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Kinetics of Chromium(II) Reduction of Nitrile-Bonded Cyanoacetate Complexes of Pentaamminecobalt(III)

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The chromium(II) reduction of cobalt(III) complexes of the type $(NH_3)_5CoNCCH_2R$, where R ≡ H, CH_2CN, CO_2CH_3, $CONH_2$, and CO_2H, have been studied. The rate law for the cyanoacetic acid complex has the form $(k_1[H^+] + k_2K_a)/(K_a + [H^+])$[cobalt(III)][chromium(II)]. The value of $k_1[H^+]$ was too small relative to k_2K_a to allow it to be accurately determined, but $k_2 = 2.1 \pm 0.1$ M^{-1} s^{-1} with $\Delta H_2^{\ddagger} = 12.5 \pm 1.1$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -15.2 \pm 3.6$ cal mol^{-1} deg^{-1}, and $K_a = 2.7 \times 10^{-2}$ M, all at 25 °C in 0.5 M $LiClO_4$–$HClO_4$. The k_2 path has been shown to produce a carboxylate-bound chromium(III) product and is assigned to have a bridged-outer-sphere mechanism. The other complexes are reduced without ligand transfer and have simple second-order rate constants independent of $[H^+]$. Results for the ester are typical with $k = 2.34 \pm 0.06 \times 10^{-2}$ M^{-1} s^{-1} (25 °C, 0.5 M $LiClO_4$–$HClO_4$), $\Delta H^{\ddagger} = 9.5 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -34.2 \pm 1.3$ cal mol^{-1} deg^{-1}.

Introduction

The chromium(II) reductions of several nitrile complexes of the general type $(NH_3)_5CoNCCH_2R$, where R ≡ H, CO_2H, $C(O)NH_2$, $C(O)OCH_3$, and CH_2CN, have been studied. Since adjacent attack at the nitrile function is not possible and there is a saturated CH_2 between the nitrile and R function, the results would be expected to reflect substituent effects on outer-sphere reactions. However, Sargeson and co-workers[1] have shown that the active methylene group in the cyanoacetate systems can lead to internal oxidation–reduction and electrophilic attack on these ligands. The active methylene might also influence the chromium(II) reduction reactions.

Experimental Section

Materials. All solutions for kinetic studies were prepared in deionized water redistilled from alkaline permanganate in an all-glass apparatus. Solutions of lithium perchlorate (Aldrich Chemical Co.) were filtered through a 0.22-μm Millipore filter (Millipore Corp.) and standardized by titration of the hydrogen ion eluted from Dowex 50W-X8 cation-exchange resin.

Chromium(III) perchlorate solutions were prepared by reduction of primary standard potassium dichromate (B.D.H., Ltd.) with hydrogen peroxide in perchloric acid.[2] The potassium perchlorate was removed by filtration on a 0.22-μm Millipore filter. The perchloric acid concentration was determined by pH titration with standardized sodium hydroxide after converting the chromium(III) to tris(oxalato)chromium(III) by treatment with sodium oxalate.

Chromium(II) solutions were prepared by reduction of chromium(III) solutions with amalgamated zinc. The chromium(II) content was determined by oxidation with ammonium ferric sulfate, and the excess iron(III) was determined iodometrically.

The cobalt(III) complexes were prepared from $[(NH_3)_5CoO_3SCF_3](O_3SCF_3)_2$ and the appropriate ligand in either acetone or tetramethylene sulfone (sulfolane)[3] containing 2–3 drops of trifluoromethanesulfonic acid. Crude product was isolated either by addition of the reaction mixture to about 600 mL of a 5:1 mixture of ether and *sec*-butyl alcohol or by addition of an equal volume of water followed by slow addition of perchloric acid. The products were purified by cation-exchange chromatography on Dowex 50W-X2 resin in the H^+ form, at 5 °C. The band of ion-exchange resin containing the desired product was separated physically and the product removed by treatment with 6 M hydrochloric acid. The solution was treated with perchloric acid and cooled to 0 °C to obtain the perchlorate salt, which was recrystallized from dilute perchloric acid. The characteristics of the electronic and proton NMR spectra are given in Table I. All samples gave satisfactory C:H:N analysis as shown by the following results.

