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Reduction of Pentaamminenitrocobalt(III) by Hexaaquachromium(II) Ion. Reinvestigation of the Mechanism

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Abstract

Products of the reduction of $[\mathrm{CoNO_2(NH_3)_5}]^{2+}$ by Cr^{2+} were separated and identified under the conditions of $[\mathrm{Cr}^{2+}]_0/[\mathrm{Co(III)}]_0 \leqslant 3$ and $0.02\ \mathrm{M} \leqslant [\mathrm{H}^+] \leqslant 0.75\ \mathrm{M}$. The product distribution was dependent on both $[\mathrm{Cr}^{2+}]_0$ and $[\mathrm{H}^+]$. The following mechanism is proposed:

$$[\mathrm{CoNO_2(NH_3)_5}]^{2+} + \mathrm{Cr}^{2+} \longrightarrow \mathrm{Co}^{2+} + [\mathrm{CrONO(H_2O)_5}]^{2+} \tag{i}$$

$$[\mathrm{CrONO(H_2O)_5}]^{2+} + \mathrm{H}^+ \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{HNO_2} \tag{ii}$$

$$[\mathrm{CrONO(H_2O)_5}]^{2+} + \mathrm{Cr}^{2+} \longrightarrow \mathrm{Cr(IV)} + [\mathrm{CrNO(H_2O)_5}]^{2+} \tag{iii}$$

$$\mathrm{Cr(IV)} + \mathrm{Cr}^{2+} \longrightarrow [\mathrm{(H_2O)_4Cr(OH)_2Cr(H_2O)_4}]^{4+} \tag{iv}$$

$$\mathrm{HNO_2} + 2\mathrm{Cr}^{2+} \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + [\mathrm{CrNO(H_2O)_5}]^{2+} \tag{v}$$

Introduction

Electron-transfer reactions of the type $[\mathrm{Co^{III}X(NH_3)_5}]^{n+}$ with hexaaquachromium(II) ions (Cr^{2+}) have been studied extensively. In some cases a chemical mechanism has been found, in which an electron is trapped in X before the electron is transferred to cobalt(III) [1]. In the reduction of $[\mathrm{CoNO_2(NH_3)_5}]^{2+}$ by Cr^{2+} a ligand reduction to NO was suggested with a formation of $[\mathrm{CrNO(H_2O)_5}]^{2+}$ (CrNO^{2+}) [2]. The stoichiometry of this reaction has been found to be [Cr(II)] : [Co(III)] = 3:1. Later the following mechanism was suggested [3]:

$$[\mathrm{Co^{III}NO_2(NH_3)_5}]^{2+} + \mathrm{Cr}^{2+} \xrightarrow{\mathrm{H^+}} \mathrm{Co}^{2+} + [\mathrm{Cr^{III}ONO(H_2O)_5}]^{2+} + 5\mathrm{NH_4}^+ \tag{1}$$

$$[\mathrm{Cr^{III}ONO(H_2O)_5}]^{2+} + \mathrm{Cr}^{2+} \longrightarrow [\mathrm{Cr(H_2O)_6}]^{3+} + [\mathrm{Cr^{III}NO_2(H_2O)_5}]^{+} \tag{2}$$

$$[\mathrm{Cr^{III}NO_2(H_2O)_5}]^{+} + \mathrm{Cr}^{2+} \longrightarrow [\mathrm{CrNO(H_2O)_5}]^{2+} + [\mathrm{Cr(H_2O)_6}]^{3+} \tag{3}$$

In this mechanism the nitro group is reduced to the nitrosyl group without a release of nitrite ion from the metal center. Matts and Moore [4] have demonstrated that the aquation of $[\mathrm{CrONO(H_2O)_5}]^{2+}$ (CrONO^{2+}) is very fast in acidic solutions. If the aquation of CrONO^{2+} competed with the reduction by Cr^{2+}, free nitrite ion would be detected. It has been reported that Cr^{2+} reduces $\mathrm{NO_3}^-$ to $\mathrm{NO_2}^-$ with a formation of $[\mathrm{(H_2O)_4Cr(OH)_2Cr(H_2O)_4}]^{4+}$ ($\mathrm{Cr(OH)_2Cr}^{4+}$) via a Cr(IV) intermediate [5, 6]. A formation of the dimer, $\mathrm{Cr(OH)_2Cr}^{4+}$, is a characteristic of the $2\mathrm{e}^-$ reduction by Cr^{2+}. We have found that $\mathrm{Cr(OH)_2Cr}^{4+}$ is also produced in the reduction of $[\mathrm{CoNO_2(NH_3)_5}]^{2+}$ by Cr^{2+} and that a free nitrite ion is detected under certain conditions. Therefore, the above mechanism should be reinvestigated. In this paper we report on the product analyses of this reaction and propose a new mechanism.

