However, it is significant that it is possible to explain the kinetics of reaction 2 by a mechanism that is the microscopic reverse of that proposed to explain reaction 1. Hence the proposed mechanisms reinforce each other, although one should note that reactions 1 and 2 are not strictly the reverse of each other because the phosphines are different. Finally it is important to note that Figure 2 is essentially identical with the well-established mechanism for the acid hydrolysis of metal chelates.[6] This further strengthens the credibility of the proposed mechanism for (2) and, by the principle of microscopic reversibility, also for (1).

Acknowledgment.—The authors are indebted to Professor R. G. Pearson for useful discussions. We thank the National Science Foundation for an award of a predoctoral fellowship to D. A. S., 1967–1970. We also thank the National Institutes of Health for awarding a predoctoral fellowship to D. G. DeW., 1968–1970. This work was also supported by NSF Grant 6341X to Northwestern University.

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Kinetics of the Chromium(II) Reduction of Isocyanatopentaamminecobalt(III)

BY R. J. BALAHURA AND R. B. JORDAN*

Received June 22, 1970

In a recent study[1] on the preparation and reactivity of (NH$_3$)$_5$CoNCO^{2+} Burmeister and DeStefano reported that the chromium(II) reduction of this complex fails to produce any (H$_2$O)$_5$CrNCO^{2+} or its linkage isomer. This conclusion, combined with a discussion of why cyanate should not be as good a bridging group as CN$^-$ or N$_3$$^-$ and the long reaction times used, leaves the impression that the reaction is quite slow and that a bridging mechanism may not be operative. However in the concluding paragraph of the paper Burmeister and DeStefano note that they may never have actually observed the chromium(II) reduction reaction due to possible oxidation and/or hydrolysis.

Our preliminary studies indicated that the reduction of (NH$_3$)$_5$CoNCO$^+$ by chromium(II) was much faster than indicated by the previous work. In fact the reaction is complete in ~10 sec at the concentrations used by Burmeister and DeStefano. In order to obtain a quantitative measure of the reduction rate, a more detailed kinetic study was undertaken as reported here.

Experimental Section

The ((NH$_3$)$_5$CoNCO)(ClO$_4$)$_2$ used in this study was prepared from aquopentaamminecobalt(III) perchlorate and either urea in trimethyl phosphate or molten urea or urea in *N,N*-dimethylacetamide as described previously.[2] The compound from the molten urea preparation has been further purified by cation-exchange chromatography on Rexyn 102(H) in the sodium ion form. The visible spectrum of the chromatographed sample had maxima at 353 (ϵ 82.6) and 501 nm (ϵ 128) and an infrared spectrum with a characteristic maximum at 2265 cm^{-1}. The chromatographed material has extinction coefficients almost identical with those reported previously[2] but somewhat different from those reported by Burmeister and DeStefano.[1]

The rate of the chromium(II) reduction was followed spectrophotometrically at 500 nm using standard syringe techniques and temperature control apparatus as described previously.[3] The lithium perchlorate, perchloric acid, and chromous perchlorate solutions were prepared and standardized also as previously described.[3] The reduction was initiated by adding a degassed solution of cobalt complex to a solution of chromous perchlorate, HClO$_4$, and LiClO$_4$, at the appropriate concentrations and temperature, in a spectrophotometric cell.

Results and Discussion

The kinetics of the reduction were studied as a function of hydrogen ion and chromium(II) concentrations. The results are summarized in Table I. The concentration dependence of the rate is given by

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} = k_1[Cr^{2+}] + k_2[H^+] \qquad (1)$$

TABLE I

KINETIC DATA FOR THE REDUCTION OF (NH$_3$)$_5$CoNCO^{2+} BY CHROMIUM(II) (1 M LiClO$_4$–HClO$_4$)

Temp, °C	10^3[oxidant]^a	10^2[reductant]^a	10^2[HClO$_4$]^a	10^2k, sec^{-1} Obsd	10^2k, sec^{-1} Calcd^b
25	1.7	1.05	5.62	1.47	1.44
25	1.7	1.05	5.62	1.47	1.44
25	2.1	1.61	5.67	1.76	1.72
25	2.0	1.61	5.67	1.76	1.72
25	1.4	2.42	5.65	2.11	2.13
25	1.4	2.91	5.58	2.31	2.36
25	1.2	3.23	5.67	2.43	2.53
25	2.0	3.88	5.56	2.94	2.84
25	1.7	4.20	5.64	3.15	3.01
25	1.2	3.23	0.87	1.58	1.76
25	1.5	3.23	3.27	2.24	2.14
25	1.5	3.23	3.27	2.27	2.14
25	1.2	3.23	8.01	2.89	2.95
25	1.3	3.23	12.8	3.59	3.69
25	1.4	3.23	19.9	4.78	4.84
25	1.4	3.23	19.9	4.47	4.84
10	1.4	1.61	5.20	0.578	0.572
10	1.7	1.50	5.59	0.533	0.565
10	1.7	1.50	5.59	0.530	0.565
10	1.8	3.00	5.57	0.856	0.894
10	1.6	3.00	5.57	0.856	0.894
10	1.7	4.50	5.56	1.22	1.22
10	1.8	6.00	5.54	1.56	1.55