Table I. Electronic and Proton Magnetic Resonance Spectral Properties of Nitrile Complexes of $(NH_3)_5Co^{3+}$

nitrile ligand	electronic spectrum[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	proton NMR, τ[b] trans NH_3	cis NH_3	other
$NCCH_3$	468 (60.4), 335 (52.6)[c]	6.71	6.26	7.46 (CH_3)
$NC(CH_2)_2CN$	467 (60.7), 333 (54.4)	6.63	6.23	6.73-7.16 (CH_2–CH_2)[d]
$NCCH_2CONH_2$	467 (63.3), 333 (58.4)	6.60	6.17	5.94 (CH_2); 2.50, 2.28 (NH_2)
$NCCH_2CO_2CH_3$	467 (64.3), 333 (58.9)	6.61	6.21	5.70 (CH_2); 6.30, (CH_3)
$NCCH_2CO_2H$	467 (69.5), 333 (62.5)	6.68	6.26	5.70 (CH_2)

[a] Recorded in 0.50 M $HClO_4$. [b] Recorded in Me_2SO-d_6 plus 1–2 drops of H_2SO_4. Shifts are relative to the residual solvent protons at τ 7.48. [c] These values are in reasonable agreement with those reported: Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* 1966, *5*, 1091. [d] Complex multiplet due to nonequivalent CH_2 groups.

Anal. Calcd for $((NH_3)_5CoNCCH_3)(ClO_4)_3$: C, 4.97; H, 3.75; N, 17.38. Found: C, 4.95; H, 3.63; N, 16.82. Calcd for $((NH_3)_5CoNCCH_2CH_2CN)(ClO_4)_3$: C, 9.19; H, 3.67; N, 18.76. Found: C, 9.14; H, 3.53; N, 18.74. Calcd for $((NH_3)_5CoNCCH_2CONH_2)(ClO_4)_3$: C, 6.84; H, 3.64; N, 18.62. Found: C, 6.60; H, 3.64; N, 18.18. Calcd for $((NH_3)_5CoNCCH_2CO_2CH_3)(ClO_4)_3$: C, 8.87; H, 3.72; N, 15.52. Found: C, 8.42; H, 3.55; N, 15.35. Calcd for $((NH_3)_5CoNCCH_2CO_2H)(ClO_4)_3$: C, 6.83; H, 3.44; N, 15.93. Found: C, 6.87; H, 3.40; N, 15.90.

The infrared spectra of all the complexes in Nujol mulls showed coordinated C≡N stretches in the 2325–2337-cm^{-1} region. The free nitrile in the succinonitrile complex was observed at 2260 cm^{-1}.

Acid Dissociation Constant of $((NH_3)_5CoNCCH_2CO_2H)^{3+}$. Spectrophotometric measurements were carried out at 260 nm at 14.6, 25.0, and 35.0 °C at an ionic strength of 0.50 M ($HClO_4$–$LiClO_4$). From 11 to 15 acidities in the range 0.0008–0.495 M were studied at each temperature. Observations were made in a 5-cm path length cell at a cobalt(III) concentration of 7.67×10^{-4} M and in one case at 25.0 °C and [cobalt(III)] = 2.39×10^{-3} M. The data were fitted by nonlinear least squares to the appropriate theoretical equation. At 14.6, 25.0, and 35.0 °C, the extinction coefficients (M^{-1} cm^{-1}) of the acidic and basic forms were found to be 35.4 and 113.4, 37.3 and 127.6, and 52.6 and 149.3, respectively. The values are temperature dependent because they are on the side of a charge-transfer band. The acid dissociation constants at 14.6, 25.0, and 35.0 °C are $(3.42 \pm 0.43) \times 10^{-2}$, $(3.58 \pm 0.27) \times 10^{-2}$, and $(3.53 \pm 0.34) \times 10^{-2}$ M, respectively.

Kinetic Measurements. All chromium(II) reductions were done in solutions deoxygenated with high-purity argon and handled by standard syringe techniques. Reactions were monitored at 467 nm on a Cary 219 spectrophotometer equipped with a water-circulating temperature-control system. Rate constants were calculated from the usual semilogarithmic plots of absorbance change vs. time. Such

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(1) Butler, D. G.; Creaser, I. I.; Dyke, S. F.; Sargeson, A. M. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 789.

(2) Nordmeyer, F. Ph.D. Thesis, Stanford University, 1967.

(3) Kupferschmidt, W. C.; Jordan, R. B., manuscript in preparation.

