The Kinetics and Mechanisms of the Reactions of Nitric and Nitrous Acids with Hexaaquochromium(II) Ions

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Stoichiometric and kinetic investigations of reactions of the nitric and nitrous acids with hexaaquochromium(II) ions have been carried out in acidic media. The stoichiometries of these reactions found in this work were consistent with the mechanisms proposed by Swaddle,[1] in which one mole of nitric acid reacts with four moles of chromium(II) and one mole of nitrous acid reacts with two moles of chromium(II). For the former reaction, it was found that the two-electron reduction of nitric acid by chromium(II) is rate-determining and that the rate constant was 2.2×10^{2} M^{-1} s^{-1} at 25 °C and at an ionic strength of 1.0 ($NaClO_4$). For the latter reaction, it was found that the one-electron reduction of nitrous acid by chromium(II) is rate-determining and that the rate constant was 4.5×10^{3} M^{-1} s^{-1} at 25 °C and at an ionic strength of 1.0 ($NaClO_4$). The rates of the reactions of chromium(II) with anionic species of the parent acids, NO_3^- and NO_2^-, were too slow to be detected under the present experimental conditions.

Ardon and Herman[2] demonstrated that the reaction products of nitrate with hexaaquochromium(II), Cr^{2+}, in acidic media were $Cr(NO)(H_2O)_5^{2+}$, $Cr(H_2O)_6^{3+}$ and $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$ and succeeded in isolating a nitrosyl complex, $[Cr(NO)(H_2O)_5]SO_4$. Swaddle[1] suggested, on the basis of the product ratios, that the reduction of the nitrate ion by Cr^{2+} in an acidic solution proceeds through the following reaction paths:

$$Cr^{2+} + NO_3^- + 2H^+ \longrightarrow Cr(IV) + NO_2^- + H_2O \quad (1)$$

$$Cr(IV) + Cr^{2+} \xrightarrow{H_2O} (H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+} \quad (2)$$

$$Cr^{2+} + NO_2^- + 2H^+ \xrightarrow{H_2O} Cr(H_2O)_6^{3+} + NO + H_2O \quad (3)$$

$$Cr^{2+} + NO \xrightarrow{H_2O} Cr(NO)(H_2O)_5^{2+} \quad (4)$$

Mori *et al.*[3] prepared several salts of $[Cr(NO)(NH_3)_5]^{2+}$ by the reaction of chromium(II) in an ammoniacal solution with sodium nitrite or nitrate. The chloride salt was prepared also by Griffith by the reaction of chromium(II) with NO in liquid ammonia.[4] In early works[2,3] on nitrosyl chromium complexes, the formulation Cr(III)–(NO^-) has been used. Later it was reported,[4,5] however, that the formulation Cr(I)–(NO^+) was more feasible.

In order to ascertain the kinetic and mechanistic details of these interesting reactions, the reactions of nitrate and nitrite with chromium(II) in acidic media have been dealt with in this study.

Experimental

Reagents. All the solutions were prepared with redistilled water. The acidic solution of hexaaquochromium(III) perchlorate was prepared by the reduction of sodium dichromate in perchloric acid with hydrogen peroxide. The chromium(II) perchlorate solutions were prepared by the reduction of hexaaquochromium(III) perchlorate with a zinc amalgam under an atmosphere of nitrogen. The chromium(II) solutions thus obtained contained known amounts of sodium perchlorate and perchloric acid. The concentration of the hydrogen ion was determined by the method reported in the literature.[6,7] A sodium perchlorate solution was prepared by the neutralization of sodium bicarbonate of a primary standard reagent grade with perchloric acid. All the other chemicals were of an analytical reagent grade and were used without further purification.

Kinetic Measurements and Apparatus. For the reaction of nitrate with Cr^{2+}, kinetic measurements were carried out by a conventional method similar to that reported previously.[8] The change in the absorbance with the time was followed at 422 nm with a Hitachi EPS-3 pen-recording spectrophotometer. Solutions containing $NaNO_3$, $NaClO_4$ and $HClO_4$ were added to the optical cell, which was then sealed with a serum cap. After the solution had been purged with nitrogen gas, chromium(II) was added with a syringe.

