The Reduction of Nitrous Acid by the Azidopentaaquochromium(III) Ion

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Abstract: The rate expression for the reaction, $(H_2O)_5CrN_3^{2+} + HNO_2 = (H_2O)_6Cr^{3+} + N_2 + N_2O$, in perchloric acid–sodium perchlorate solution ($[H^+] = 0.13–1.0\ M$) is $-d[(H_2O)_5CrN_3^{2+}]/dt = k_0[(H_2O)_5CrN_3^{2+}]\cdot[HNO_2][H^+]$. At 25° and 1.00 *M* ionic strength, the value of k_0 is $(2.40 \pm 0.01) \times 10^3\ M^{-2}\ sec^{-1}$, and the associated activation parameters are $\Delta H^{\ddagger} = 13.4 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = 1.9 \pm 2.2$ eu. Addition of Cl^- or Br^- increases the reaction rate but results in the formation of only traces of $(H_2O)_5CrX^{2+}$. The results are compared to those reported for related systems.

The empirical form of the rate law reported for the reduction of nitrous acid by hydrazoic acid[1] and the azidopentaamminecobalt(III) ion[2] is $-d[HNO_2]/dt = k[\text{reductant}][HNO_2][H^+]$. Thus, the rate expressions for these two systems are formally similar despite the difference in the coordination site for the azide ion. In this paper we report the results of a study employing the azidopentaaquochromium(III) ion[3] as the reducing agent. Although our primary interest is the comparative redox kinetics of the azide ion coordinated to a hydrogen ion and to substitution inert metal ion centers, we have also tested the possible formation of the pentacoordinated intermediate $(H_2O)_5Cr^{3+}$.

Experimental Section

Reagents. The water used was doubly distilled in an all-glass apparatus after distillation of deionized water from an alkaline permanganate still. The sodium perchlorate was recrystallized three times after preparation by the neutralization of reagent grade sodium carbonate with perchloric acid. Azidochromium(III) ion was prepared by the method of Swaddle and King.[4] Fresh working stock solutions of this reactant were separated by ion-exchange techniques daily and kept frozen to prevent aquation. The positions and molar extinction coefficients for azidochromium(III) ion were: 5850 Å, 67.7 $cm^{-1}\ M^{-1}$; 4340 Å, 67.7 $cm^{-1}\ M^{-1}$; and 2710 Å, 3740 $cm^{-1}\ M^{-1}$, in excellent agreement with published values.[4] All other chemicals were reagent grade and were used without further purification. The sodium nitrite solutions were standardized by the hypochlorite procedure.[5]

Stoichiometric Studies. The ratio ([azidochromium(III)] reacted)/([nitrous acid] reacted) was determined by injecting a known amount of standard sodium nitrite solution into a small excess of azidochromium(III) ion in molar perchloric acid. The amount of the latter reactant that was consumed was determined spectrophotometrically.

The chromium(III) product of the reaction in the absence of added anions other than perchlorate ion, as determined by ion exchange procedures, was solely the hexaaquochromium(III) ion. Preliminary analysis of reaction solutions containing 0.50 *M* NaCl or NaBr indicated that only traces of the anated chromium(III) species were produced. The analytical problems in accurately determining approximately 2% $(H_2O)_5CrX^{2+}$ ($X = Cl^-$ or Br^-) and 98% $(H_2O)_6Cr^{3+}$ (based on the total chromium content) in dilute solution proved to be considerable. Conditions were finally found in which 90–95% of the anated species could be quantitatively separated from the hexaaquochromium(III), and the remainder could be separated with 10–20% contamination (based on total chromium in this eluent) by the 3+ ion. In a typical experiment, a small excess of sodium nitrite solution was rapidly mixed with 100 ml of a solution containing $2.0 \times 10^{-3}\ M\ (H_2O)_5CrN_3^{2+}$, 0.50 *M* $HClO_4$, and 0.50 *M* NaCl or NaBr at 0°. The spent reaction mixture was then placed on an optimum sized Dowex-50WX-8, 50–100 mesh ion exchange column, and any anated chromium(III) product was eluted with a predetermined amount of ice-cold 2 *M* perchloric acid. Any anation of the hexaaquochromium(III) ion by the halide ion present is negligible under these conditions in the time period required to wash the halide ion off the column (0.5 hr),[6,7] and aquation of the anated chromium(III) species in the *ca.* 2 hr required for the elution is very slight.[7,8] Matts and Moore[9] have reported that nitrous acid catalyzes the rate of aquation of $(H_2O)_5CrCl^{2+}$ and $(H_2O)CrBr^{2+}$. However, their data indicate that under the conditions employed in the present study, aquation by this catalytic path is negligible during the time required to elute the small excess of nitrous acid. Analysis of the eluent containing all the anated species (with ≤2% contamination by $(H_2O)_6Cr^{3+}$) was made for chromium by spectrophotometry after conversion to chromate with alkaline peroxide.[10]