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Table II. Rate Constants and Activation Parameters for the Reduction of Nitrile Complexes of Pentaamminecobalt(III) by Chromium(II)

	10^2k, M^{-1} $s^{-1\,a,b}$			
temp, °C	$NCCH_3$	$NC(CH_2)_2$-CN	$NCCH_2$-$CONH_2$	$NCCH_2$-CO_2CH_3
25	0.943 (0.944)	2.54 (2.52)	2.61 (2.58)	2.34 (2.34)
35	1.73 (1.71)	4.35 (4.40)	4.25 (4.37)	4.07 (4.06)
45	3.04 (3.05)	7.72 (7.67)^c	7.40 (7.27)	6.96 (6.96)
$\Delta H^{\ddagger}$, kcal mol^{-1} ^{d}	10.3 ± 0.4	9.5 ± 0.4	9.0 ± 0.6	9.5 ± 0.5
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1} ^{d}	−33.1 ± 1.4	−34.1 ± 1.1	−35.6 ± 1.9	−34.2 ± 1.3

[a] Experimental rate constants are the average of four to six determinations at each temperature agreeing to within about 2% of each other. Reagent concentration ranges: [Co(III)], (1.12–6.02) × 10^{-3} M; [Cr(II)], (2.00–7.36) × 10^{-2} M; [H^+], 0.040–0.329 M; in 0.50 M $LiClO_4$-$HClO_4$. [b] Values in parentheses are calculated from the least-squares fit to the transition-state theory equation. [c] The temperature is actually 45.9 °C. [d] Errors quoted are 95% confidence limits and are about 3 times larger than 1 standard deviation.

Table III. Product Distribution from the Chromium(II) Reduction of Pentaamminecobalt(III) Cyanoacetate

reactant concn, M			prod distrib, %^{a,b}	
[H^+]	10^{-3} × [Co(III)]	10^{-2} × [Cr(II)]	$(H_2O)_5CrO_2$-CCH_2CN^{2+}	$NCCH_2$-CO_2^-
0.400	4.56	1.41	82.9 (86)	19.8 (14)
0.300	7.76	1.56	85.1 (89)	
0.300	7.78	1.58	85.7 (89)	
0.050	2.99	0.93	99.2 (98)	8.2 (2)

[a] Chromium(III) product was determined by ion-exchange separation and oxidation to CrO_4^{2-}. The free cyanoacetate was determined in the initial eluate from ion-exchange separation by the sulfanilic acid test. [b] Values in parentheses are calculated from the kinetic parameters and the proposed reaction scheme.

Table IV. Kinetic Data for the Reduction of N-Bonded (Cyanoacetato)pentaamminecobalt(III) by Chromium(II)^a

[H^+], M	10^3 × [Co(III)], M	10^2 × [Cr(II)], M	k_{obsd}, M^{-1} s^{-1}
0.445	0.84	1.01	0.147
0.375	1.43	2.02	0.167
0.299	1.69	3.01	0.199
0.240	1.43	2.02	0.236
0.200	0.84	1.01	0.274
0.141	1.69	2.03	0.354
0.102	2.03	4.25	0.465
0.0740	2.00	2.13	0.574
0.0500	0.84	1.01	0.739
0.0400	0.80	2.20	0.882
0.0300	0.42	1.01	1.03

[a] These are data representative of a total of 42 kinetic runs done on this system at 25 °C in 0.50 M $LiClO_4$-$HClO_4$.

plots were linear to more than 95% of reaction.

Product Analysis. After the reduction reaction was complete, the excess chromium(II) was air oxidized and the solution subjected to ion-exchange chromatography at 5 °C on Dowex 50W-X2. The free organic product was collected in the initial eluent, and the cobalt(II) and chromium(III) species were eluted with a solution of increasing concentration from 0.12 M $NaClO_4$ in 0.025 M $HClO_4$ to 0.50 M $NaClO_4$ in 0.10 M $HClO_4$. The electronic spectra of chromium-containing fractions were recorded and the chromium content was determined spectrophotometrically as CrO_4^{2-} (ϵ = 4815 M^{-1} cm^{-1} at 372 nm) after hydrogen peroxide oxidation.

The cyanoacetate ligands were determined by a modification of the procedure of Lovelady.[4] Two milliliters of aqueous sulfanilic acid (1.2 × 10^{-2} M in 0.36 M HCl) in a 10.0-mL volumetric flask was cooled in a refrigerator, and 0.20 mL of 1.2 M $NaNO_2$ was added. The solution was allowed to stand in the refrigerator for 10 min, and then it was treated with 1 mL of 6 M NaOH and an aliquot of the cyanoacetate solution. The solution at room temperature was diluted to 10 mL and the absorbance recorded at 490 nm, 2.5 min after adding the cyanoacetate. Tests showed that Beer's law was obeyed for up to 2.44 μg mL^{-1} of cyanoacetic acid and for up to 3.30 μg mL^{-1} of cyanoacetamide. Since the color is not very stable, the analyses were always done in parallel with solutions of known concentration. However, the results were quite reproducible from day to day if the same procedure was followed strictly. Since ethyl cyanoacetate is known to hydrolyze rapidly[5] in the basic conditions of the analysis, the methyl ester was assumed to be similarly reactive, and cyanoacetic acid standards were used for comparison in the ester analysis.

