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The Aquation of Nitritopentaamminechromium(III) Catalyzed by Hydrogen, Chloride, and Bromide Ions[1]

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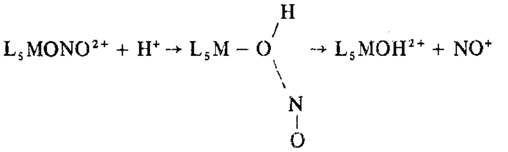
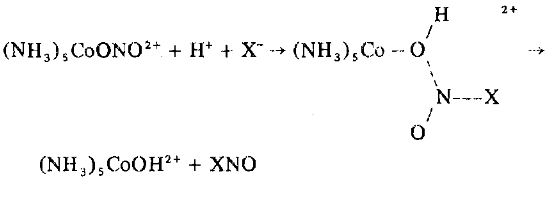
Kinetic and mechanistic studies of diazotization and deamination reactions[2] have established that nitrosation can proceed via the species N_2O_3, NO^+ (or H_2ONO^+), and XNO ($X^- = Cl^-, Br^-, I^-, SCN^-$). In the coordination chemistry of nitrite ion, the N_2O_3 pathway has been uncovered in the formation reactions of nitritopentaammine complexes of cobalt(III), chromium(III), rhodium(III), iridium(III), and platinum(IV).[3-5] The NO^+ pathway is featured in the acid-catalyzed aquations of nitrite complexes of chromium(III), cobalt(III), rhodium(III), and iridium(II).[6-9] We previously[10] reported the operation of the XNO pathway in the halide-catalyzed aquation of $Co(NH_3)_5ONO^{2+}$.



$$L_5MONO^{2+} + H^+ \rightarrow L_5M-\underset{\substack{N\\|\\O}}{\overset{H}{O}} \rightarrow L_5MOH^{2+} + NO^+ \qquad (1)$$



$$(NH_3)_5CoONO^{2+} + H^+ + X^- \rightarrow \left[(NH_3)_5Co-\underset{\substack{N---X\\/\\O}}{\overset{H}{O}}\right]^{2+} \rightarrow (NH_3)_5CoOH^{2+} + XNO \qquad (2)$$

In the present note, we report that chloride and bromide ions catalyze the aquation of $Cr(NH_3)_5ONO^{2+}$, and thus we provide evidence for the generality of the XNO pathway in the coordination chemistry of nitrite ion.

Experimental Section

Nitritopentaamminechromium(III) nitrate was prepared by reaction of aquopentaamminechromium(III) with nitrite ion.[11] This salt was transformed into the corresponding perchlorate by dissolution in the minimum amount of water followed by precipitation with a saturated solution of sodium perchlorate.[12] Anal. Calcd for $[Cr(NH_3)_5ONO](ClO_4)_2$: Cr, 13.61. Found: Cr, 13.50, 13.75.

Table I. Kinetics of the Acid-Catalyzed Aquation of $Cr(NH_3)_5ONO^{2+}$ [a]

$10^2[H^+]$, M	10^3k_{obsd}, sec^{-1}	10^2k_H, M^{-1} sec^{-1} [e]
2.50	1.66 ± 0.14[b]	6.64
5.02	3.49 ± 0.10[c]	6.95
9.99	6.96 ± 0.21[d]	6.97
20.0	14.0 ± 0.7[d]	7.00

[a] At 10°, $\mu = 1.00$ M, [Cr(III)] ~ 3×10^{-4} M. [b] Average of seven measurements. [c] Average of three measurements. [d] Average of four measurements.. [e] $k_H \equiv k_{obsd}/[H^+]$.

Lithium perchlorate was obtained as a solid from solutions prepared by dissolution of lithium carbonate in perchloric acid. The solid was recrystallized twice from water. The water used was purified as described previously.[10] Lithium chloride and sodium bromide were reagent grade and were used as received.

The lithium perchlorate solutions were standardized acidimetrically by an ion-exchange procedure. Chromium analyses were carried out spectrophotometrically following oxidation of chromium to CrO_4^{2-} in alkaline solution.

All kinetic measurements were carried out spectrophotometrically in a Cary 118 recording spectrophotometer equipped with a thermostated cell compartment and a modified thermostated cell holder. The cell holder ends were sealed with Suprasil windows (Amersil Inc., Hillside, N.J.) and the holder was filled with water. The temperature of the water was monitored continuously by means of a Digitec Model 581C digital thermistor thermometer. A solution containing all the desired components (lithium perchlorate, perchloric acid, and the halide salt when necessary) except the chromium(III) complex was prepared and 3.00 ml was placed in a square 1-cm cell. The cell was placed in the cell compartment. The precautions given by Matts and Moore[6] in handling $Cr(NH_3)_5ONO^{2+}$ were followed. The solutions of the chromium(III) complex were prepared at 0° and were used within 1–2 hr. Just before the start of a kinetic run, the chromium(III) solution was allowed to reach temperature equilibrium and approximately 0.1 ml was added to the 1-cm cell by means of a Cuvette Add-A-Mixer (Precision Cells, Inc., Hicksville, N.Y.). All measurements were carried out at 10° and ionic strength 1.00 M, and were followed at 240 nm. Pseudo-first-order rate constants were obtained from ln $(A_t - A_\infty)$ vs. time plots. A_t and A_∞ are the absorbances at time t and at the completion of the reaction, usually 8–10 half-lives.