As the rate of the reaction of HNO_2 with Cr^{2+} was too fast to be measured by a conventional method, the stopped-flow method was employed by the use of a Hitachi EPS-2 rapid-scanning spectrophotometer which was equipped with two syringes as reactant containers. One of the syringes was filled with a deoxygenated $NaNO_2$ solution, and the other, with a solution containing Cr^{2+}, $NaClO_4$ and $HClO_4$. The change in the transmittance at 443 nm was recorded on a storage-type oscilloscope (Hitachi V-018 Memoriscope) as a function of time after the mixing of the two reactant solutions.

In the kinetic measurements, the temperature was controlled at 25 °C and the ionic strength was adjusted to 1.0 with sodium perchlorate.

Product Analyses. The chromium species in the reaction products were separated by SP-Sephadex C-25 (Pharmacia, Sweden) column chromatography. The column used was 2.5 cm^2 in cross-section and 4 cm in height. The separation of the products with the Sephadex column was much more convenient than that with Dowex 50W used by previous workers.[1,2]

After the completion of the reaction between nitrate and Cr^{2+}, the reaction mixture was passed through the column. When the initial concentration of Cr^{2+} was smaller than that of nitrate, the chromium species were adsorbed in three bands···brown at the bottom, bluish-violet in the middle, and green at the top. The brown-colored species was eluted with a 0.1 M $HClO_4$–0.1 M $NaClO_4$ solution and was identified as $Cr(NO)(H_2O)_5^{2+}$ ($CrNO^{2+}$) spectrophotometrically. The bluish-violet species was eluted with a 0.1 M $HClO_4$–0.5 M $NaClO_4$ solution and was identified as $Cr(H_2O)_6^{3+}$ (Cr^{3+}). The green species was eluted with a 0.1 M $HClO_4$–0.9 M $NaClO_4$ solution and was identified as $(H_2O)_4Cr(OH)_2$–$Cr(H_2O)_4^{4+}$ ($(Cr(OH)_2Cr^{4+}$). When the initial concentration of Cr^{2+} exceeded that of nitrate, the column gave four bands···of brown, bluish-violet and two kinds of green··· from the bottom to the top of the column. The lower three

products were identified as $CrNO^{2+}$, Cr^{3+}, and $Cr(OH)_2Cr^{4+}$ respectively. The uppermost green species was considered to be produced by the reaction between $CrNO^{2+}$ and Cr^{2+}. Sephadex column chromatography revealed that this green species moves slightly slower than $Cr(OH)_2Cr^{4+}$. This species has not been identified, but the spectrum shows absorption maxima at 584 nm and 422 nm which are very close to those of $Cr(OH)_2Cr^{4+}$.[9]

In the nitrous acid system, the chromium species produced during the reaction were adsorbed on the Sephadex column in two bands···an upper bluish-violet band and a lower brown band, unless the initial concentration of nitrous acid was smaller than that of Cr^{2+}. The brown species was eluted with a 0.1 M $HClO_4$–0.1 M $NaClO_4$ solution and was identified as $CrNO^{2+}$. The bluish-violet species was eluted with a 0.1 M $HClO_4$–0.5 M $NaClO_4$ solution and was identified as Cr^{3+}. Under these experimental conditions the formation of $Cr(OH)_2Cr^{4+}$ was not observed. The chromium content in each effluent was determined spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.

Results

Reaction of $CrNO^{2+}$ with Cr^{2+}. Stoichiometric and kinetic studies of this reaction were reported by Armor and Buchbinder very recently.[10] According to their results, the stoichiometry is:

$$4Cr^{2+} + 2CrNO^{2+} + 6H_2O + 2H^+ \longrightarrow 3Cr(OH)_2Cr^{4+} + 2NH_3OH^+ \quad (5)$$

The present authors have also investigated the reaction between $CrNO^{2+}$ and Cr^{2+} and found that the rates of the reaction were in agreement with those reported by Armor and Buchbinder. However, a green species which is different from $Cr(OH)_2Cr^{4+}$ and which can not be expected from the stoichiometry of Eq. (5) was found in this work. From the chromatographic behavior described in the Experimental section, the positive charge of this species seems not to be smaller than 4. Further extensive work has not been made of this system, however.