Experimental

Materials

$[\mathrm{CoNO_2(NH_3)_5}](\mathrm{ClO_4})_2$ and $[\mathrm{CrONO(NH_3)_5}](\mathrm{ClO_4})_2$ were prepared according to the literature method [7]. A solution of hexaaquachromium(III) perchlorate was prepared by the reduction of chromium trioxide in perchloric acid with hydrogen peroxide. Chromium(II) perchlorate solutions were prepared by a Zn/Hg reduction in a nitrogen atmosphere. The concentrations of the hydrogen ions in chromium(III) and chromium(II) solutions were determined by the method in the literature [8, 9]. The remaining chemicals used were the purest commercial products.

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Product Analyses

Solutions containing a cobalt(III) complex were added to an optical cell, which was sealed with a serum cap. After the solution had been purged with nitrogen gas for 20 min, the reaction was initiated by the addition of the chromium(II) solution containing $HClO_4$ and $NaClO_4$ by means of a syringe. The reaction was completed within 5 s under the present experimental conditions ($[Cr^{2+}]_0/[Co(III)]_0 \leqslant 3$ at room temperature). The solution was diluted ten times with water and poured onto an SP-Sephadex C-25 column (H^+ form). HNO_2 was passed through the column by washing with water when Cr^{2+} was used in less than three times excess over Co(III). HNO_2 was identified and analyzed spectrophotometrically [10]. Five species were adsorbed on the column. The first reddish-brown and the second pink species were eluted with a 0.1 M $HClO_4$ solution and identified as $CrNO^{2+}$ and Co^{2+}, respectively. $CrNO^{2+}$ moved faster than Co^{2+} on the column, but these could not be separated completely with a 0.1 M $HClO_4$ solution. Therefore, these were collected together for the analyses of the contents of chromium and cobalt. The third yellow-brown species was completely separated from $CrNO^{2+}$ and Co^{2+} with a 0.1 M $HClO_4$ solution and finally eluted out with a 0.1 M $HClO_4$–0.2 M $NaClO_4$ solution. It was identified as $[CoNO_2(NH_3)_5]^{2+}$. The fourth blue-violet species was eluted with a 0.1 M $HClO_4$–0.4 M $NaClO_4$ solution and identified as $[Cr(H_2O)_6]^{3+}$-(Cr^{3+}). The final green band was further separated into two bands with a 0.1 M $HClO_4$–0.6 M $NaClO_4$ solution. These are $Cr(OH)_2Cr^{4+}$ and/or $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$. However these were collected together for the analysis.

The chromium content was determined spectrophotometrically in the form of CrO_4^{2-} after oxidation with an alkaline hydrogen peroxide solution. For the solution of $CrNO^{2+}$ containing Co^{2+}, cobalt oxide was removed by filtration. The cobalt(II) content was determined by Kitson's method [11]. The chromium(III) species did not interfere in the analysis of the cobalt(II) species. The cobalt(III) complex was reduced to cobalt(II) with Zn/Hg.

Absorption spectra were recorded on a Hitachi 200-20 spectrophotometer.

Results and Discussion

It is known that $CrNO^{2+}$ reacts slowly with Cr^{2+} to form a dimeric species which contains a hydroxyamino group [12]. Therefore, the product analyses were carried out at $[Cr^{2+}]_0/[Co(III)]_0 \leqslant 3$. The results are summarized in Table I. When Cr^{2+} reacted with $[CoNO_2(NH_3)_5]^{2+}$ in the ratio of $[Cr^{2+}]_0/[Co(III)]_0 = 3$, almost of all the Co(III) ions were consumed and HNO_2 was not detected. Moreover excess of Cr^{2+} ions was not detected, because the spectrum was not changed by the introduction of air after the reaction was completed. If an excess of Cr^{2+} remained, Cr^{2+} should be converted to $Cr(OH)_2Cr^{4+}$ by O_2 [13]. In agreement with earlier work, we found that the reactions are consumed in the ratio 3Cr(II) to 1Co(III).

