Kinetic Investigations of the Cleavage of One Hydroxo Bridge in the Tri-μ-hydroxo-bis[triamminechromium(III)] Ion

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The kinetics of the first cleavage step of the trihydroxo-bridged dimer, $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$, was investigated spectrophotometrically at 10.0 and 25.0°C in 1.0 M $NaClO_4$ in the $[H^+]$ range 10^{-11}–10^{-4} M. The initial product is the cis-isomer of the dihydroxo-bridged dimer. The observed pseudo-first-order rate constants vs. $[H^+]$ data were interpreted as three pathways without back-reactions: an acid-catalyzed one involving a μ-H_2O bridge, an uncatalyzed one and a base-catalyzed one involving a μ–O bridge, respectively.

The rate constants and activation parameters for the three pathways are compared with those of other trihydroxo-bridged dimers, and the present bridge cleavage is found to be considerably faster than for the other systems in the investigated $[H^+]$ range. The magnitude of the rate constant for the uncatalyzed bridge cleavage of the present 3+ charged ion is 0.0364(5) s^{-1} at 25.0°C.

The trihydroxo-bridged dimer, $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$, was isolated as a perchlorate salt a few years ago, and the synthesis, crystal structure and magnetic properties are described elsewhere,[1,2] together with the ESR and optical spectra. When this salt is dissolved in water at room temperature, cleavage of one of the hydroxo bridges takes place with a rate comparable to the rate of dissolution. This is in contrast to other trihydroxo-bridged chromium(III) dimers with tridentate amine ligands, such as N,N',N''-trimethyl-1,4,7-triazacyclononane (metacn),[3] 1,5,9-triazadodecane (tacd)[4] and N,N',N''-trimethyl-1,1,1-tris(aminomethyl)ethane (metame),[5] for which bridge cleavage in aqueous neutral solution is considerably slower. The equilibria and kinetics associated with bridge formation and cleavage in mono- and dihydroxo-bridged chromium(III) dimers with $(NH_3)_3$ coordinated facially were described recently,[6,7] and to conclude the series we present here a kinetic investigation of the first step in the bridge cleavage of $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3]^{3+}$.

Experimental

The experimental details are very similar to those given previously.[6,7] The specific conditions for the present kinetic experiments were as follows: 50 μl of a solution containing 100 mg of $[(NH_3)_3Cr(OH)_3Cr(NH_3)_3](ClO_4)_3$ in 1 ml dimethyl sulfoxide (dmso), in which the complex can be kept unchanged for several hours, were added to a 1 cm cell containing 3 ml of thermostatted 1.0 M $NaClO_4$

with the appropriate buffer. Absorbance (A) vs. time (t) data were collected at a fixed wavelength (typically 550 nm) with a Perkin-Elmer Lambda 17 spectrophotometer from ca. 6 s after mixing and for ca. 7 half-lives. After that no trihydroxo-bridged dimer could be detected.

The observed pseudo-first-order rate constants, k_{obs}, were calculated by least-squares refinements to eqn. (1).

$$A(t)_{obs} = (A_0 - A_\infty)\, e^{-k_{obs}t} + A_\infty + at \qquad (1)$$

The last term in eqn. (1) makes allowance for a small linear correction due to a slower cis–trans isomerization of the initial product (see later) and loss of ammonia in the basic solutions. Reliable values of k_{obs} were determined in this way in a $[H^+]$ range from 10^{-11} to 10^{-4} M at 10.0 and 25.0°C, and the results are given in Fig. 1.

The experiments were checked for buffer interference and other possible sources of error as described elsewhere.[6] The small amount of dmso had no influence on the observed rates, as checked by experiments without dmso.

Results

It was previously shown[1,2,6,7] that the initial product in the investigated $[H^+]$ range is the cis-isomer of the dihydroxo-bridged dimer, where cis refers to the positions of the nonbridging coordinated oxygen atoms relative to the $Cr(\mu\text{-}OH)_2Cr$ plane. At $[H^+] = 10^{-5}$ M the rate of cis–trans isomerization of the dihydroxo-bridged dimer equals that of bridge cleavage to the monohydroxo-bridged dimer.[6,7] The preceding bridge cleavage of the trihydroxo-bridged dimer is, however, 30–40 times faster, and at lower $[H^+]$ the cis–trans isomerization is

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still slower. The equilibrium amount of monohydroxo-bridged relative to dihydroxo-bridged species is only a few per cent in the investigated [H$^+$] range. Accordingly the reaction scheme of relevance to k_{obs} is given as Scheme 1.
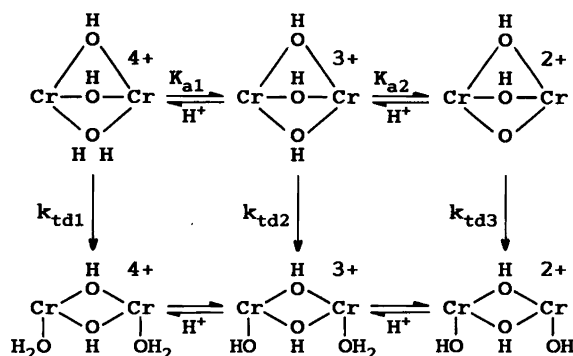
Scheme 1. Reaction scheme for the proposed model for the bridge cleavage showing the symbols used for the rate and equilibrium constants. t = trihydroxo-bridged dimer and d = dihydroxo-bridged dimer.