Reaction of Nitrate with Cr^{2+}. The results of the product analyses are summarized in Table 1. If the initial concentration of nitrate is higher than that of Cr^{2+}, nitrate is found to react with four equivalents of Cr^{2+} to produce $CrNO^{2+}$, Cr^{3+}, and $Cr(OH)_2Cr^{4+}$ in the ratio of 1 : 1 : 1. The overall reaction of nitrate with Cr^{2+} is expressed by Eq. (6), which is the same as that reported by Swaddle:[1]

$$NO_3^- + 4Cr^{2+} + 2H^+ \longrightarrow CrNO^{2+} + Cr^{3+} + Cr(OH)_2Cr^{4+} \quad (6)$$

When the initial concentration of nitrate is smaller than that of Cr^{2+}, the yield of $CrNO^{2+}$ is much lower than those of Cr^{3+} and $Cr(OH)_2Cr^{4+}$, as is shown in Table 1. This can be understood in view of the fact that there is a slow reaction between the $CrNO^{2+}$ produced by Reaction (6) and the Cr^{2+} remaining in excess.

The kinetics for the reaction of nitrate with Cr^{2+} were studied under second-order conditions. If it is assumed that the rate equation (7) is valid for this system:

$$\text{Rate} = k[NO_3^-][Cr^{2+}] \quad (7)$$

Eq. (8) is then derived:

$$\log \frac{4\varepsilon_{app}[NO_3^-]_0 - D_t}{D_\infty - D_t} = \frac{4[NO_3^-]_0 - [Cr^{2+}]_0}{4\times 2.303} kt + \log \frac{4[NO_3^-]_0}{[Cr^{2+}]_0} \quad (8)$$

where $[NO_3^-]_0$ and $[Cr^{2+}]_0$ indicate the initial concentrations of nitrate and Cr^{2+} respectively. D_t is the absorbance measured at time t, and D_∞ is the final absorbance. The symbol, ε_{app}, is the apparent extinction coefficient of the products at 422 nm, which was determined from the absorbance after the completion of the reaction. The plots of the left-hand side of Eq. (8) *vs.* t gave a good linear relation for three half-lives. The second-order rate constant, k, was determined from the slope of this straight line. The kinetic results under the experimental condition of nitrate in excess of Cr^{2+} are given in Table 2. The rate constants were independent of the initial concentrations of both nitrate and Cr^{2+} at a given hydrogen-ion concentration. Therefore, the reaction is strictly second-order. Under the condition of Cr^{2+} in excess of nitrate, the second-order rate constants are very different from the values given Table 2. This can be attributed to the fact that the $CrNO^{2+}$ produced reacts further with the Cr^{2+} remaining in the solution. The observed second-order rate constants were considerably dependent on the hydrogen-ion concentrations, as is shown in Table 2. This dependency can be explained by considering the following mechanism:

$$HNO_3 \overset{K_a}{\rightleftharpoons} H^+ + NO_3^- \quad (9)$$

Table 1. Products of the reaction of HNO_3 with Cr^{2+} a)

Initial concentrations of reactants		Products				
					Ratios	
$[Cr^{2+}]_0$/mM	$[NO_3^-]_0$/mM	$[CrNO^{2+}]$/mM	$[Cr^{3+}]$/mM	$[Cr_2(OH)_2^{4+}]$/mM	$[CrNO^{2+}]$:	$[Cr^{3+}]$: $[Cr_2(OH)_2^{4+}]$
15.7	4.00	1.98	3.71	5.32	0.53 :	1.00 : 1.43 b)
15.7	16.0	3.50	4.52	4.20	0.77 :	1.00 : 0.93
15.7	32.0	3.53	4.22	4.10	0.84 :	1.00 : 0.97
15.7	50.0	3.93	4.42	4.25	0.89 :	1.00 : 0.96

a) The experiments were made under the following conditions: $[H^+]=0.207$ M, at 25 °C and at an ionic strength of 1.0 ($NaClO_4$). b) In this case, two green species (see Experimental) were observed and were collected together.