Results

Because of the kinetic differences, the reduction of the cyanoacetic acid complex will be described separately. For all other systems studied here, the rate law was found to be

$$-d[\text{cobalt(III)}]/dt = k[\text{cobalt(III)}][\text{chromium(II)}] \qquad (1)$$

The kinetic results for the acetonitrile, succinonitrile, cyanoacetamide, and methyl cyanoacetate are summarized in Table II.

Product analysis studies were carried out as described in the Experimental Section. The reaction of the cyanoacetamide complex (9.66 × 10^{-3} M) with chromium(II) (5.85 × 10^{-2} M) in 9.66 × 10^{-2} M perchloric acid for 66 min at 25 °C gave 95.3 ± 2.5% free ligand. A similar experiment (7.75 × 10^{-3} M cobalt(III), 3.72 × 10^{-2} M chromium(II), 0.100 M perchloric acid) at 5 °C for 8 h gave 96.5 ± 2.5% free ligand and 111% $Cr(OH_2)_6^{3+}$. The high chromium(III) yield is due to the production of some $Cr(OH_2)_6^{3+}$ during the air oxidation of the excess chromium(II). The electronic spectrum shows that the product is $Cr(OH_2)_6^{3+}$ with maxima at 575 and 407 nm and extinction coefficients of 13.3 and 15.6 M^{-1} cm^{-1}, respectively, in agreement with Laswick and Plane.[6]

Similar product results were obtained for the methyl cyanoacetate complex. The reaction of the ester complex (7.54 × 10^{-3} M) and chromium(II) (3.72 × 10^{-2} M) in 0.10 M perchloric acid for 162 min at 25 °C gave 106 ± 2.4% free ligand and 123% $Cr(OH_2)_6^{3+}$.

Product analysis was not attempted with the acetonitrile and succinonitrile systems because of the lack of a satisfactory method of analysis for these ligands. However, reduction of the succinonitrile complex (7.86 × 10^{-3} M) by chromium(II) (1.24 × 10^{-2} M) yielded 98% $Cr(OH_2)_6^{3+}$ as the sole chromium(III) product.

The reduction of the cyanoacetic acid complex is qualitatively faster than that of the four systems described above. Several product analysis studies showed that a dipositive chromium(III) product is formed. This species was separated from $Cr(OH_2)_6^{3+}$ by ion-exchange chromatography and was found to have absorbance maxima at 411 and 570 nm, with molar extinction coefficients of 22.4 and 22.3 M^{-1} cm^{-1}, respectively. This spectrum is essentially the same as that of $(H_2O)_5CrO_2CCH_3^{2+}$ [7] and serves to identify the product as $(H_2O)_5CrO_2CCH_2CN^{2+}$.

The product distribution for the cyanoacetate system was studied as a function of acid concentration with the results shown in Table III. The fraction of ligand-transfer product increases as the acidity decreases. The chromium(III) product

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(4) Lovelady, H. G. *Anal. Chem.* **1962**, *34*, 1344.
(5) Lienhard, G. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1965**, *87*, 3863.
(6) Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3564.
(7) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

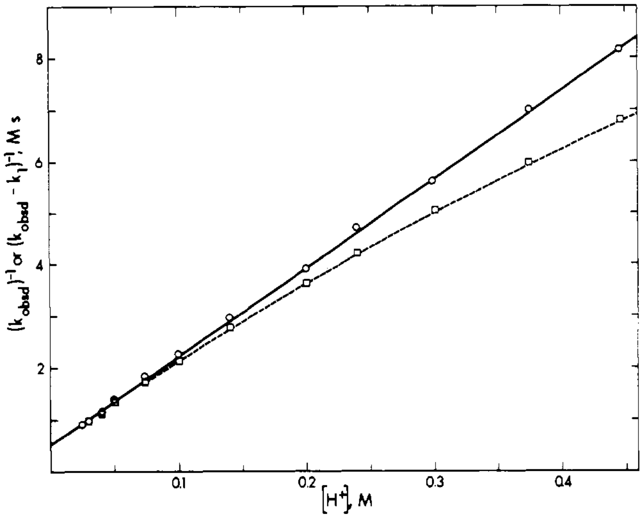


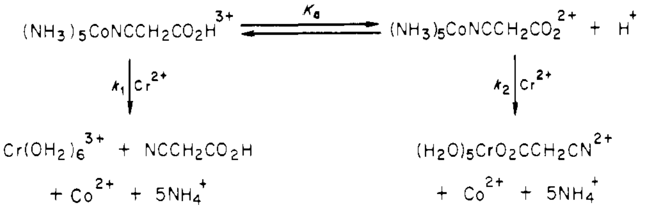
Figure 1. Variation of k_{obsd}^{-1} (□) and $(k_{obsd} - k_1)^{-1}$ (○) with $[H^+]$ for the reduction of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ by Cr^{2+} at 25 °C in 0.5 M $LiClO_4$–$HClO_4$. The value of $k_1 = 2.34 \times 10^{-2}$ M^{-1} s^{-1} was taken from the reduction of the ester complex. The dashed curve is an eye guide only.

is stable from the experimental conditions, so that the product variation with acidity represents the change in product from the reduction reaction.