Kinetic Studies. The rate measurements were carried out spectrophotometrically at the 2710-Å absorption maximum of the azidochromium(III) ion. Spectral interference by the other species present in the reaction solutions is negligible at this wavelength. A Zeiss PMQ11 spectrophotometer equipped with a thermostated (±0.1°) and rapid-mixing sample compartment was used. The azidochromium(III), perchloric acid, and sodium perchlorate were allowed to reach temperature equilibrium in the sample compartment; in the experiments with added sodium chloride or bromide, a suitable aliquot of a solution containing the halide salt at the working temperature was added just prior to initiation of the reaction. The reaction was initiated by rapidly injecting and mixing (<1 sec) the sodium nitrite solution. Spontaneous decomposition of nitrous acid in the acidic reaction solution is negligible[11] relative to the rate of the oxidation of azidochromium(III). The hydrogen ion concentration of the reaction medium was determined by titration of the spent reaction solution with standard base.

Results

The ratio ($[(H_2O)_5CrN_3^{2+}]$ reacted)/($[HNO_2]$ reacted) was determined to be 0.99 ± 0.01. Hexaaquochromium(III) ion is the only detectable chromium(III) product in the absence of anions other than perchlorate ion. On the basis of these data, the observed gas evolution, and the results of the corresponding hydrazoic acid reaction,[1] the stoichiometry can be represented by eq 1.

$$(H_2O)_5CrN_3^{2+} + HNO_2 + H^+ = (H_2O)_6Cr^{3+} + N_2 + N_2O \quad (1)$$

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[1] G. Stedman, *J. Chem. Soc.*, 2943 (1959).

[2] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

[3] Hereafter called azidochromium(III) in this paper.

[4] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

[5] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Vol. 3, The Macmillan Co., New York, N. Y., 1952, p 560.

[6] H. S. Gates and E. L. King, *J. Amer. Chem. Soc.*, **80**, 5011 (1958).

[7] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

[8] T. W. Swaddle and E. L. King, *ibid.*, **4**, 531 (1965).

[9] T. C. Matts and P. Moore, *Chem. Commun.*, 29 (1969).

[10] G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 414 (1952).

[11] E. Abel, H. Schmidt, and E. Romer, *Z. Phys. Chem.*, **148**, 337 (1930).

At constant $[HClO_4]$, the rate expression $-d[\text{complex}]/dt = k^1[\text{complex}][HNO_2]$ was obeyed for all of the kinetic experiments for at least three half-lives of the reaction. Values of k^1 were determined from a least-squares analysis of the integrated form of this expression; the standard deviation in k^1 was $\leq 1.5\%$. Values of k^1 at 25° are listed in Table I.

Table I. Kinetic Results[a] at 25°

Experiment no.	$[H^+]$, M	k^1, $M^{-1}\ sec^{-1}$
1	0.130	301 ± 4
2	0.162	375 ± 5
3	0.236	629 ± 1
4	0.326	731 ± 3
5	0.492	1160 ± 20
6	0.642	1530 ± 20
7	0.957	2350 ± 30
8	0.988	2440 ± 40[b]
9	0.130	103 ± 4[c]
10	0.130	177 ± 3[d]

[a] $[HNO_2]_0 = 1.12 \times 10^{-4}–3.73 \times 10^{-5}\ M$, $[(H_2O)_5CrN_3^{2+}]_0 = 1.12 \times 10^{-4}–5.70 \times 10^{-5}\ M$. All runs at $I = 1.00$ (maintained with $NaClO_4$) and monitored at 2710 Å unless otherwise noted. Uncertainties are average deviations of duplicate runs. [b] Monitored at 2225 Å. [c] $I = 0.13$. [d] $I = 0.50$.

The invariance of the rate parameter k^1 with the wavelength used to monitor the reaction is illustrated by experiments 7 and 8. Experiments 9, 10, and 1 indicate a substantial increase in k^1 as the ionic strength is increased at constant $[HClO_4]$, a feature noted in the $(NH_3)_5CoN_3^{2+}$ system.[2]

The empirical dependence of the rate parameter with variation in hydrogen ion concentration at $I = 1.00$ can be expressed as

$$\log k^1 = \log k_0 + n \log [H^+] \qquad (2)$$

Values of $n = 1.00 \pm 0.01$ and $k_0 = (2.40 \pm 0.01) \times 10^3\ M^{-2}\ sec^{-1}$ were computed from the data listed for experiments 1–8. The empirical composition of the activated complex (uncertain as to the number of water molecules) is therefore defined as one molecule of HNO_2, one $(H_2O)_5CrN_3^{2+}$ ion, and one more than the usual number of hydrogen ions associated with the reactants.