Table 2. Rate constants of the reaction between HNO_3 and Cr^{2+} at 25 °C and at an ionic strength of 1.0

$[Cr^{2+}]_0$/mM	$[NO_3^-]_0$/mM	$[H^+]$/M	k/($M^{-1}\,s^{-1}$)
5.03	32.0	0.204	2.73
7.86	32.0	0.199	2.71
10.1	32.0	0.197	2.61
15.7	16.0	0.207	2.61
15.7	18.0	0.207	2.70
15.7	20.0	0.207	2.71
15.7	22.0	0.207	2.96
15.7	24.0	0.207	2.77
15.7	26.0	0.207	2.71
15.7	28.0	0.207	2.85
15.7	30.0	0.207	2.84
15.7	32.0	0.207	2.71
15.7	20.0	0.110	1.66
15.7	20.0	0.301	4.06
15.7	20.0	0.395	5.49
15.7	20.0	0.512	7.05
15.7	20.0	0.599	8.65

$$NO_3^- + Cr^{2+} \xrightarrow{k_1} \text{products} \quad (10)$$

$$HNO_3 + Cr^{2+} \xrightarrow{k_2} \text{products} \quad (11)$$

On the basis of this mechanism, the following rate law was derived:

$$\text{Rate} = \frac{k_1 + k_2 K_a^{-1}[H^+]}{1 + K_a^{-1}[H^+]}[NO_3^-]_T[Cr^{2+}] \quad (12)$$

where

$$[NO_3^-]_T = [NO_3^-] + [HNO_3]$$

$$K_a = \frac{[H^+][NO_3^-]}{[HNO_3]}$$

Many values for the dissociation constant, K_a, of nitric acid have been reported.[11,12] They are in good agreement with each other, almost all of the values ranging from 15 to 34 M at 25 °C and at an ionic strength of zero. Of them, the value of 15.4 which was revised by Davis and de Bruin[13] was used for the analysis of the rate constants without any correction of the ionic strength. The plots of $k(1+K_a^{-1}[H^+])$ *vs.* $[H^+]$ show a linear relation, which is given in Fig. 1. The value of the intercept is practically zero. This means that the contribution of Reaction (10) is negligible and that the whole reaction proceeds almost entirely through the path represented by Eq. (11). The rate constant, k_2, is $2.2\times10^2\ M^{-1}\,s^{-1}$, and the value of k_1 is less than $0.2\ M^{-1}\,s^{-1}$.

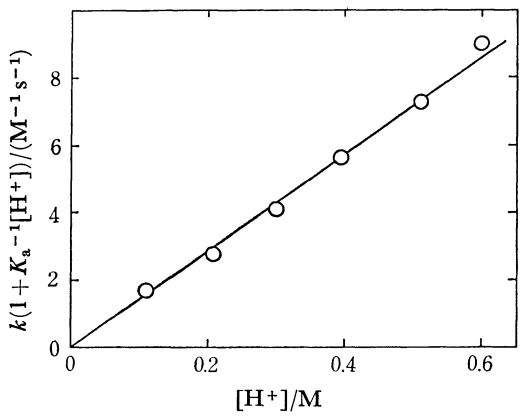

Fig. 1. The plots of $k(1+K_a^{-1}[H^+])$ *vs.* $[H^+]$ at 25 °C. and at an ionic strength of 1.0.

Reaction of Nitrous Acid with Cr^{2+}. Nitrous acid was found to react with two equivalents of Cr^{2+} to produce $CrNO^{2+}$ and Cr^{3+} in the ratio of 1 : 1 under the condition of a higher concentration of nitrous acid than of Cr^{2+}. Therefore, the overall reaction of nitrous acid with Cr^{2+} is as follows:

$$HNO_2 + 2Cr^{2+} + H^+ \longrightarrow CrNO^{2+} + Cr^{3+} + H_2O \quad (13)$$

In order to avoid the interference of the reaction between $CrNO^{2+}$ and Cr^{2+}, the kinetics of the reaction of nitrous acid with Cr^{2+} were studied under the condition that the concentration of nitrous acid exceeded that of Cr^{2+}. When the second-order rate equation:

$$\text{Rate} = k[HNO_2][Cr^{2+}] \quad (14)$$

holds in this case, Eq. (15) is derived:

$$\log\frac{2\varepsilon_{app}[HNO_2]_0 - D_t}{D_\infty - D_t} = \frac{2[HNO_2]_0 - [Cr^{2+}]_0}{2\times2.303}kt + \log\frac{2[HNO_2]_0}{[Cr^{2+}]_0} \quad (15)$$