TABLE I. Product Analyses of the Reduction of $[CoNO_2(NH_3)_5]^{2+}$ by Cr^{2+} at $\mu = 1$ M ($HClO_4$–$NaClO_4$) and at Room Temperature

$[Cr^{2+}]_0$ × 10^3 (M)	$[Co(III)]_0$ × 10^3 (M)	$[H^+]$ (M)	$[CrNO^{2+}]$ × 10^3 (M)	$[Cr^{3+}]$ × 10^3 (M)	$[Cr(OH)_2Cr^{4+}]$ × 10^3 (M)	$[Co^{2+}]$ × 10^3 (M)	[Co(III)] × 10^3 (M)	$[HNO_2]$[a] × 10^3(M)
8.63	6.53	0.021	3.01	1.08	2.23	3.80	2.71	⩾0.89
8.63	8.20	0.13	1.65	4.11	1.27	4.93	2.84	⩾3.1
6.53	6.53	0.20	1.31	2.85	1.13	4.00	2.20	⩾1.9
6.53[b]	6.53	0.20	1.87	4.01	0.22	3.01	3.55	–[c]
8.63	8.35	0.25	1.49	6.25	0.80	5.52	2.37	–[c]
8.63	8.28	0.38	1.36	4.98	0.56	5.27	3.04	⩾4.7
8.63	8.32	0.50	0.99	6.60	0.40	5.49	2.74	–[c]
8.63	8.38	0.62	1.01	6.80	0.24	6.59	2.05	–[c]
17.3	8.47	0.13	3.86	4.14	4.50	7.40	1.13	–[c]
17.3	8.29	0.26	4.73	5.83	3.55	7.85	0.24	–[c]
17.3	8.30	0.48	5.83	7.30	1.92	6.73	1.05	–[c]
17.3	8.38	0.75	4.56	9.64	1.09	7.10	1.24	–[c]
3.45	8.34	0.25	0.51	2.31	0.31	2.83	5.01	–[c]
8.63	14.0	0.25	1.13	5.59	0.62	5.03	8.29	–[c]
13.8	7.94	0.25	2.49	6.37	2.00	6.62	0.23	–[c]
20.7	8.38	0.25	5.66	5.76	3.90	6.73	0.48	–[c]
24.6	8.20	0.25	8.06	3.37	6.74	8.10	0.08	0[d]

[a] Minimum values, some were lost as an HNO_2 gas during the solution was bubbled with a nitrogen gas. [b] In the presence of 6.53×10^{-3} M sodium nitrite. [c] Not determined. [d] Not detected.

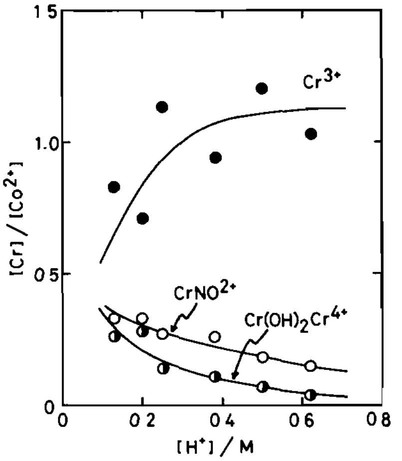


Fig. 1. Plots of $[Cr]/[Co^{2+}]$ vs. $[H^+]$ at $[Cr^{2+}]_0/[Co(III)]_0 \simeq 1$. (○) $CrNO^{2+}$, (●) Cr^{3+}; (◑) $Cr(OH)_2Cr^{4+}$.

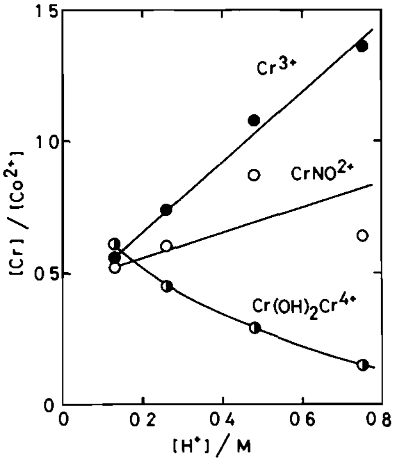


Fig. 2. Plots of $[Cr]/[Co^{2+}]$ vs. $[H^+]$ at $[Cr^{2+}]_0/[Co(III)]_0 \simeq 2$. (○) $CrNO^{2+}$; (●) Cr^{3+}, (◑) $Cr(OH)_2Cr^{4+}$.