Results and Discussion

The earlier studies[6] of the acid-catalyzed aquation of $Cr(NH_3)_5ONO^{2+}$ were carried out using sodium perchlorate to adjust the ionic strength. Since lithium perchlorate appears to be a better background electrolyte when acid-dependent pathways are operative,[10] we repeated the measurements at ionic strength 1.00 M using lithium perchlorate, and the results are summarized in Table I. It is seen that k_{obsd} is proportional to $[H^+]$ in the range 0.0250–0.200 M and, therefore, in agreement with the earlier work, the rate law is $k_H[Cr(NH_3)_5ONO^{2+}][H^+]$. Taking into account the difference in ionic media, our value of k_H, $6.89 \pm 0.12 \times 10^{-2}$ M^{-1} sec^{-1}, in $LiClO_4$ compares favorably with the value reported previously,[6] $5.34 \pm 0.1 \times 10^{-2}$ M^{-1} sec^{-1} in $NaClO_4$.

Addition of chloride or bromide strongly accelerates the rate of aquation, and the results of the kinetic measurements are presented in Tables II and III, respectively. It is seen that when k_{obsd} is corrected for the contribution of the acid-catalyzed path, the corrected values increase linearly with $[H^+]$ and with the concentration of halide ion. Therefore, the halide-catalyzed paths obey a rate law of the form $k_X[H^+][X^-][Cr(III)]$, with $k_X = 3.12 \pm 0.10$ and 27.9 ± 1.3 M^{-2} sec^{-1} for chloride and bromide ions, respectively.

The results obtained in the present work parallel exactly those obtained previously[10] for the acid- and halide-catalyzed aquations of $Co(NH_3)_5ONO^{2+}$. Indeed, a plot of log k for $Co(NH_3)_5ONO^{2+}$ vs. log k for $Cr(NH_3)_5ONO^{2+}$ is a straight line of slope 1.09 (see Figure 1). Consequently, we infer that

Table II. Kinetics of the Chloride-Catalyzed Aquation of $Cr(NH_3)_5ONO^{2+}$ [a]

$10^2[H^+]$, M	$10^2[Cl^-]$, M	$10^3 k_{obsd}$, sec^{-1} [b]	k_{Cl},[e] M^{-2} sec^{-1}
2.26	2.10	3.13 ± 0.15[c]	3.31
2.26	6.29	6.14 ± 0.13	3.22
2.26	10.5	8.83 ± 0.31[d]	3.06
1.36	6.29	3.59 ± 0.19	3.10
4.52	6.29	11.7 ± 0.1	3.02
9.04	6.29	23.4 ± 1.4	3.02

[a] At 10°, $\mu = 1.00\ M$ ($LiClO_4$), [Cr(III)] ~ $3 \times 10^{-4} M$. [b] Average of three measurements, unless indicated otherwise. [c] Average of five measurements. [d] Average of six measurements. [e] $k_{Cl} \equiv (k_{obsd} - k_H[H^+])/[H^+][Cl^-]$.

Table III. Kinetics of the Bromide-Catalyzed Aquation of $Cr(NH_3)_5ONO^{2+}$ [a]

$10^2[H^+]$, M	$10^2[Br^-]$, M	$10^3 k_{obsd}$, sec^{-1} [b]	k_{Br},[d] M^{-2} sec^{-1}
0.452	6.36	7.88 ± 0.25	26.3
0.452	10.6	13.4 ± 1.2	27.3
1.36	2.12	9.40 ±0.18	29.4
1.36	6.36	24.8 ± 1.1	27.6
1.36	10.6	37.2 ± 2.8	25.1
2.26	2.12	15.7 ± 0.4	29.5
2.26	6.36	41.7 ± 1.4	27.9
2.26	10.6	72.2 ± 3.1[c]	30.1

[a] At 10°, $\mu = 1.00\ M$ ($LiClO_4$), [Cr(III)] ~ $3 \times 10^{-4} M$. [b] Average of three measurements, unless indicated otherwise. [c] Average of four measurements. [d] $k_{Br} \equiv (k_{obsd} - k_H[H^+])/[H^+][Br^-]$.

