

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

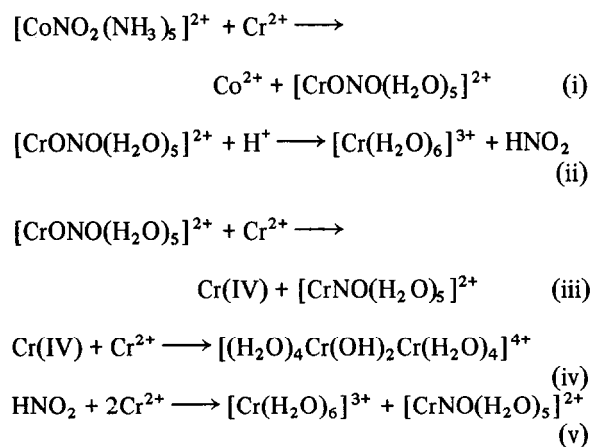
KEIICHI TSUKAHARA

Department of Chemistry, Faculty of Science, Shimane University, Matsue 690, Japan

(Received January 31, 1986; revised May 14, 1986)

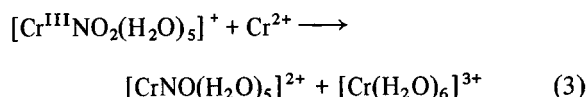
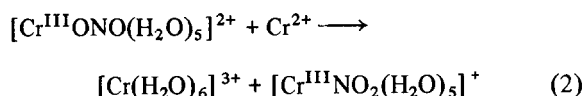
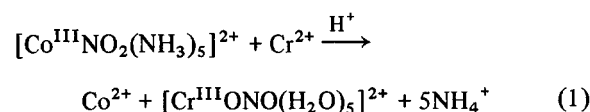
Abstract

Products of the reduction of $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$ by Cr^{2+} were separated and identified under the conditions of $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \leq 3$ and $0.02 \text{ M} \leq [\text{H}^+] \leq 0.75 \text{ M}$. The product distribution was dependent on both $[\text{Cr}^{2+}]_0$ and $[\text{H}^+]$. The following mechanism is proposed:



Introduction

Electron-transfer reactions of the type $[\text{Co}^{\text{III}}\text{X}(\text{NH}_3)_5]^{n+}$ 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 $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$ by Cr^{2+} a ligand reduction to NO was suggested with a formation of $[\text{CrNO}(\text{H}_2\text{O})_5]^{2+}$ (CrNO^{2+}) [2]. The stoichiometry of this reaction has been found to be $[\text{Cr(II)}]:[\text{Co(III)}] = 3:1$. Later the following mechanism was suggested [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 $[\text{CrONO}(\text{H}_2\text{O})_5]^{2+}$ (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 NO_3^- to NO_2^- with a formation of $[(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$ ($\text{Cr}(\text{OH})_2\text{Cr}^{4+}$) via a Cr(IV) intermediate [5, 6]. A formation of the dimer, $\text{Cr}(\text{OH})_2\text{Cr}^{4+}$, is a characteristic of the $2e^-$ reduction by Cr^{2+} . We have found that $\text{Cr}(\text{OH})_2\text{Cr}^{4+}$ is also produced in the reduction of $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$ 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

$[\text{CoNO}_2(\text{NH}_3)_5](\text{ClO}_4)_2$ and $[\text{CrONO}(\text{NH}_3)_5](\text{ClO}_4)_2$ 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.

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 ($[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \leq 3$ 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 $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$. The fourth blue-violet species was eluted with a 0.1 M HClO_4 –0.4 M NaClO_4 solution and identified as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (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 $\text{Cr}(\text{OH})_2\text{Cr}^{4+}$ and/or $[(\text{H}_2\text{O})_5\text{CrO}(\text{Cr}(\text{H}_2\text{O})_5)]^{4+}$. However these were collected together for the analysis.