Values of the third-order rate constant k_0 determined at other temperatures are: 519 ± 12 $M^{-2}\ sec^{-1}$ at 7.0°, 905 $M^{-2}\ sec^{-1}$ at 12.6°, 1030 $M^{-2}\ sec^{-1}$ at 13.2°, and 1610 ± 10 $M^{-2}\ sec^{-1}$ at 19.1°. Values for the associated activation parameters as calculated in the usual manner by means of absolute reaction rate theory[12] are: $\Delta H^{\ddagger} = 13.4 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = 1.9 \pm 2.2$ eu.

A series of experiments was performed in the presence of added NaCl and NaBr, and the results are summarized in Table II. The entries in the fourth column indicate a marked enhancement of the rate parameter k^1 upon addition of chloride ion, and an even greater effect with bromide ion. The $k_0{}^1$ values listed in the last column were calculated from the expression

$$k^1 = k_0[H^+] + k_0{}^1[H^+][Cl^-] \qquad (3)$$

Table II. Kinetic Results[a] in the Presence of Added Anions at 25°

Experiment no.	Anion, M	$[H^+]$, M	k^1, $M^{-1}\ sec^{-1}$	$k_0{}^1$, $M^{-3}\ sec^{-1}$ [b]
20	Cl^-, 0.056	0.051	309 ± 5	6.6×10^4
21	Cl^-, 0.056	0.124	850 ± 2	8.0×10^4
22	Cl^-, 0.138	0.051	618 ± 3	7.0×10^4
23	Cl^-, 0.269	0.047	835 ± 21	5.7×10^4
24	Cl^-, 0.465	0.044	1190 ± 40	5.3×10^4
25	Br^-, 0.059	0.050	532 ± 15	1.4×10^5
26	Br^-, 0.059	0.126	1510 ± 40	1.6×10^5
27	Br^-, 0.145	0.050	1060 ± 20	1.3×10^5
28	Br^-, 0.282	0.046	1550 ± 10	1.1×10^5
29	Br^-, 0.487	0.043	2050 ± 10	9.3×10^4

[a] $I = 1.00$, maintained with $NaClO_4$ and either NaCl or NaBr. Uncertainties are average deviations of duplicate runs. [b] Calculated from eq 3.

The value of $k_0 = 2400\ M^{-2}\ sec^{-1}$ as determined in the absence of any anions other than perchlorate ion at 25° and $I = 1.00$ was used. The values for $k_0{}^1$ listed for experiments 20, 21 and 25, 26 indicate that the anion-catalyzed path is approximately first order in $[H^+]$ for both chloride and bromide ions. The remaining data indicate, however, that the dependence of the reaction rate upon anion concentration for this path apparently becomes less than first order as the anion concentration increases. This latter effect was also observed by Haim and Taube in the $(NH_3)_5CoN_3^{2+}$ system.[2]

The ion-exchange experiments designed to determine any $(H_2O)_5CrX^{2+}$ product in addition to $(H_2O)_6Cr^{3+}$ revealed that $\leq 2.1\%$ of the azidochromium(III) was converted to $(H_2O)_5CrCl^{2+}$ in 0.50 M NaCl (0.5 M $HClO_4$), and $\leq 1.4\%$ was converted to $(H_2O)_5CrBr^{2+}$ in 0.50 M NaBr (0.5 M $HClO_4$). These results are in sharp contrast to the 9.6% conversion of $(NH_3)_5CoN_3^{2+}$ to the anated complex in 0.5 M HCl and 19.6% conversion in 1.0 M HBr.[13]

Discussion

The empirical form of the rate law for the reduction of HNO_2 by HN_3, $(NH_3)_5CoN_3^{2+}$, and $(H_2O)_5CrN_3^{2+}$ in perchloric acid solution is

$$-d[HNO_2]/dt = k_0[\text{reductant}][HNO_2][H^+] \qquad (4)$$

The values of the third-order rate constant k_0 for these systems are summarized in Table III.

Table III. Kinetic Data for the Reduction of Nitrous Acid

Reductant	T, deg	I, M	k_0, $M^{-2}\ sec^{-1}$	Ref
HN_3	0	[a]	33.7	1
$(H_2O)_5CrN_3^{2+}$	0	1.00	274[b]	This work
$(H_2O)_5CrN_3^{2+}$	25	1.00	2400	This work
$(NH_3)_5CoN_3^{2+}$	25	1.00	4000	2
$(H_2O)_5CrN_3^{2+}$	25	0.50	1360	This work
$(NH_3)_5CoN_3^{2+}$	25	0.50	1600	2

[a] k_0 is apparently nearly ionic strength independent for HN_3. [b] Calculated by using the activation parameters reported in this study.

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(12) S. Glasstone, R. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp 195–199.