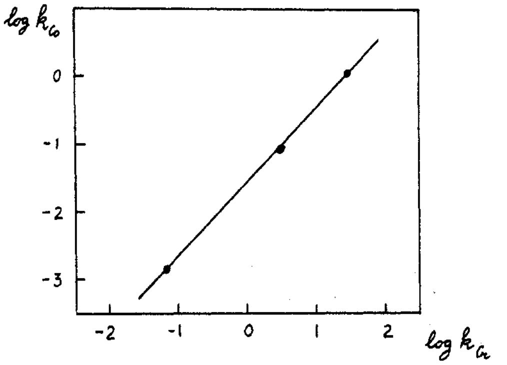


Figure 1.

the mechanisms of the two sets of reactions are identical, namely, rapid equilibrium protonation of the adjacent oxygen atom, followed by unassisted loss of NO^+ in the k_H pathway (eq 1) or assisted removal of NO^+ by Cl^- or Br^- in the k_{Cl} and k_{Br} pathways (eq 2).

Registry No. $Cr(NH_3)_5ONO^{2+}$, 22269-22-3; Cl^-, 16887-00-6; Br^-, 24959-67-9.

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A New Zerovalent Nickel Complex. Bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0)

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We have recently reported the photoreaction of tetrafluorodiphosphine with various olefins.[1-3] Our investigation of the reaction of the resulting bidentate ligand 1,2-bis(difluorophosphino)cyclohexane with tetracarbonylnickel(0) has resulted in the high-yield preparation of a new zerovalent nickel complex under relatively mild conditions.

Experimental Section

Into a 50-ml heavy-walled Pyrex vessel equipped with a Teflon stopcock, 1.71 mmol of $Ni(CO)_4$ (Strem Chemicals) and 4.90 mmol of $P_2F_4C_6H_{10}$[3] were condensed using standard vacuum techniques. Dry, air-free tetrahydrofuran (ca. 30 ml) was condensed into the reaction vessel, and the mixture was allowed to warm slowly to room temperature. Liberated CO was removed while holding the mixture at −196°. Upon warming, the vessel was placed in an oil bath with occasional shaking at 60° to ensure complete reaction. After 48 hr, the volatile material was pumped off and the remaining white solid was collected and sublimed. The reaction appeared to be essentially complete within 20 hr due to the absence of CO emerging from the solution. Recovery of 4.0 equiv of CO/equiv of $Ni(CO)_4$ substantiated the occurrence of complete substitution. Decomposition occurs upon melting at 169° (uncorrected). Anal. Calcd for $NiP_4F_8C_{12}H_{20}$: Ni, 11.77; C, 28.91; H, 4.01. Found: Ni, 11.61; C, 28.83, H, 4.16. (Galbraith Laboratories, Knoxville, Tenn.). NMR spectra were recorded on a Varian XL-100 spectrometer operating in the CW mode. Infrared spectra were recorded on a Beckman IR-20A spectrometer as KBr pellets. Mass spectra were recorded at 70 eV on a Hitachi Perkin-Elmer RMU-6E spectrometer.

Results and Discussion

Bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) was obtained as a dry, white powder which was stable in air for long periods of time with no apparent decomposition, in contrast to the rapid decomposition of the ligand in air.

The 40.5-MHz phosphorus-31 NMR spectrum of $Ni(P_2F_4C_6H_{10})_2$ in dry THF gives a broad triplet centered at −244.0 ppm (85% H_3PO_4 external reference) with J_{F-P} = 1115 Hz resulting from the two fluorine nuclei directly attached to the phosphorus. The free ligand shows two triplets, a large one (trans, diequatorial conformation) at −234.1 ppm and a small triplet (trans, diaxial), which disappears at low temperatures, at −241.1 ppm, with J_{F-P} = 1218 and 1203 Hz, respectively.[3] The absence of the second triplet in the complex is attributable to the absence of the trans, diaxial ligand configuration; models show the latter configuration to be nonamenable to bidentate bonding to metals. The downfield coordination shift δ_P(complex) − δ_P(ligand) = −9.9 ppm is in agreement with the observations reported in the literature for tetrakis(fluorophosphine)nickel(0) complexes.[4]

The ^{19}F NMR spectrum (94.1 MHz) of $Ni(P_2F_4C_6H_{10})_2$ in dry benzene suggests the presence of a mixture of isomers. A large doublet centered at 71 ppm (CCl_3F external standard) and two small doublets centered at approximately 65 and 63 ppm were observed with $J_{P-F} \simeq$ 1150 Hz for each doublet. All are shifted downfield from the uncoordinated ligand which displays a complex doublet at 81.3 ppm with $J_{P-F} \simeq$ 1174 Hz. These shifts are consistent with other fluorophosphine–metal complexes.[5] Though the peaks were quite broad and noisy, the three sets of doublets were clearly observed with area ratio of ~5:1 (combined area of smaller doublets). The small doublets were in a 1:1 area ratio. The doublets appear to result from the presence of coordinated trans and cis difluorophosphino groups in the ligand. The large doublet is assigned