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 hydroxylamino group [12]. Therefore, the product analyses were carried out at $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \leq 3$. The results are summarized in Table I. When Cr^{2+} reacted with $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$ in the ratio of $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 = 3$, 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 $\text{Cr}(\text{OH})_2\text{Cr}^{4+}$ by O_2 [13]. In agreement with earlier work, we found that the reactions are consumed in the ratio 3 Cr(II) to 1 Co(III) .

TABLE I. Product Analyses of the Reduction of $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$ by Cr^{2+} at $\mu = 1$ M (HClO_4 – NaClO_4) and at Room Temperature

$[\text{Cr}^{2+}]_0$ $\times 10^3$ (M)	$[\text{Co(III)}]_0$ $\times 10^3$ (M)	$[\text{H}^+]$ (M)	$[\text{CrNO}^{2+}]$ $\times 10^3$ (M)	$[\text{Cr}^{3+}]$ $\times 10^3$ (M)	$[\text{Cr}(\text{OH})_2\text{Cr}^{4+}]$ $\times 10^3$ (M)	$[\text{Co}^{2+}]$ $\times 10^3$ (M)	$[\text{Co(III)}]$ $\times 10^3$ (M)	$[\text{HNO}_2]^a$ $\times 10^3$ (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

^aMinimum values, some were lost as an HNO_2 gas during the solution was bubbled with a nitrogen gas. ^bIn the presence of 6.53×10^{-3} M sodium nitrite. ^cNot determined. ^dNot detected.

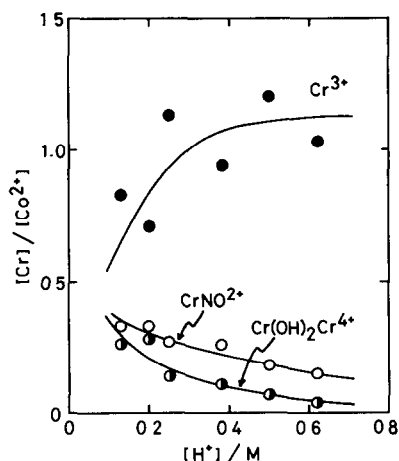


Fig. 1. Plots of $[\text{Cr}]/[\text{Co}^{2+}]$ vs. $[\text{H}^+]$ at $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \approx 1$. (○) CrNO_2^{2+} , (●) Cr^{3+} , (◐) $\text{Cr(OH)}_2\text{Cr}^{4+}$.

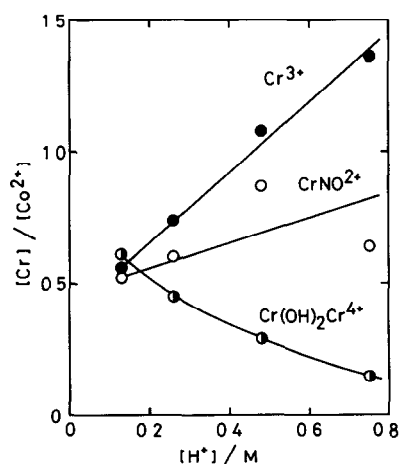


Fig. 2. Plots of $[\text{Cr}]/[\text{Co}^{2+}]$ vs. $[\text{H}^+]$ at $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \approx 2$. (○) CrNO_2^{2+} , (●) Cr^{3+} , (◐) $\text{Cr(OH)}_2\text{Cr}^{4+}$.

Hydrogen ion dependences of the product distribution ($[\text{Cr}]/[\text{Co}^{2+}]$) are shown in Fig. 1 ($[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \approx 1$) and in Fig. 2 ($[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \approx 2$). When $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \approx 1$, $[\text{CrNO}_2^{2+}]$ and $[\text{Cr(OH)}_2\text{Cr}^{4+}]$ decrease with an increase in $[\text{H}^+]$, while $[\text{Cr}^{3+}]$ increases and reaches to ~ 1 . This suggests that CrNO_2^{2+} and $\text{Cr(OH)}_2\text{Cr}^{4+}$ are produced through a different path from that for Cr^{3+} ; the latter path must be dependent on $[\text{H}^+]$. When $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0$ increases to 2, $[\text{CrNO}_2^{2+}]$ increases with an increase in $[\text{H}^+]$ in contrast with $\text{Cr(OH)}_2\text{Cr}^{4+}$. This means that an additional path, dependent on both $[\text{H}^+]$ and $[\text{Cr}^{2+}]_0$, produces Cr^{3+} and CrNO_2^{2+} . When $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \sim 1$, 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^{2+} . The second-order rate constant of the reduction of HNO_2 by Cr^{2+} to form Cr^{3+} and CrNO_2^{2+} has been reported