The kinetic results for the chromium(II) reduction of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ at 25 °C are summarized in Table IV. The reaction is first order in oxidant and reductant, and the second-order rate constant (k_{obsd}) increases with decreasing $[H^+]$. However, a plot of $(k_{obsd})^{-1}$ vs. $[H^+]$ is not linear as shown in Figure 1. The direction of the curvature is consistent with the rate law

$$k_{obsd} = (a[H^+] + b)/(c + [H^+]) \qquad (2)$$

The plot should be linear if $a = 0$, but the magnitude of the curvature is not large enough to allow a realistic evaluation of "a". However, the form of the rate law and the product distribution results (Table III) are consistent with the reaction scheme given by eq 3. The dependence of the amount of ligand-transfer product, $(H_2O)_5CrO_2CCH_2CN^{2+}$, on acidity is attributed to only the unprotonated cobalt(III) complex reacting with ligand transfer.



(3)

The predicted rate law gives the second-order rate constant

$$k_{obsd} = (k_1[H^+] + k_2K_a)/(K_a + [H^+]) \qquad (4)$$

which has a form consistent with the experimental rate law (eq 2). Unfortunately, the value of k_1 ($=a$) cannot be established from the data, but the reaction scheme leads to the expectation that k_1 should be similar to the rate constant for the corresponding ester or amide complexes. These complexes have the same charge and similar structure and are reduced without ligand transfer to chromium. In addition, the ester and amide have very similar rate constants for reduction (Table II). If k_1 is assumed to be equal to the rate constant for reduction of the ester, then a plot of $(k_{obsd} - k_1)^{-1}$ vs. $[H^+]$ should be linear as shown in Figure 1. Since the k_1 correction to k_{obsd} is about 15% at most, it makes no real difference whether the ester or amide rate constants are used. With k_1 fixed at the values for the ester, a least-squares analysis of the data gives the values for k_2 and K_a shown in Table V.

Table V. Kinetic Results for the Reduction of N-Bonded (Cyanoacetato)pentaamminecobalt(III) by Chromium(II)[a]

temp, °C	$10^2 \times k_1$, M^{-1} s^{-1} [b]	k_2, M^{-1} s^{-1}	10^2K_a, M	
14.9	1.29	0.903 ± 0.053	3.02 ± 0.20	3.42 ± 0.43[c,d]
25.0	2.34	2.11 ± 0.10	2.73 ± 0.17	3.58 ± 0.27[c]
35.0	4.06	4.00 ± 0.35	2.81 ± 0.32	3.53 ± 0.34[c]
$\Delta H^\ddagger$, kcal mol^{-1} [e]		12.5 ± 1.1		
$\Delta S^\ddagger$, cal mol^{-1} deg^{-1} [e]		−15.2 ± 3.6		
ΔH°, kcal mol^{-1} [e]			−0.74 ± 1.4	
ΔS°, cal mol^{-1} deg^{-1} [e]			−9.6 ± 4.7	

[a] Errors quoted are 95% confidence limits. [b] Values for the reduction of the methyl ester complex, held constant during the data analysis. [c] Values obtained from the spectrophotometric study. [d] Value at 14.6 °C. [e] Values obtained by simultaneously fitting all the data at three temperatures.

The proposed reaction scheme and analysis can be tested by independently measuring K_a and by comparing the experimental product distribution to that predicted from the rate constants k_1 and k_2.

The experimental and predicted product distributions are compared in Table III. At least at the higher acidities, the predicted amount of ligand-transfer product is 3–4% greater than observed. The essentially quantitative recovery of ligand-transfer product at the lowest acidity indicates that product aquation and incomplete ion-exchange separation are not problems. Probably the observed differences are due to the uncertainty in k_1 and possibly to some reduction of the unprotonated complex by an outer-sphere path. If this outer-sphere path has the same rate constant as the ester, then the ligand-transfer percentage is lowered by about 1% at each acidity. In any case, the differences between observed and predicted values are rather small, and the results support the proposed reaction scheme.