[a] Initial concentrations in molar units. [b] Calculated from eq 1 with $k_1 = 0.500\ M^{-1}\ sec^{-1}$ and $k_2 = 0.162\ M^{-1}\ sec^{-1}$ at 25° and with $k_1 = 0.22\ M^{-1}\ sec^{-1}$ and $k_2 = 0.042\ M^{-1}\ sec^{-1}$ at 10°. The activation parameters for k_1 are $\Delta H^* = 8.8$ kcal mol^{-1} and $\Delta S^* = -30.4$ eu, calculated from k_1 at 25 and 10°.

The results in Table I give $k_1 = 0.51\ M^{-1}\ sec^{-1}$ and $k_2 = 0.162\ M^{-1}\ sec^{-1}$ at 25° in 1 M LiClO$_4$–HClO$_4$, while at 10° $k_1 = 0.22\ M^{-1}\ sec^{-1}$ and $k_2 = 0.042\ M^{-1}\ sec^{-1}$.

It would seem most probable that the k_2 path, which

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(2) R. J. Balahura and R. B. Jordan, *ibid.*, **9**, 1567 (1970).

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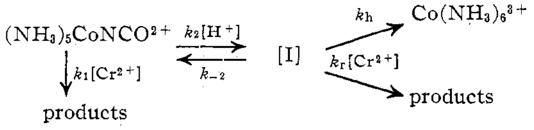
is independent of chromium(II), represents a hydrolysis reaction. A study of the hydrolysis reaction has been reported[2] and the reaction was found to yield $Co(NH_3)_6^{3+}$ as a product. However no $Co(NH_3)_6^{3+}$ has been found under the conditions used to study the kinetics of the reduction. It has also been found that 1 mol of chromium(II) is consumed for each mole of cobalt(III) even under conditions when the reaction proceeds 75% by the k_2 path.

Ion-exchange analysis of the chromium(III) product indicates that at least 75% is $(H_2O)_5$–$CrO_2CNH_2^{2+}$, when the reaction proceeds either 66 or 50% by the k_2 path. The chromium(III) product was identified by comparison of its visible spectrum to that of the product from reduction of $(NH_3)_5CoO_2CNH_2^{2+}$.[4] It seems likely that the 25% of product unaccounted for is hydrolyzed on the ion-exchange column to give $Cr(OH_2)_6^{3+}$.

The following reaction scheme will account for these observations under certain limiting conditions as discussed later



(2)

If a steady-state assumption is made for the concentration of the intermediate [I], then

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} =$$

$$\frac{k_1[Cr^{2+}](k_{-2} + k_h + k_r[Cr^{2+}]) + k_2[H^+](k_h + k_r[Cr^{2+}])}{k_{-2} + k_h + k_r[Cr^{2+}]} \quad (3)$$

If it is assumed that $(k_h + k_r[Cr^{2+}]) \gg k_{-2}$, then

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} = k_1[Cr^{2+}] + k_2[H^+] \quad (4)$$

Comparison of eq 1 and 4 shows that the proposed reaction scheme is consistent with the observed rate law.

It should also be noted that when $[Cr^{2+}] = 0$, *i.e.*, when only hydrolysis is being observed, then eq 3 reduces to

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} = \frac{k_2 k_h}{k_{-2} + k_h}[H^+] \quad (5)$$

If it is assumed that $k_h \gg k_{-2}$, then eq 5 gives

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} = k_2[H^+] \quad (6)$$

Therefore the rate constant obtained in the hydrolysis study[2] should agree with the value of k_2 obtained in the present work. In fact the values are in good agreement, being 0.162 M^{-1} sec^{-1} at 25° from both studies and 0.046 (by interpolation) and 0.042 M^{-1} sec^{-1} at 10° from the hydrolysis and reduction studies, respectively.