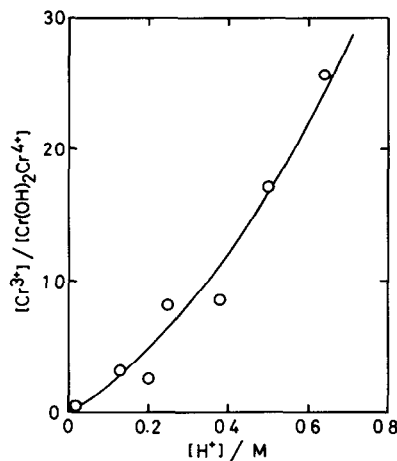


Fig. 3. Plot of $[\text{Cr}^{3+}]/[\text{Cr(OH)}_2\text{Cr}^{4+}]$ vs. $[\text{H}^+]$ at $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \approx 1$.

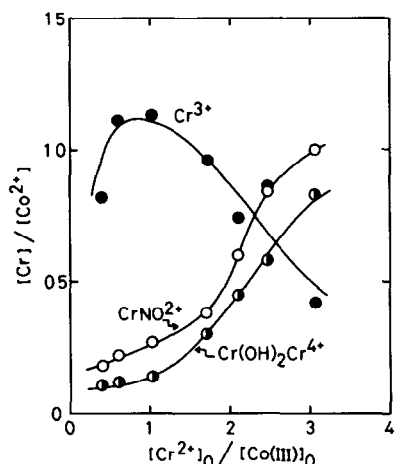
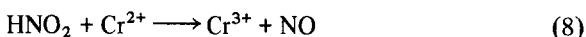
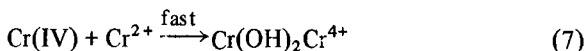
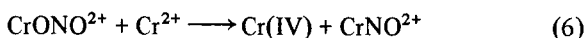
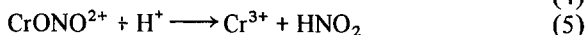
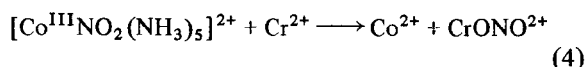


Fig. 4. Plots of $[\text{Cr}]/[\text{Co}^{2+}]$ vs. $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0$ at $[\text{H}^+] = 0.25 \text{ M}$. (○) CrNO_2^{2+} , (●) Cr^{3+} , (◐) $\text{Cr(OH)}_2\text{Cr}^{4+}$.

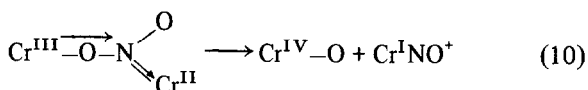
to be $4.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and $\mu = 1$ and is independent of $[\text{H}^+]$ [6]. The aquation of CrONO_2^{2+} in acidic solutions is fast and the rate constant at 25°C and $\mu = 1$ is $k (\text{s}^{-1}) = 2.0[\text{H}^+] + 4.6[\text{H}^+]^2$ [4]. Therefore, HNO_2 must be produced through the aquation of CrONO_2^{2+} formed by the Cr^{2+} reduction of $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$. This is also supported by the result that a quadratic curve with a zero intercept is obtained when $[\text{Cr}^{3+}]/[\text{Cr(OH)}_2\text{Cr}^{4+}]$ is plotted against $[\text{H}^+]$ as shown in Fig. 3 ($[\text{Cr}^{3+}]/[\text{Cr(OH)}_2\text{Cr}^{4+}] = 18[\text{H}^+] + 32[\text{H}^+]^2$). Figure 4 shows the $[\text{Cr}^{2+}]_0$ dependence of the product distribution at $[\text{H}^+] = 0.25 \text{ M}$. $[\text{Cr(OH)}_2\text{Cr}^{4+}]$ and $[\text{CrNO}_2^{2+}]$ increase with an increase in $[\text{Cr}^{2+}]_0$, while $[\text{Cr}^{3+}]$ decreases. This suggests that $\text{Cr(OH)}_2\text{Cr}^{4+}$ and CrNO_2^{2+} are produced in a $[\text{Cr}^{2+}]_0$ -dependent path. It is known that the reactions of Cr^{2+} with HNO_3 , Ti(III) and O_2 produced $\text{Cr(OH)}_2\text{Cr}^{4+}$ 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:



