Polish J. Chem., **78**, 457–462 (2004) **COMMUNICATION**

Kinetics of Nitrito-O Substitution in a Macrocyclic Chromium(III) Complex in Alkaline Media

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Nitrito-O anion is a commonly used ligand in coordination chemistry. There is a number of NO_2^- bonding modes [1], where the terminal η^1 coordination through the N-donor atom results in a strong ligand field, whereas the O-end bonding locates the ligand left to H_2O molecule in the spectrochemical series [2]. Recently, NO_2^- anion gains a new interest, because of importance of NO_3^- reduction in solution [3], nitrito-O bonding by vitamin B_{12} [4] and application of the photochemical intramolecular Cr(III) – ONO process in tetraazamacrocyclic complexes for generation of chromium(IV) and chromium(V) species [5]. It is well known, [6], that ONO^- belongs to such class of ligands, which can be substituted from transition metals complexes also without breaking the metal-ligand bond. However, this mechanism operates in acidic media for the O-bonded nitrito-O, where protonation of the coordinated ligand activates its central atom, making possible a nucleophilic attack on it.

Before [7], we have studied base hydrolysis of several hexamethylcyclam ligands (cyc), where cyc*a* = *meso*-5,5,7,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and cyc*b* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane of the general formula $[Cr(cyc)(OH)X]^+$, with $X^- = NCS^-$, N_3^- and Cl^-. The robustness and stereochemical rigidity of the Cr(cyc) units allowed to examine the monodentate ligand substitution without complication, caused by isomerization or the complex decomposition. The other macrocyclic kinetic effects – among them exceptionally slow outcoming of the X ligand – have been discussed [7].

The aim of this work is to examine kinetics of NO_2^- ligand liberation from the *cis*-$[Cr(cycb)(OH)ONO]^+$ complex. The results obtained in two electrolytes have been presented, because of observed before [7] importance of outersphere interactions in determining values of kinetic parameters and – within a wider hydroxide anion concentration range – also in determining the rate law. A simplified structure of the macrocyclic ligand is shown in Scheme.

Scheme

cyc*b* – ligand

The reactant – a novel complex – was prepared *via* anation of the aquahydroxo reactant according to the reaction (1):

$$cis\text{-}[\mathrm{Cr(cyc}b)(\mathrm{H_2O})(\mathrm{OH})]^{2+} + \mathrm{NO_2^-} \underset{}{\overset{\mathrm{pH} = 5\text{–}6}{\rightleftarrows}} cis\text{-}[\mathrm{Cr(cyc}b)(\mathrm{ONO})(\mathrm{OH})]^{+} + \mathrm{H_2O} \qquad (1)$$

Spectral changes observed during reaction (1) are presented in Figure 1.

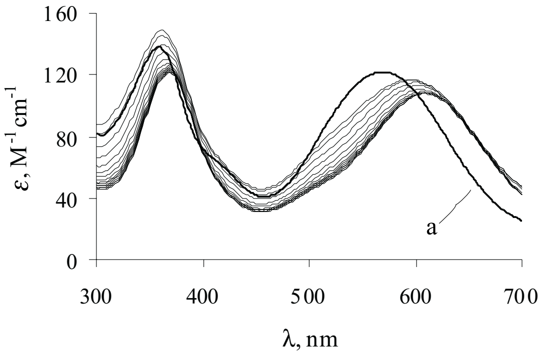

Figure 1. Changes in electronic spectra of *cis*-$[\mathrm{Cr(cyc}b)(\mathrm{H_2O})(\mathrm{OH})]^{2+}$ during anation by $\mathrm{ONO^-}$ ligand, pH = 5–6, T = 298 K, scans taken every 120 s, "a" – spectrum of the starting complex.

The following procedure was applied: About 0.15 $\mathrm{cm^3}$ 1 M NaOH was added to 100 mg of *cis*-$[\mathrm{Cr(cyc}b)(\mathrm{H_2O})_2]\mathrm{Br_3}\cdot 2\mathrm{H_2O}$ [6] dissolved in 10 $\mathrm{cm^3}$ $\mathrm{H_2O}$, colour of the solution changed from red to magenta, due to deprotonation of one of the coordinated $\mathrm{H_2O}$ molecules [8]. Then, about three fold molar excess of $\mathrm{NaNO_2}$ (30 mg) was added. The resulting solution was kept in dark for about half an hour at pH = 5–6, and then was passed through a column (15×2 cm) of cationit, Sephadex SP C-25, $\mathrm{Na^+}$. Elution, at 275 K, with 0.01–0.5 M NaBr in 0.001 M NaOH resulted in separation of the nitrito-O complex from the dihydroxo species. Composition of the complex was established by determination of the molar ratio Cr:NO_2^-. Content of chromium was analysed, using a Varian ABQ-20 ASA spectrometer and NO_2^- was determined iodometrically. The average value of the ratio Cr:NO_2^- was 1:0.96 and was consistent with expected *cis*-$[Cr(cycb)(OH)ONO]^+$ formula. Coordination of nitrito-O ion through the oxygen atom is proposed, basing on position of the lower energy d-d transition band of the complex which is shifted red in comparison with the *cis*-$[Cr(cycb)(H_2O)(OH)]^{2+}$, 592 and 612 nm respectively, what is consistent with a weaker ligand field strength of ONO^- than H_2O molecule. The attempts to transform the *cis*-$[Cr(cycb)(OH)(ONO)]^+$ complex into its conjugate acid (the aqua form) were unsuccessful, because of substitution and the redox decomposition of the NO_2^- ligand.