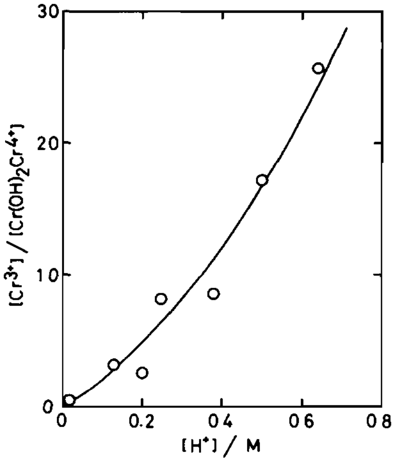


Fig. 3. Plot of $[Cr^{3+}]/[Cr(OH)_2Cr^{4+}]$ vs. $[H^+]$ at $[Cr^{2+}]_0/[Co(III)]_0 \simeq 1$.

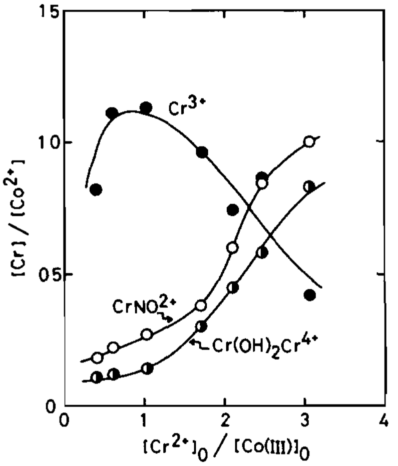


Fig. 4. Plots of $[Cr]/[Co^{2+}]$ vs. $[Cr^{2+}]_0/[Co(III)]_0$ at $[H^+]$ = 0.25 M. (○) $CrNO^{2+}$, (●) Cr^{3+}; (◑) $Cr(OH)_2Cr^{4+}$.

Hydrogen ion dependences of the product distribution ($[Cr]/[Co^{2+}]$) are shown in Fig. 1 ($[Cr^{2+}]_0/[Co(III)]_0 \simeq 1$) and in Fig. 2 ($[Cr^{2+}]_0/[Co(III)]_0 \simeq 2$). When $[Cr^{2+}]_0/[Co(III)]_0 \simeq 1$, $[CrNO^{2+}]$ and $[Cr(OH)_2Cr^{4+}]$ decrease with an increase in $[H^+]$, while $[Cr^{3+}]$ increases and reaches to ~1. This suggests that $CrNO^{2+}$ and $Cr(OH)_2Cr^{4+}$ are produced through a different path from that for Cr^{3+}; the latter path must be dependent on $[H^+]$. When $[Cr^{2+}]_0/[Co(III)]_0$ increases to 2, $[CrNO^{2+}]$ increases with an increase in $[H^+]$ in contrast with $Cr(OH)_2Cr^{4+}$. This means that an additional path, dependent on both $[H^+]$ and $[Cr^{2+}]_0$, produces Cr^{3+} and $CrNO^{2+}$. When $[Cr^{2+}]_0/[Co(III)]_0 \sim 1$, HNO_2 was always detected. Therefore, it is suggested that HNO_2 is released which reacts with Cr^{2+} to generate Cr^{3+} and $CrNO^{2+}$. The second-order rate constant of the reduction of HNO_2 by Cr^{2+} to form Cr^{3+} and $CrNO^{2+}$ has been reported to be 4.5×10^3 M^{-1} s^{-1} at 25 °C and $\mu = 1$ and is independent of $[H^+]$ [6]. The aquation of $CrONO^{2+}$ in acidic solutions is fast and the rate constant at 25 °C and $\mu = 1$ is k $(s^{-1}) = 2.0[H^+] + 4.6[H^+]^2$ [4]. Therefore, HNO_2 must be produced through the aquation of $CrONO^{2+}$ formed by the Cr^{2+} reduction of $[CoNO_2(NH_3)_5]^{2+}$. This is also supported by the result that a quadratic curve with a zero intercept is obtained when $[Cr^{3+}]/[Cr(OH)_2Cr^{4+}]$ is plotted against $[H^+]$ as shown in Fig. 3 ($[Cr^{3+}]/[Cr(OH)_2Cr^{4+}] = 18[H^+] + 32[H^+]^2$). Figure 4 shows the $[Cr^{2+}]_0$ dependence of the product distribution at $[H^+] = 0.25$ M. $[Cr(OH)_2Cr^{4+}]$ and $[CrNO^{2+}]$ increase with an increase in $[Cr^{2+}]_0$, while $[Cr^{3+}]$ decreases. This suggests that $Cr(OH)_2Cr^{4+}$ and $CrNO^{2+}$ are produced in a $[Cr^{2+}]_0$-dependent path. It is known that the reactions of Cr^{2+} with HNO_3, Tl(III) and O_2 produced $Cr(OH)_2Cr^{4+}$ via a Cr(IV) intermediate [5, 6, 13–15]. In the present system, therefore, the Cr(IV) intermediate must be contained. From the above results the following mechanism is suggested:

$$[Co^{III}NO_2(NH_3)_5]^{2+} + Cr^{2+} \longrightarrow Co^{2+} + CrONO^{2+} \quad (4)$$

$$CrONO^{2+} + H^+ \longrightarrow Cr^{3+} + HNO_2 \quad (5)$$

$$CrONO^{2+} + Cr^{2+} \longrightarrow Cr(IV) + CrNO^{2+} \quad (6)$$

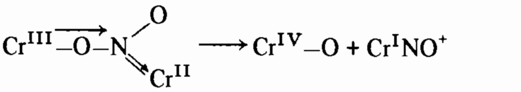
$$Cr(IV) + Cr^{2+} \xrightarrow{\text{fast}} Cr(OH)_2Cr^{4+} \quad (7)$$

$$HNO_2 + Cr^{2+} \longrightarrow Cr^{3+} + NO \quad (8)$$

$$NO + Cr^{2+} \xrightarrow{\text{fast}} CrNO^{2+} \quad (9)$$

This mechanism contains the inner-sphere electron transfer through a NO_2 bridge followed by competition of the aquation of $CrONO^{2+}$ with the inner-sphere type reduction by Cr^{2+}. The first step is the same as that proposed previously [3]. Fraser [3] investigated this reaction over the $[H^+]$ range between 0.2 M and 0.6 M and at $[Cr^{2+}]_0/[Co(III)]_0 \leqslant 3$, but did not take acccount of the rapid aquation of $CrONO^{2+}$. In the presence of an equimolar amount of HNO_2 to Co(III), $[Co^{2+}]$ decreased compared with that in the absence of HNO_2 (see Table I), indicating that the rate of reaction (4) is comparable with that of reaction (8).

It has been reported that the formulation Cr^I-NO^+ is more feasible than $Cr^{III}NO^-$ for the oxidation state of $CrNO^{2+}$ [2, 16]. In the formation of Cr(IV) and $CrNO^{2+}$, therefore, the following $2e^-$ reduction may be contained:



$$Cr^{III}\!-\!O\!-\!N(\!=\!O)\!-\!Cr^{II} \longrightarrow Cr^{IV}\!-\!O + Cr^INO^+ \quad (10)$$

When a solid sample of $[CrONO(NH_3)_5](ClO_4)_2$ was dissolved in a Cr^{2+} solution at $[H^+] = 0.02$ M and $[Cr^{2+}]_0/[Cr(III)]_0 = 1$ in nitrogen gas, $[CrH_2O(NH_3)_5]^{3+}$, $CrNO^{2+}$ and Cr^{3+} were detected. There was no evidence for the formation of $Cr(OH)_2Cr^{4+}$. This shows that a rapid aquation of $[CrONO(NH_3)_5]^{2+}$ occurred and that this is followed by the reduction of HNO_2 by Cr^{2+}. This may arise from the fact that the aquation of $[CrONO(NH_3)_5]^{2+}$ is faster than that of $CrONO^{2+}$ [4].

It is interesting to make a comparison with pentaamminenitratocobalt(III), $[CoNO_3(NH_3)_5]^{2+}$, whose system has been examined by Swaddle [5]. Thirty-three percent of the reaction proceeds through the reduction of the central cobalt(III) ion to the cobalt(II) ion with a formation of $[CrNO_3(H_2O)_5]^{2+}$-($CrNO_3{}^{2+}$) when $[Cr^{2+}]_0/[Co(III)]_0 = 1$. The remaining sixty-seven percent of the reaction proceeds through the reduction of the coordinated nitrato ligand to generate $Cr(OH)_2Cr^{4+}$ as one of the products. The reaction of $CrNO_3{}^{2+}$ with Cr^{2+} also proceeds through the reduction of the coordinated nitrato ligand to generate $Cr(OH)_2Cr^{4+}$, Cr^{3+} and $CrNO^{2+}$. The aquation of $CrNO_3{}^{2+}$ is sufficiently slow for the reduction by Cr^{2+} to go to completion [5].

In conclusion, the $2e^-$ reduction step is contained in the reductions by Cr^{2+} of $CrONO^{2+}$, $CrNO_3{}^{2+}$, $[CoNO_3(NH_3)_5]^{2+}$ and HNO_3, but not in those of $[CoNO_2(NH_3)_5]^{2+}$ and HNO_2.

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