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 $[\text{H}^+]$ range between 0.2 M and 0.6 M and at $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 \leq 3$, but did not take account of the rapid aquation of CrONO^{2+} . In the presence of an equimolar amount of HNO_2 to Co(III) , $[\text{Co}^{2+}]$ 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 $\text{Cr}^{\text{I}}\text{NO}^+$ is more feasible than $\text{Cr}^{\text{III}}\text{NO}^-$ 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:



When a solid sample of $[\text{CrONO}(\text{NH}_3)_5](\text{ClO}_4)_2$ was dissolved in a Cr^{2+} solution at $[\text{H}^+] = 0.02$ M and $[\text{Cr}^{2+}]_0/[\text{Cr(III)}]_0 = 1$ in nitrogen gas, $[\text{CrH}_2\text{O}(\text{NH}_3)_5]^{3+}$, CrNO^{2+} and Cr^{3+} were detected. There was no evidence for the formation of $\text{Cr(OH)}_2\text{Cr}^{4+}$. This shows that a rapid aquation of $[\text{CrONO}(\text{NH}_3)_5]^{2+}$ 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 $[\text{CrONO}(\text{NH}_3)_5]^{2+}$ is faster than that of CrONO^{2+} [4].

It is interesting to make a comparison with pentaamminenitratocobalt(III), $[\text{CoNO}_3(\text{NH}_3)_5]^{2+}$, 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 $[\text{CrNO}_3(\text{H}_2\text{O})_5]^{2+}$ (CrNO_3^{2+}) when $[\text{Cr}^{2+}]_0/[\text{Co(III)}]_0 = 1$. The remaining sixty-seven percent of the reaction proceeds through the reduction of the coordinated nitrate ligand to generate $\text{Cr(OH)}_2\text{Cr}^{4+}$ as one of the products. The reaction of CrNO_3^{2+} with Cr^{2+} also proceeds through the reduction of the coordinated nitrate ligand to generate $\text{Cr(OH)}_2\text{Cr}^{4+}$, 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+} , $[\text{CoNO}_3(\text{NH}_3)_5]^{2+}$ and HNO_3 , but not in those of $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$ and HNO_2 .

Acknowledgement

The author would like to thank Ms. Junko Uesako for her experimental assistance.

References

- 1 E. S. Gould, *Acc. Chem. Res.*, **18**, 22 (1985) and refs. therein.
- 2 W. P. Griffith, *J. Chem. Soc.*, 3286 (1963).
- 3 R. T. M. Fraser, *J. Chem. Soc.*, 3641 (1965).
- 4 T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1997 (1969).
- 5 T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).
- 6 H. Ogino, K. Tsukahara and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **47**, 308 (1974).
- 7 M. Linhard, H. Siebert and M. Weigel, *Z. Anorg. Allg. Chem.*, **278**, 287 (1955).
- 8 E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).
- 9 K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).
- 10 C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 2440 (1958).
- 11 R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).
- 12 J. N. Armor and M. Buchbinder, *Inorg. Chem.*, **12**, 1086 (1973).
- 13 R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).
- 14 M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).
- 15 R. M. Sellers and M. G. Simic, *J. Chem. Soc., Chem. Commun.*, 401 (1975).
- 16 I. Bernal, S. D. Robinson, L. S. Meriwether and G. Wilkinson, *Chem. Commun.*, 571 (1965).