The failure to observe any $Co(NH_3)_6^{3+}$ product under the kinetic conditions used must be due to a high ratio of k_r to k_h. Reaction scheme 2, assuming steady-state conditions for [I] and also that $(k_h + k_r[Cr^{2+}]) \gg k_{-2}$, predicts the product ratio

$$\left\{\frac{[Co(NH_3)_6^{3+}]}{[Cr^{3+}]}\right\}_\infty = \frac{k_2 k_h[H^+]}{\{k_2 k_r[H^+] + k_1(k_h + k_r[Cr^{2+}])\}[Cr^{2+}]} \quad (7)$$

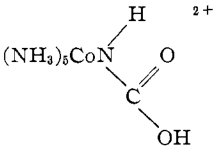
Rearrangement of eq 7 gives

$$\frac{k_r}{k_h} = \frac{\frac{k_2[H^+]}{[Cr^{2+}]}\left(\frac{[Cr^{3+}]}{[Co(NH_3)_6^{3+}]}\right)_\infty - k_1}{k_1[Cr^{2+}] + k_2[H^+]}$$

In a kinetic run with initial concentrations of 0.032 M Cr^{2+}, 0.20 M H^+, and 1.38×10^{-3} M $(NH_3)_5CoNCO^{2+}$, an upper limit of 3×10^{-4} M was placed on the amount of $Co(NH_3)_6^{3+}$ product.[5] Assuming that $[Cr^{3+}]$ equals the initial amount of $(NH_3)_5CoNCO^{2+}$, as indicated by the stoichiometry studies, then $k_r/k_h \gtrsim 60$. Since no buildup of intermediates was observed in the hydrolysis study, it can be concluded that k_h is at least 5 times greater than the maximum value of $k_2[H^+]$ in the hydrolysis study. Therefore $k_h \gtrsim 5$ (0.014) sec^{-1} and $k_r \gtrsim 4.2$ M^{-1} sec^{-1}.

The estimated value of k_r seems to be a reasonable lower limit for chromium(II) reduction through a simple bridging group. The Cr(II) reduction constants of the N-bonded formamide and O-bonded carbamate complexes are 1.7[3] and 2.4[4] M^{-1} sec^{-1}, respectively, at 25°.

The nature of the intermediate I has not been specified but it seems most probable that the acid-catalyzed hydration of cyanate would yield



This would decompose to $Co(NH_3)_6^{3+}$ in acidic solution and the N-bonded carbamate could serve as a good bridging group for electron transfer.

It should be noted that our previous work on other simple amide bridging ligands[3,4] would predict that the protonated form of the proposed intermediate, $(NH_3)_5CoNH_2CO_2H^{3+}$, would undergo slow reduction by chromium(II). It is therefore necessary to assume that the $-NH_2$ proton is quite acidic. This is not unreasonable in view of the fact that the analogous N-bonded formamide complex, $(NH_3)_5CoNH_2CHO^{3+}$, has a pK_a of ~2.2. The $-CO_2H$ group would be expected to increase the acidity of the carbamate complex relative to that of formamide.

It would be of interest to compare the rate of electron transfer through cyanate to the rate through other isoelectronic bridging groups. However it should be noted first that a mechanism other than simple bridging is available in the cyanate case. It is possible that the slow step in the reduction of $(NH_3)_5CoNCO^{2+}$ involves initial hydration of the coordinated cyanate by a water molecule in the hydration sphere of the chromium(II) ion. This would give a carbamate-bridged intermediate in which facile electron transfer could occur to

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[4] R. J. Balahura and R. B. Jordan, submitted for publication.

[5] The upper limit was established by the failure to detect any precipitate of $Co(NH_3)_6(ClO_4)_3$. Blank experiments indicate that a 3×10^{-4} M solution of $Co(NH_3)_6^{3+}$ in 1 M $LiClO_4$–$HClO_4$ gives a readily visible precipitate.

give $(H_2O)_5CrO_2CNH_2^{2+}$ as product. Admittedly this mechanism does not seem favorable compared to hydration by a free water molecule when reactant charges and the relative nucleophilicity of free and coordinated water molecules are considered. In any case, if hydration from the coordination sphere of another metal ion were operative, then metal ions should catalyze the hydrolysis of $(NH_3)_5CoNCO^{2+}$ to $Co(NH_3)_6^{3+}$. However no catalysis by aqueous copper(II) at pH 4 has been observed and it is concluded that this type of hydration is not important in the electron-transfer reaction with chromium(II).

It is concluded that the k_1 path for reduction of $(NH_3)_5CoNCO^{2+}$ involves a simple inner-sphere mechanism with $-NCO^-$ acting as the bridging ligand. The $(H_2O)_5CrOCN^{2+}$ formed initially must hydrate to give the observed product $(H_2O)_5CrO_2CNH_2^{2+}$.