On the basis of Scheme 1 the expression for the pseudo-first-order rate constant as a function of [H$^+$] is as given in eqn. (2). Inspection of the k_{obs} vs. $-\log$ [H$^+$] data

$$k_{calc} = \frac{k_{td1}K_{a1}^{-1}[H^+] + k_{td2} + k_{td3}K_{a2}[H^+]^{-1}}{K_{a1}^{-1}[H^+] + 1 + K_{a2}[H^+]^{-1}} \qquad (2)$$

shows that the $K_{a1}^{-1}[H^+]$ and $K_{a2}[H^+]^{-1}$ terms in the denominator of eqn. (2) are insignificant compared to unity in the investigated [H$^+$] range. This is not unexpected, as the μ-H$_2$O group in similar compounds is a strong acid and the μ-OH group is a very weak acid (see later). Eqn. (2) is therefore reduced to eqn. (3). Least-

$$k_{calc} = k_{td1}K_{a1}^{-1}[H^+] + k_{td2} + k_{td3}K_{a2}[H^+]^{-1} \qquad (3)$$

squares refinements using eqn. (3) with three parameters gave the values of $k_{td1}K_{a1}^{-1}$, k_{td2} and $k_{td3}K_{a2}$ shown in Table 1 and the curves in Fig. 1.
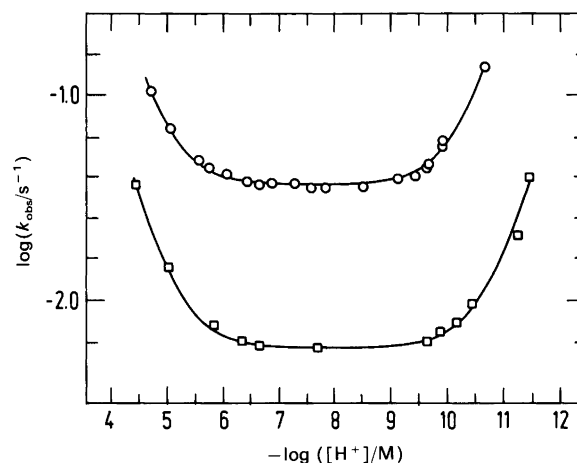

Fig. 1. $\log(k_{obs}/s^{-1})$ vs. $-\log([H^+]/M)$ for the bridge cleavage in 1.0 M NaClO$_4$ at 25.0°C (upper part) and 10.0°C (lower part). The curves through the experimental points are based on eqn. (3) using the constants from Table 1.

Discussion

At [H$^+$] > 10^{-5} M the dominating pathway for the bridge cleavage is the acid-catalyzed one ($k_{td1}K_{a1}^{-1}$). From a comparison with other systems[7,8] one must assume that the aqua bridge is a strong acid, i.e. $K_{a1} > 1$ M, and consequently $k_{td1} > 3 \times 10^3$ s^{-1}. Concerning the enthalpy of activation, the value of $\Delta H^*(k_{td1}) - \Delta H°(K_{a1}) = 64$ kJ mol^{-1} probably represents an upper limit for $\Delta H^*(k_{td1})$, because one would expect the strong acid to have a negative $\Delta H°$. The relatively low enthalpy of activation is characteristic when aqua bridges are involved, these being good leaving groups in substitution reactions: $\Delta H^*(k_{td1}) - \Delta H°(K_{a1}) = 47(8)$ kJ mol^{-1} for the ammine-cobalt(III) analogue,[9] and low values are found also for the acid-catalyzed cleavage of di- and monohydroxo-bridged dimers.[8]

Table 1. The rate constants and activation parameters (ΔH/kJ mol^{-1} and ΔS/J mol^{-1}K^{-1}) referring to Scheme 1 for the present ammine system in 1.0 M NaClO$_4$ at 25.0°C and for other comparable systems.