The OH^- catalysed transformation of the ONO^- complex into the dihydroxo product:

$$cis\text{-}[Cr(cyc\mathit{b})(OH)(ONO)]^+ \xrightarrow{H_2O,\ OH^-} cis\text{-}[Cr(cyc\mathit{b})(OH)_2]^+ \qquad (2)$$

was monitored spectrophotometrically, using a Hewlett Packard HP 89090A diode-array instrument equipped with a Peltier HP 89090A digital temperature controller. A simple reaction course expressed by (2) was proved by chromatographic products analysis. Only one complex was isolated after acidification of the reaction mixture and was identified as the *cis*-$[Cr(cycb)(H_2O)_2]^{3+}$ isomer basing on its spectral data [8]: λ_{max}/nm ($\varepsilon_{max}/M^{-1}\ cm^{-1}$) 529 (169) and 388 (82). Most of the kinetic runs were repeated at least three times. Pseudo-first order rate constants, k_{obs}, were calculated by nonlinear regression analysis. Absorbance-time data were processed up to 4–5 half-lives. The relative error for a single rate constant was about 1% and reproducibility of the runs was characterized by relative standard deviations about 3%. The data obtained at several different wavelengths and at $(1–3)\cdot10^{-3}$ M initial concentrations of the reactant were practically the same. Freshly prepared samples of the chromium complex were used every day.

Kinetic experiments were carried out at $[OH^-] = 0.05–0.5$ M at four temperatures within 289.4–319.2 K at $I = 1.0$ M (Na^+, OH^-, ClO_4^-) or at three temperatures (299.4–319.2 K) using NaBr as the supporting electrolyte. Values of the k_{obs} are collected in Table 1.

A linear dependence of the pseudo-first order rate constants on $[OH^-]$, obtained at ≥ 50-fold excess of $[OH^-]$ over [Cr(III)], is illustrated in Figure 2 for NaBr media. An analogous dependence was found using $NaClO_4$.

Table 1. The pseudo-first order rate constants (k_{obs}) for base hydrolysis of *cis*-[Cr(cyc*b*)(OH)(ONO)]$^+$, I = 1.0 M (NaClO$_4$ or NaBr*).

Temperature, K	[OH$^-$], M	$10^3 \cdot k_{obs}$, s^{-1}	$10^3 \cdot k_{obs}$, s^{-1}*
319.2	0.05	37.1	34.6
	0.10	41.2	36.1
	0.15	45.2	38.2
	0.20	48.0	40.5
	0.30	62.0	43.2
	0.40	70.0	49.1
	0.50	81.0	52.0
309.3	0.05	10.6	9.59
	0.10	11.6	10.7
	0.15	12.8	11.2
	0.20	13.4	11.7
	0.30	15.0	13.0
	0.40	17.3	14.3
	0.50	18.8	15.7
299.3	0.05	2.80	2.97
	0.10	2.97	3.13
	0.15	3.25	3.33
	0.20	3.61	3.52
	0.30	3.92	3.90
	0.40	4.60	4.15
	0.50	5.00	4.55
289.4	0.05	0.77	–
	0.10	0.85	
	0.15	0.93	
	0.20	1.01	
	0.30	1.12	
	0.40	1.31	
	0.50	1.47	

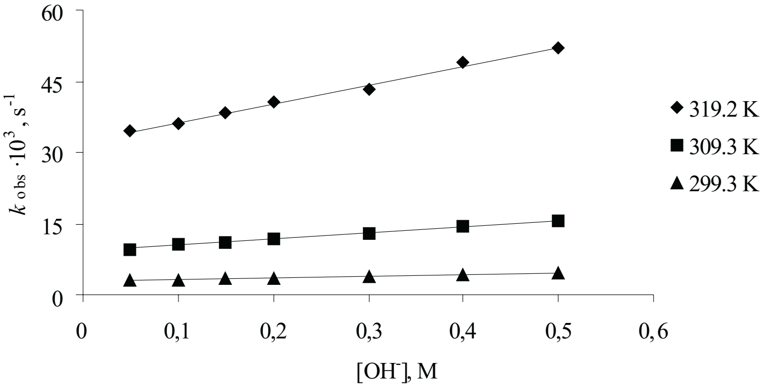

Figure 2. Dependence of the pseudo-first order rate constant on [OH$^-$] for base hydrolysis of *cis*-[Cr(cyc*b*)(OH)(ONO)]$^+$, I = 1.0 M (NaBr).

The results of the linear least-squares fitting of the k_{obs} *vs*. $[OH^-]$ data to

$$k_{obs} = k_o + k_{OH}[OH^-] \tag{3}$$

are summarized in Table 2.

