steric crowding of the non-participating ligands, control the substitution mechanism. In the case of the Co(III) complexes, bond breakage on the leaving group is followed by bond formation with OH^- which is accompanied by protonation of the amido ligand via the hydrogen bonding effect described above. For the Cr(III) systems there seems to be a fine balance between the ligand packing and ability of the metal center to form a metal–hydroxy bond and to break the bond with the leaving ligand. This process may be visualised as indicated below (M = Co, Cr).



We conclude that steric effects can account for the observed changeover in the substitution behaviour of conjugate base species of Co(III) and Cr(III) amine complexes.

Acknowledgements

We thank the New Zealand Universities Grants Committee for funds to purchase instruments used in this research. Rudi van Eldik gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. K. Bal Reddy appreciates a fellowship from DAAD that enabled him to participate in this study.

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