	[L$_3$M(OH)$_3$ML$_3$]$^{3+}$				
M:	Cr	Cr^a	Co^b	Co^c	Co^c
L$_3$:	(NH$_3$)$_3$	tacd	(NH$_3$)$_3$	dien	tach
Ref.:	This work	4	9	12	13
$k_{td1}K_{a1}^{-1}$/M^{-1} s^{-1}	3.36(9)×10^3		4.22	11.4	260
k_{td2}/s^{-1}	3.64(5)×10^{-2}				
$k_{td3}K_{a2}$/M^{-1} s^{-1}	2.24(4)×10^{-12}	2.02(5)×10^{-13}			
$\Delta H^*(k_{td1}) - \Delta H°(K_{a1})$	64(4)		47(8)		
$\Delta H^*(k_{td2})$	83(6)				
$\Delta H^*(k_{td3}) + \Delta H°(K_{a2})$	138(3)				
$\Delta S^*(k_{td1}) - \Delta S°(K_{a1})$	36(13)		−77(28)		
$\Delta S^*(k_{td2})$	5(19)				
$\Delta S^*(k_{td3}) + \Delta S°(K_{a2})$	−6(10)				

^{a}25.0°C, 0.4 M (Li,H)ClO$_4$. ^{b}25.0°C, 1.0 M (Li,H)ClO$_4$. ^{c}20.0°C, 1.4 M (Li,H)ClO$_4$, dien = diethylenetriamine, tach = cis,cis-1,3,5-cyclohexanetriamine.

At $[H^+] < 6 \times 10^{-11}$ M the dominating pathway for the bridge cleavage is the base-catalyzed one ($k_{td3}K_{a2}$). The hydroxo bridge in the trihydroxo-bridged dimer is a very weak acid; from comparison with similar systems[8] K_{a2} for this dimer is estimated to be less than 10^{-12} M, and accordingly $k_{td3} > 2\,s^{-1}$. The magnitude of $\Delta H^*(k_{td3}) + \Delta H^\circ(K_{a2}) = 138$ kJ mol^{-1} probably represents an upper limit for $\Delta H^*(k_{td3})$, since one would expect the weak acid to have a positive ΔH°.

In neutral solution the present dimer undergoes bridge cleavage to the dihydroxo-bridged dimer with a rate which has not been observed to be as high for other trihydroxo-bridged dimers. After 8–10 half-lives there is no sign of the reactant, so the equilibrium ratio between $[(NH_3)_3Cr(\mu\text{-}OH)_3Cr(NH_3)_3]^{3+}$ and $[(NH_3)_3Cr(\mu\text{-}OH)_2(\mu\text{-}H_3O_2)Cr(NH_3)_3]^{3+}$ can be estimated to be less than ca. 0.01. ($\mu\text{-}H_3O_2$ is the hydrogen-bonded arrangement between a non-bridging hydroxide ligand at one chromium and a water ligand at the other chromium center.[1,6,8,10])

A review including investigations of the bridge cleavage of trihydroxo-bridged dimers was given recently.[8] It refers to the rather few equilibrium and kinetic studies of these compounds with chromium(III), cobalt(III) and rhodium(III). The systems for which cleavage rate constants have been determined are shown for comparison in Table 1. The general observation is that bridge cleavage of the present chromium(III) dimer is considerably faster in the investigated $[H^+]$ range than for the other trihydroxo-bridged dimers. An extreme example of a robust $[L_3Cr(OH)_3CrL_3]^{3+}$ dimer is that with $L_3 = $ metacn, where no bridge cleavage takes place, either in acidic or in basic solution.[3] A major reason for this robustness was suggested to be of a steric nature, ligand–ligand interactions being a hindrance to the formation of the dihydroxo-bridged dimer. Such interactions may also be partly responsible for the relatively high activation energies of the bridge cleavage of trihydroxo-bridged dimers with L_3 representing other tridentate amines: there is no reaction in neutral or acidic solution when L_3 is tacd,[4] and when L_3 is metame the reaction is relatively slow (see below). In the acid- and base-catalyzed pathways the acidities of the aqua and hydroxo bridges are included, but differences in these acidities are hardly sufficient to explain the observed rate differences.

Further aspects. The trihydroxo-bridged chromium(III) dimer with $L_3 = $ metame has appeared an interesting

example of the series. This compound was recently synthesized and characterized structurally, spectroscopically and magnetically by Glerup and Weihe.[5] Preliminary investigations show that this compound has a rate of bridge cleavage which, compared with the ammonia compound, is ca. 10^6 times slower in acidic solution and ca. 10^3 times slower in basic solution. Furthermore, in weakly basic solution at room temperature it is possible, within hours, to establish equilibrium between measurable amounts of the trihydroxo-bridged dimer and the mononuclear amine complex.[11] It is our hope that ongoing investigations of this system will bring further clarification of what is, in some respects, the rather complicated hydrolysis of chromium (III).

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