The k_1 value can be compared to that for other isoelectronic bridging ligands. The rate constants (25°), with ΔH^* and ΔS^* values in parentheses, for the chromium(II) reduction of $(NH_3)_5CoN_3^{2+}$, $(NH_3)_5CoNCNH^{2+}$, $(NH_3)_5CoNCS^{2+}$, and $(NH_3)_5CoNCO^{2+}$ are $\sim 3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$,[6] $3.3 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ (4.3 kcal mol^{-1}, −28 eu),[4] 19 $M^{-1}\ \text{sec}^{-1}$ (6.9 kcal mol^{-1}, −29 eu),[6] and 0.5 $M^{-1}\ \text{sec}^{-1}$ (8.8 kcal mol^{-1}, −30 eu), respectively. The ΔS^* values are remarkably constant, indicating a common mechanism. It has been noted by Burmeister and DeStefano[1] that N-bonded cyanate is not likely to be a good bridging group because the negative charge of the ligand is largely localized on the nitrogen atom bonded to cobalt(III). Therefore the oxygen atom will not be very basic and will not form a very stable bridge to the reducing agent. This may explain the low rate for cyanate bridging.

It should be noted that the conclusions about charge density in the NCO^- ion are based on the theoretical calculations of Wagner[7] in which only the π system was considered. In fact pK_a correlations with the theory predict that HSCN should have a pK_a of 5.4, which is certainly not the case. Such a result should be cause for more caution than seems to have been the case in applying Wagner's results.[8]

In any case it may still be that the strength of the bridge to chromium(II) is largely responsible for the difference in reactivity of these complexes, as has been argued previously[9,10] for the $-N_3$ and $-NCS$ complexes. This factor would be consistent with the fact that the rate differences are primarily due to ΔH^* differences. However changes in the electronic energy levels of the ligands and the cobalt may also be important factors.

Acknowledgment.—The authors wish to thank the National Research Council of Canada for the financial support of this research and for scholarship support to R. J. B.

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The Microwave Spectrum of Trimethylamine–Boron Trifluoride. The Boron–Nitrogen Distance

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Received June 27, 1970

Very few donor–acceptor complexes between boron and nitrogen have been studied by microwave spectroscopy because they are often either very involatile or highly dissociated compounds.[1-3] Trimethylamine–boron trifluoride, however, is sufficiently volatile and is undissociated at 177°.[4] We have observed the spectra of three isotopic species and have determined the boron–nitrogen bond distance of the complex in the gas phase.

Prokhorov and Shipulo[2] have reported an average B value of 1750 MHz for this complex based on the observation of ten rotational transitions. They stated that the low J lines appeared as broad unresolved transitions. We have investigated the $J = 8 \rightarrow J = 9$ and the $J = 9 \rightarrow J = 10$ rotational transitions for $(CH_3)_3N \cdot BF_3$, $(CH_3)_3{}^{15}N \cdot BF_3$, and $(CH_3)_3N \cdot {}^{10}BF_3$ at sufficiently low pressures to resolve the broad bands into the typical pattern expected for a symmetric-top molecule. Each transition region consisted of an intense ground-state line and a number of weaker lines arising from rotational transitions in excited vibrational states. Although the vibrational satellite patterns were similar for both J regions in each isotopic species, no extensive attempt was made to measure and assign these transitions. At the pressures employed, line widths were reduced to half-widths of about 1 MHz. No splitting of the ground state was observed due to centrifugal distortion, boron quadrupole coupling, or methyl torsion.

Experimental Section

The transitions were measured at room temperature with a Stark-modulated spectrometer described previously.[5] The uncertainties in the frequency measurements were estimated as ±0.2 MHz. The assigned transitions and the average B values are listed in Table I. The effect of centrifugal distortion was small ($D_J \simeq 0.1 \pm 0.1$ kHz) and was neglected. The assignments were facilitated by the isotopic enrichment of the samples: $(CH_3)_3{}^{15}N \cdot BF_3$ was 90% ^{15}N and 99% ^{11}B; $(CH_3)_3N \cdot {}^{10}BF_3$ was

TABLE I

OBSERVED TRANSITIONS AND ROTATIONAL CONSTANTS (MHz)

$J \rightarrow J + 1$	$(CH_3)_3N \cdot BF_3$	$(CH_3)_3N \cdot {}^{10}BF_3$	$(CH_3)_3{}^{15}N \cdot BF_3$
8–9	31,609.35	31,675.94	31,529.18
9–10	35,121.42	35,195.38	35,032.40
B	1,756.073	1,759.772	1,751.621

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