Product studies at $[H^+] \leq 0.025$ M showed that some secondary reactions do occur. Preliminary studies indicate that some aquation is accompanied by formation of a more strongly absorbing species, which is suspected to be chelated malonic acid amide.

The acid dissociation constant of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ was determined spectrophotometrically as described in the Experimental Section. Unfortunately, the only significant difference in the spectra of the protonated and unprotonated forms occurs on the side of the charge-transfer band. At the wavelength used the absorbance of the protonated form is only moderately dependent on wavelength, but for the unprotonated form, the absorbance increases rapidly with decreasing wavelength. Although these are far from ideal conditions for a spectrophotometric analysis, the data can be fitted so that observed and calculated absorbances agree within 1%, to yield the values of K_a given in Table V.

The agreement between the spectrophotometric and kinetic K_a values (Table V) is considered satisfactory. The spectrophotometric values are about 20% larger, but the values at 14.9 and 35.0 °C agree within their respective 95% confidence limits. It should be noted that the spectrophotometric values are concentration constants, and comparison to the kinetic values involves the assumption that the ratios of the activity coefficients of the protonated and unprotonated forms remain

Table VI. Summary of Kinetic Parameters for the Reduction of Nitrile Complexes of Pentaamminecobalt(III) by Chromium(II)

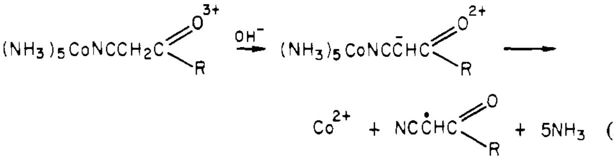
nitrile ligand	10^2k(25 °C),[a] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal $mol^{-1}\ deg^{-1}$
$NCCH_3$	0.94 (2.0)[b]	10.3 ± 0.4	−33.1 ± 1.4
$NC(CH_2)_2CN$	2.54	9.5 ± 0.4	−34.1 ± 1.1
$NCCH_2CONH_2$	2.61 (5.3)[e]	9.0 ± 0.6	−35.6 ± 1.9
$NCCH_2CO_2CH_3$	2.34	9.5 ± 0.5	−34.2 ± 1.3
$NCCH_2CO_2^-$	211	12.5 ± 1.1	−15.2 ± 3.6
cinnamonitrile[c]	2.2	8.8 ± 0.9	−37 ± 3
furanacrylonitrile[c]	2.0	9.5 ± 0.8	−34 ± 3
4-acetoxybenzonitrile[c]	2.1	9.1 ± 1.2	−36 ± 4
benzonitrile[d]	4.27		

[a] Values in 0.5 M $LiClO_4$-$HClO_4$ unless otherwise noted.
[b] Measured in 0.10 M $HClO_4$–0.90 M $LiClO_4$ at 25 °C; value agrees with that reported in 1.0 M $HClO_4$: Hua, L. H.-C.; Balahura, R. J.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* 1978, *17*, 3692.
[c] Purcell, W. L.; Balahura, R. J. *J. Am. Chem. Soc.* 1976, *98*, 4457.
[d] In 1.0 M $HClO_4$: Balahura, R. J.; Wright, G. B.; Jordan, R. B. *Ibid.* 1973, *95*, 1137. [e] Measured in ionic strength 1.0 M ($HClO_4$-$LiClO_4$).

constant as the medium is changed from essentially 0.5 M $HClO_4$ to 0.5 M $LiClO_4$.

Discussion

Nitrile complexes of pentaamminecobalt(III) are known to be very sensitive to base-catalyzed hydrolysis to the N-bonded amide complex.[8] The cyanoacetate complexes have additional reactivity toward base due to the active methylene group. Sargeson and co-workers[1] have shown that these systems can undergo electrophilic attack as well as intramolecular oxidation–reduction due to the reactions shown by eq 5. These reactions indicate that mild and acidic conditions would be preferable for preparation and purification of these cobalt(III) complexes. The reactivity of the starting material ($(NH_3)_5CoO_3SCF_3)(O_3SCF_3)_2$ and the use of trifluoromethanesulfonic acid have been particularly helpful in the preparation of these and other nitrile complexes.[3]



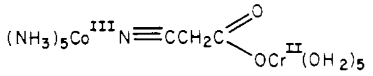
(5)

The spectroscopic properties of these complexes, summarized in Table I, show that d–d transitions on cobalt(III) are not sensitive to the substituents on the nitrile.