Table 2. Results of the least-squares fitting of k_{obs}-$[OH^-]$ data to eq. (3), $I = 1.0$ M ($NaClO_4$ or NaBr*).

Temperature, K	$10^3\cdot k_{OH}$, $s^{-1}\cdot M^{-1}$	$10^3\cdot k_{OH}$, $s^{-1}\cdot M^{-1}$*	$10^3\cdot k_o$, s^{-1}	$10^3\cdot k_o$, s^{-1}*
319.2	99±4	39.7±1.6	31±1	32.3±0.5
309.3	18.2±0.5	12.9±0.4	9.8±0.2	9.2±0.1
299.3	5.0±0.2	3.5±0.1	2.52±0.05	2.80±0.02
289.4	1.53±0.04	–	0.69±0.01	–

As it is seen (Table 2), (3) is satisfied well for a narrow OH^- concentration range (up to 0.5 M). It is characteristic, that the intercepts are significantly different from zero. In terms of a simple base hydrolysis mechanism model [6,7] the k_o parameter is interpreted as the rate constant for spontaneous aquation of the *cis*-$[Cr(\mathrm{cyc}b)(OH)(ONO)]^+$ complex and the k_{OH} parameter is a composite quantity: $k_1\cdot K$, where K is the equilibrium constant for deprotonation of the amine nitrogen of the macrocyclic ligand and k_1 is the aquation rate constant of the resulting conjugate base.

The activation parameters calculated from k_o and the apparent activation parameters obtained from k_{OH} are given in Table 3.

Table 3. Activation parameters for base hydrolysis (ONO^- substitution) of *cis*-$[Cr(\mathrm{cyc}b)(OH)(ONO)]^+$, $I = 1.0$ M ($NaClO_4$ or NaBr*).

	Data obtained from k_o (eq. 2)	
$\Delta H^{\#}$, $kJ\cdot mol^{-1}$	93.7± 1.7	99.9±2.8*
$\Delta S^{\#}$, $J\cdot mol^{-1}\cdot K^{-1}$	19.1± 5.3	38.8± 8.9*
k_{298}, $s^{-1}\cdot M^{-1}$	$2.4\cdot10^{-3}$	$2.1\cdot10^{-3}$*
	Data obtained from k_{OH} (eq. 2)	
$\Delta H^{\#}$, $kJ\cdot mol^{-1}$	134.4±6.3	91.4±2.1*
$\Delta S^{\#}$, $J\cdot mol^{-1}\cdot K^{-1}$	156.3± 19.8	13.9±6.8*
k_{298}, $s^{-1}\cdot M^{-1}$	$2.6\cdot10^{-3}$	$3.2\cdot10^{-3}$*

Positive values of the activation entropy for the k_o reaction path in the both media (Table 3) are consistent with a dissociative interchange mechanism for spontaneous aquation of the monohydroxocomplex. Three terms in $\Delta S^{\#}$ can be distinguished: one reflecting the ligand dissociation in the activated complex and the two others, describing differences in the solvation and the outersphere interactions between the activated complex and the reactant. The second and the third terms are negative, because liberation of ONO^- ligand leads to electric charge separation, causing an increase of solvation and the outersphere interactions with counter-ions. Thus, the obtained positive values of the $\Delta S^{\#}$ results from a high positive value of the first term. Mechanism of the

k_{OH} reaction path cannot be deduced, basing on the obtained activation parameters, because of the mentioned before composite character of the k_{OH} and also due to large errors in $\Delta S^{\#}$. Comparing the results obtained for NaBr and $NaClO_4$ media at 298 K (Table 3) one can evaluate the magnitude of the specific kinetic salt effect. For OH^- independent reaction path (k_o), the rate is slightly (~15%) faster in perchlorates than in bromides, due to the lower activation enthalpy. On the other hand, for the OH^- dependent path, the specific kinetic effect is opposite and k_{298} in NaBr solution is *ca* 25% higher than in $NaClO_4$ solution also, because of the more favourable (apparent) enthalpy of activation.

Remarkable are large differences in the $\Delta H^{\#}$ (and in $\Delta S^{\#}$) values, obtained from the k_{OH} parameter between the two media in spite of very close the $\Delta G^{\#}$ values – a characteristic compensation effect. For that reason the observed specific kinetic salt effect is small at 298 K, but substantially increases at higher temperatures.

Comparing the results of this work with those published before [7], it is seen that the rate of base hydrolysis for a series of $[Cr(cyc)(OH)X]^-$ type complexes increases for the monodentate ligands as follows:

$$NCS^- < N_3^- < ONO^- << Cl^-$$

what correlates with their decreasing ligand field strength. This correlation is quite frequently obeyed for ligand substitution in Cr(III) or Co(III) complexes [6]. Within a narrow concentration range of hydroxide anion, arbitrary taken up to 0.5 M, the two parameters rate aquation (3) can be applied. The outersphere interaction between the cationic reactant and the anion of the „inert electrolyte" causes the specific kinetic salt effect, affecting the both parameters of (3), but larger differences are observed for the k_{OH}, especially at higher temperatures (Table 2) – up to 150% at 319 K.

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