(13) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967). These data have been cited, rather than those in ref 1, due to the more accurate analytical procedures employed.

Unfortunately, activation parameters are available only for the present system. Also, the rates of the reduction of HNO_2 by $(H_2O)_5CrN_3^{2+}$ and $(NH_3)_5CoN_3^{2+}$ are markedly dependent upon the ionic strength, whereas there is apparently little such dependence in the case of HN_3. The values of the rate parameter k_0 are quite similar for the two metal ion complexes under identical conditions, and are of the same order of magnitude as that for HN_3. In fact, at low ionic strength the rate data suggest that the coordination center for the azide ion is not of major kinetic importance in the reduction of nitrous acid. Loeliger and Taube[14] have reported values of $k_0 = 110\ M^{-2}\ \text{sec}^{-1}$ and $440\ M^{-2}\ \text{sec}^{-1}$ for *trans*- and *cis*-$(en)_2CoN_3H_2O^{2+}$, respectively, at 25° and $I = 0.05\ M$. Rather drastic extrapolations of k_0 for $(NH_3)_5CoN_3^{2+}$ and $(H_2O)_5CrN_3^{2+}$ to an ionic strength of 0.05 suggest that the rate parameters for all four of these monoazido complexes lie within a factor of 4 of each other.[15]

The following reaction scheme is consistent with the kinetic data obtained in this study

$$H^+ + HNO_2 \overset{K}{\rightleftharpoons} H_2NO_2^+ \qquad (5)$$

$$H_2NO_2^+ + (H_2O)_5CrN_3^{2+} \overset{k}{=} (H_2O)_6Cr^{3+} + N_2 + N_2O \qquad (6)$$

where (5) is rapid equilibrium and reaction 6 is rate-determining. The equilibrium 5 has been previously postulated in a number of nitrous acid systems.[16] However, the present data cannot distinguish between the nitrous acidium ion as the reactive form of nitrous acid as shown in reaction 5, or alternatively the nitrosonium ion as selected by Haim and Taube in the $(NH_3)_5CoN_3^{2+}$ system.[2] An equilibrium involving the protonation of $(H_2O)_5CrN_3^{2+}$ is considered less likely to have kinetic significance, although it cannot be rejected. Swaddle and King[4] were unable to find any spectral evidence for such a protonation, but the aquation rate law does have a term proportional to $[H^+]$.

Equation 6 could be amplified by the inclusion of the formation of a nitrosyl azide intermediate that would hydrolyze in a subsequent rapid step to the observed products. There is considerable evidence for this intermediate in the HN_3–HNO_2 system.[1,17]

A plausible additional kinetic path in the presence of chloride or bromide ions would invoke the additional rapid equilibrium

$$X^- + H_2NO_2^+ = NOX + H_2O \qquad (7)$$

with NOX being a more reactive species than $H_2NO_2^+$. However, the order on $[X^-]$ for this path should not become less than unity as the $[X^-]$ is increased, as the data in the last column of Table II seem to indicate. The solution composition in terms of $[X^-]$ and $[ClO_4^-]$ at constant ionic strength changes markedly over the experiments listed in Table II. If there is a medium effect superimposed on the molecular paths, then the deviations from first-order dependence on the added anion may be more apparent than real.

Considerable evidence has been presented for the formation of the pentacoordinated intermediate $(NH_3)_5Co^{3+}$ in a variety of systems, and in particular in the $(NH_3)_5CoN_3^{2+}$–HNO_2 reaction.[2,13] However, the production of only barely detectable quantities of $(H_2O)_5CrX^{2+}$ even in 0.5 M X^+ in the present study renders the formation of a $(H_2O)_5Cr^{3+}$ intermediate far less likely. Arguments such as a much lower discrimination ability toward water and halide ions of $(H_2O)_5Cr^{3+}$ as compared to $(NH_3)_5Co^{3+}$ or the smaller ion pair association constants of aquo complexes compared to ammine complexes[18] could be invoked. In summary, though, the present data are not consistent with the concept that a pentacoordinated intermediate is produced, after the rate-determining step, which competes preferentially for the halide ion.

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[14] D. Loeliger and H. Taube, *Inorg. Chem.*, **4**, 1032 (1965).

[15] In addition, C. S. Davis and G. C. Lalor (*J. Chem. Soc.*, 1095 (1968)) report a value of $k_0 = 402\ M^{-2}\ \text{sec}^{-1}$ at 25° and low ionic strength for one pathway in the $(NH_3)_5RhN_3^{2+}$–HNO_2 reaction.

[16] For example, see T. A. Turney, "Oxidation Mechanisms," Butterworth Inc., Washington, D. C., 1965, pp 80–84, and the references cited.

[17] (a) K. Clusius and E. Effenberger, *Helv. Chim. Acta*, **38**, 1843 (1955); (b) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers.

[18] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).