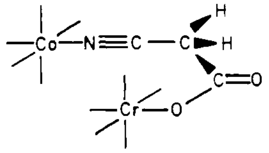
The acid dissociation constant of nitrile-coordinated cyanoacetic acid (3 × 10^{-2} M, 25 °C) is about 10 times larger than that of cyanoacetic acid (3.4 × 10^{-3} M, 25 °C).[9] There appears to be a greater increase in acidity when $(NH_3)_5CoNH_2CH_2CO_2H^{3}$ ($pK_a = 2.43$)[10] is compared to $NH_2CH_2CO_2H$ ($pK_a \approx 4.3$).[11]

The kinetic parameters for the chromium(II) reductions of a number of cobalt(III) nitrile complexes are given in Table VI. For many of these systems the rate constants are remarkably constant at ~2.3 × 10^{-2} $M^{-1}\ s^{-1}$ with correspondingly similar activation parameters. The benzonitrile complex will fit this pattern if the ionic strength effect is the same as that for the acetonitrile and cyanoacetamide complexes. All of the systems falling in this category are thought to be reduced by an outer-sphere mechanism, either from product studies or from a lack of remote substituents on the nitrile. Only the acetonitrile complex, with about a 2.5 times smaller rate constant and a 1 kcal mol^{-1} larger activation enthalpy, seems to deviate from this pattern for outer-sphere reduction.

Clearly the cyanoacetate anion complex differs from the pattern just described. The rate constant is about 100 times larger, and the reaction has been shown to proceed with ligand transfer to chromium(III). These results would imply the formation of a bridged intermediate such as


$$(NH_3)_5Co^{III}N{\equiv}CCH_2C{\overset{\displaystyle O}{\underset{\displaystyle OCr^{II}(OH_2)_5}{\lessgtr}}}$$

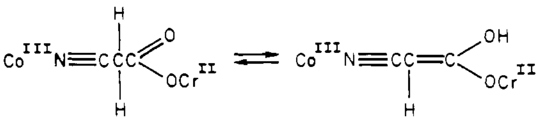
Such an intermediate is unusual in that it seems to require electron transfer through a saturated CH_2 group. However, this need not be the case when it is realized that the geometry of the bridged intermediate can be pictured as



This representation shows that the coordination spheres of cobalt(III) and chromium(II) can be in close contact in the bridged intermediate. Thus, electron transfer can occur by an outer-sphere mechanism within the bridged intermediate or by a bridged-outer-sphere mechanism.

A similar proposal has been made by Sykes et al.[12] for the chromium(II) reduction of $(NH_3)_5CoNH_2CH_2CO_2^{2+}$ and the analogous β-alanine complex. It is noteworthy that the rate constants for reduction of the glycine complex (2.5 $M^{-1}\ s^{-1}$)[12] and cyanoacetate complex (2.1 $M^{-1}\ s^{-1}$) are very similar. However, contrary to the assertions of Sykes et al., the reported electronic spectrum of the chromium(III) product, with maxima at 402 and 560 nm, does not correspond to that of $(H_2O)_5CrO_2CCH_2NH_3^{3+}$, which has maxima at 411–412 and 572–574 nm.[13,14] The product analysis experiment of Sykes et al. has been repeated in our laboratories to yield a product with maxima at 410 and 574 nm in reasonable agreement with results expected for $(H_2O)_5CrO_2CCH_2NH_3^{3+}$. We are unable to account for the observations of Sykes et al.[12]

The bridged-outer-sphere mechanism seems to be the simplest way to account for the observation with cyanoacetate and glycine. However, the active methylene group in the former presents an alternative via the tautomeric equilibrium



I II

Structure II has a conjugated system between the metal center to permit electron transfer through the organic ligand. It might be argued that this path is not effective because with the ester the oxygen atoms are not sufficiently basic to coordinate to chromium(II), and in the amide the expected proton transfer to oxygen[15] leaves the metal on the amide nitrogen not in conjugation with cobalt(III). However, this

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(8) Pinnell, D.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6104.

(9) Feates, F. S.; Ives, D. J. G. *J. Chem. Soc.* **1956**, 2798.

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(11) The value is based on the assumption that the amino group pK_a of $NH_3CH_2CO_2H^+$ is the same as that of $NH_3CH_2CO_2CH_3^+$. Intramolecular hydrogen bonding might make $NH_2CH_2CO_2H$ less acidic than expected from the cobalt(III) complex.

(12) Glennon, C. S.; Edwards, J. D.; Sykes, A. G. *Inorg. Chem.* **1978**, *17*, 1654.

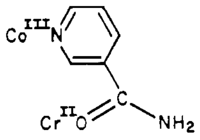
(13) Lane, R. H.; Sedor, F. A.; Gilroy, M. J.; Bennett, L. E. *Inorg. Chem.* **1977**, *16*, 102.