where $[HNO_2]_0$ and $[Cr^{2+}]_0$ are the initial concentrations of HNO_2 and Cr^{2+} respectively. The symbol, ε_{app} is the apparent extinction coefficient of the products at 443 nm. The plots of the left-hand side of Eq. (15) *vs.* t gave a good linear relation for three half-lives. The second-order rate constant, k, was obtained from the slopes of the plots. The results are given in Table 3. The rate was independent of the hydrogen-ion concentration. The pK_a value of nitrous acid has been reported to be 2.8.[11,12] HNO_2 is the predominant species under the present experimental conditions where the hydrogen-ion concentrations were varied from 0.10 to 0.65 M. Therefore, the mechanism of the reaction can be expressed as:

$$HNO_2 + Cr^{2+} \xrightarrow{k} Cr^{3+} + NO + OH^- \quad (16)$$

$$Cr^{2+} + NO \xrightarrow{\text{fast}} CrNO^{2+} \quad (17)$$

The second-order rate constant, k, was determined to be $(4.5\pm0.3)\times10^3\ M^{-1}\,s^{-1}$. The analysis of the data given in Table 3 revealed that the rate constant of NO_2^- with Cr^{2+} was less than $5\times10^4\ M^{-1}\,s^{-1}$.

Table 3. Rate constants of the reaction between HNO_2 and Cr^{2+} at 25 °C and at an ionic strength of 1.0

$[Cr^{2+}]_0$/mM	$[HNO_2]_0$/mM	$[H^+]$/M	k/($10^3\ M^{-1}\,s^{-1}$)
4.4	6.0	0.10	4.1
4.4	6.0	0.30	4.7
4.3	6.0	0.50	4.9
5.8	6.0	0.65	4.4

Discussion

It is known that the reactions of Cr^{2+} with Tl(III) and O_2 produce $Cr(OH)_2Cr^{4+}$.[9] In the Tl(III) system, the following mechanism has been proposed:

$$Cr^{2+} + Tl(III) \longrightarrow Cr(IV) + Tl(I)$$

$$Cr(IV) + Cr^{2+} \longrightarrow Cr(OH)_2Cr^{4+}$$

A kinetic study of the reaction of molecular oxygen with Cr^{2+} showed that the reaction rate is of the second-order in Cr^{2+} and of the first-order in O_2.[14] From these results, the formation of a μ-peroxo dimer was suggested. In the reaction of HNO_3 with Cr^{2+}, however, the reaction rate is of the first-order in both reactants. Product analysis revealed that $CrNO^{2+}$, Cr^{3+}, and $Cr(OH)_2Cr^{4+}$ were produced in the ratio of 1 : 1 : 1. In the reaction of HNO_2 with Cr^{2+}, only $CrNO^{2+}$ and Cr^{3+} were produced, in the ratio of 1 : 1. Therefore, it is considered that $Cr(OH)_2Cr^{4+}$ is produced in the first step of the reaction between HNO_3 and Cr^{2+}. The experimental results lead to the conclusion that the mechanism expressed by Eqs. (1) to (4) is effective in the reaction between HNO_3 and Cr^{2+} when the contribution of the reaction between $CrNO^{2+}$ and Cr^{2+} is negligibly small.

Table 4 summarizes the rate constants obtained or estimated in this work. It is interesting to note that Cr^{2+} reacts with HNO_3 but not the NO_3^- ion, which is the predominant species under the present experimental conditions. Swaddle reported that $[Co(NO_3)(NH_3)_5]^{2+}$ was reduced by Cr^{2+}.[1] Thirty-three percent of the reaction proceeds through the reduction of the central cobalt(III) ion to the cobalt(II) ion, while the remaining sixty-seven percent of the reaction proceeds through the reduction of the coordinated nitrato ligand instead of the central cobalt(III) ion. Therefore, when the NO_3^- ion is bound to the proton or is coordinated to the pentaamminecobalt(III) ion, which is a Lewis acid, the reduction of nitrate by Cr^{2+} is accelerated.

Table 4. Rate constants of the reactions of Cr^{2+} with some reactants obtained in this work at 25 °C and at an ionic strength of 1.0 ($NaClO_4$)

Reactant	Rate constant/(M^{-1} s^{-1})
HNO_3	2.2×10^2
NO_3^-	<0.2
HNO_2	$(4.5\pm0.3)\times10^3$
NO_2^-	$<5\times10^4$
NO	$>4.5\times10^3$

It was found in this work that the rates of the reactions of Cr^{2+} with HNO_3, HNO_2, and NO are in the following order: $HNO_3<HNO_2<NO$.

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