(14) Williams, R. D.; Pennington, D. E. *J. Coord. Chem.* **1978**, *7*, 187.

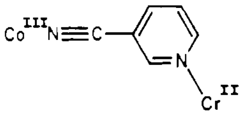
(15) Brown, R. S.; Tse, A. *J. Am. Chem. Soc.* **1980**, *102*, 5222 and references therein.

tautomerism is most unlikely with glycine because of the lack of activating organic groups, and it would not provide a conjugated system between metal centers because of the NH_2 group. In view of the great kinetic similarity of the glycine and cyanoacetate systems, the bridged-outer-sphere mechanism is the best way to rationalize the results.

The bridged-outer-sphere mechanism is difficult to distinguish from the inner-sphere mechanism, with electron transfer through the bridging group, because both result in ligand transfer to chromium(III). The outer-sphere path would only be expected when the substituent coordinated to chromium(II) is not in conjugation with the ligand atom bonded to cobalt(III) and when the bridged intermediate can attain a conformation in which chromium(II) and cobalt(III) have a normal outer-sphere interaction distance. Thus, the nicotinamide complex[16] was found to give 70% ligand transfer and could be using a bridged outer-sphere intermediate such as III. Presumably the cyanoacetamide complex does not do this because the amide group is much less basic and complex formation there is unfavorable. On the other hand, with 3-cyanopyridine (IV),[17] close contact of cobalt and chromium is not possible, and the observed 55% ligand transfer would seem to require electron transfer through the bridging ligand.



III



IV

Taube and Gould[18] observed that dicarboxylate bridging groups on cobalt(III) show an $[H^+]^{-1}$ term in the rate law for chromium(II) reduction only when there is potential for chelation between the remote and adjacent (to cobalt) carboxylates. But the chromium(III) products have extinction coefficients typical of monodentate carboxylate complexes. The ability to form a chelate with the adjacent carboxylate is tantamount to the ability to bring the remotely attached chromium(II) close to the cobalt(III). Thus, these observations could be explained by a bridged-outer-sphere mechanism without chelation in the transition state.

These few examples are just meant to illustrate some of the problems that the bridged-outer-sphere mechanism may raise and sometimes resolve.

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Registry No. $((NH_3)_5CoNCCH_3)(ClO_4)_3$, 15663-50-0; $((NH_3)_5CoNCCH_2CH_2CN)(ClO_4)_3$, 78128-40-2; $((NH_3)_5CoNCCH_2CONH_2)(ClO_4)_3$, 78128-42-4; $((NH_3)_5CoNCCH_2CO_2CH_3)(ClO_4)_3$, 78128-44-6; $((NH_3)_5CoNCCH_2CO_2H)(ClO_4)_3$, 77906-13-9; Cr^{2+}, 22541-79-3.

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Reaction between Epoxides and β-Diketonate Complexes of Low-Valent Vanadium and Molybdenum

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A series of epoxides were deoxygenated with the use of β-diketonate complexes of low-valent vanadium and molybdenum to give olefins and oxidized metallic species. Stereospecificity of deoxygenation was variable and was found to depend on the size of substituents on the oxirane ring and on the β-diketonate ligands. A mechanism is proposed for deoxygenation based on a metallooxetane intermediate.

Introduction

Deoxygenation of epoxides with the use of reagent systems obtained by reduction of metal halides is a subject of continuing interest in which attention has been focused historically on obtaining procedures attractive to the synthetic organic chemist.[1-10] The resulting lack of information concerning either the metallic starting materials or the metallic products in utilized reagents, however, hampers rational evolution of new systems of enhanced utility. We have therefore studied deoxygenation reagent systems in which at least partial characterization of critical metallic species and systematic modification thereof can be accomplished and in which trends can be discerned relating parameters of the metallic complex starting material to the specificity of deoxygenation. In this context we describe the reaction between epoxides and β-diketonate complexes of V(II) and Mo(II) which have been prepared with reference to known routes.

Experimental Section

Preparation of Starting Materials. Dichlorobis(β-diketonato)vanadium(IV) complexes were prepared according to published routes by reacting the corresponding bis(β-diketonato)oxovanadium(IV) compounds with thionyl chloride[11] or by reacting VCl_4 with β-diketones.[12] Dihalobis(β-diketonato)molybdenum(IV) species were obtained from $MoCl_5$ and β-diketones.[13] Treatment of $Cl_2(acac)_2V$

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[1] For example, see: Harrison, I. T.; Harrison, S. "Compendium of Organic Synthetic Methods"; Wiley-Interscience: New York, 1971; pp 502-504.

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