greater than about 5.5 and the electron transfer is very rapid, as is the case, for example, in the presence of azide and thiocyanate ions (and also when ferricytochrome *c* reacts with hydrated electrons[16,26]), the reaction proceeds predominantly by a remote pathway.

These conclusions must be regarded as tentative at this time and need to be confirmed with a larger variety of reducing agents. Particular attention will have to be paid to the various forms of ferricytochrome *c* and the rate at which equilibrium between these forms is established.

Acknowledgment. The authors wish to thank Dr. Keith Rowley for valuable discussions.

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(26) I. Pecht and M. Faraggi, *FEBS* (*Fed. Eur Biochem. Soc.*) *Lett.*, 13, 221 (1971).

Chromium(II) Reductions of Aromatic Nitrile Complexes of Pentaamminecobalt(III)

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Abstract: The kinetics of the reduction of the pentaamminecobalt(III) complexes of terephthalonitrile, and 3- and 4-cyanophenol have been studied. In all cases the rate law is $-\mathrm{d}\ln[\text{cobalt(III) complex}]/\mathrm{d}t = k[\mathrm{Cr(II)}]$. The rate constant ($M^{-1}$ sec^{-1}) at 25° in 1.0 M $HClO_4$-$LiClO_4$, the activation energy (kcal mol^{-1}), and activation entropy (cal mol^{-1} deg^{-1}) respectively are for the terephthalonitrile complex 0.92, 5.5 ± 0.3, −40 ± 2; for the 3-cyanophenol complex 4.17×10^{-2}, 9.4 ± 1.0, −34 ± 3; and for the 4-cyanophenol complex 2.96×10^{-2}, 11.1 ± 1.0, −28 ± 3. At 25° the rate constants (M^{-1} sec^{-1}) for reduction of the benzonitrile and 4-cyanobenzoic acid (nitrile bonded to cobalt) are found to be 4.27×10^{-2} and 0.28 M^{-1} sec^{-1}, respectively. The reaction proceeds with only 10–15% ligand transfer for the cyanophenol systems and with no detectable ligand transfer with terephthalonitrile. The variation in rates is considered to be inconsistent with a normal outer-sphere electron transfer mechanism and is explained by an outer-sphere nitrile ligand reduction mechanism.

Since the original observation by Taube, *et al.*,[2] that the reduction of some $(NH_3)_5Co^{III}X$ complexes by chromium(II) proceeds with transfer of the X ligand to the chromium(III) product, a wide range of X groups have been studied in this reaction. This work has been reviewed by Gould and Taube.[3] In the present investigation a series of aromatic nitrile ligands have been studied in the general reaction

$$((NH_3)_5Co^{III}N{\equiv}CC_6H_4Y)^{3+} + Cr^{2+} \xrightarrow{H^+} Co^{2+} + Cr^{3+} + N{\equiv}CC_6H_4Y + 5NH_4^+$$

It was of interest to determine if the reaction proceeded with ligand transfer and to determine how the rate and amount of ligand transfer varied with the Y substituent of the nitrile.

From the point of view of electron transfer these nitrile ligands have the advantage that the reducing agent cannot attack at the atom or group directly bonded to cobalt(III) since there are no free electron pairs available for bonding to the reducing agent. They are similar, in this respect, to the substituted pyridine systems[3] studied previously and differ from the carboxylic acid ligands.[3] The nitriles have the further advantage that their relative reducibilities have been systematized by polarographic studies.[4] The latter data may prove useful if ligand reduction is important in the electron transfer process.

Experimental Section

Aquopentaamminecobalt(III) perchlorate was prepared by slowly adding solid carbonatopentaamminecobalt(III) nitrate[5] to warm 1 M perchloric acid. The product was recrystallized twice from 1 M perchloric acid.

$(NH_3)_5Co$(terephthalonitrile)$(ClO_4)_3$. Terephthalonitrile (15 g), aquopentaamminecobalt(III) perchlorate (20 g), and Linde 3A molecular sieves (~20 g) were mixed in 200 ml of trimethyl phosphate (TMP). The mixture was heated on a steam bath for 3 hr. The orange solution was cooled, filtered, and mixed with 800 ml of *sec*-butyl alcohol. The product tended to separate as an oil which could be converted to solid by stirring with *sec*-butyl alcohol. The solid was slurried in methanol for 24 hr to remove any TMP complex. The product was recrystallized from warm water with added sodium perchlorate. Ion-exchange chromatography indicated that the product contained a small amount (<5%) of higher charged impurity suspected to be the symmetrical dimeric product. *Anal.* Calcd for $(NH_3)_5CoNCC_6H_4CN(ClO_4)_3$: C, 16.8; H, 3.33; N, 17.2. Found: C, 16.9; H, 3.29; N, 17.3.

$(NH_3)_5Co$(4-cyanophenol)$(ClO_4)_3$. Aquopentaamminecobalt(III) perchlorate (10 g), 4-cyanophenol (18 g), and Linde 3A molecular sieve (30 g) were mixed in 120 ml of TMP and heated on a steam bath for 45 min. The yellowish brown solution was cooled, filtered, and treated with 900 ml of *sec*-butyl alcohol. Precipitate formed and was collected by filtration and recrystallized from warm water and dilute perchloric acid. The freshly recrystallized material is bright yellow. However, during 1 week at room temperature the solid becomes yellowish brown and has a phenolic odor. The product can be stored in a refrigerator without apparent decomposition for several months. *Anal.* Calcd for $(NH_3)_5Co(NCC_6H_4OH)(ClO_4)_3$: C, 15.0; H, 3.56; N, 15.0. Found: C, 15.0; H, 3.46; N, 14.8.

This compound has also been prepared and purified by the procedure given for the 3-cyanophenol complex. The product had the

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(2) H. Taube, H. Myers, and R. L. Rich, *J. Amer. Chem. Soc.*, 75, 4118 (1953).

(3) H. Taube and E. S. Gould, *Accounts Chem. Res.*, 2, 231 (1969).

(4) O. Manousek, P. Zuman, and O. Exner, *Collect. Czech. Chem. Commun.*, 33, 3979 (1968).

(5) A. B. Lamb and K. J. Mysels, *J. Amer. Chem. Soc.*, 67, 468 (1945).

Table I. Wavelengths and Extinction Coefficients of Maxima in the Electronic Spectra of Aromatic Nitrile Complexes of $(NH_3)_5Co^{3+}$

Nitrile ligand	Medium	Wavelength, nm (extinction coefficient, M^{-1} cm^{-1})
Terephthalonitrile	H_2O	469 (78.5), 329 (86.5), 255 (1.89×10^4), 244 (2.33×10^4)
4-Cyanophenol	H_2O^a	473 (108), 295 (2.32×10^4)
	1 M $HClO_4$	472 (95.5), 257 (2.16×10^4)
3-Cyanophenol	H_2O^a	469 (80), 299 (2.8×10^3), 245
	1 M $HClO_4$	469 (79), 301 (3.53×10^3), 237 (1.33×10^4)
Benzonitrile	H_2O	469 (79), 330 (82), 233 (2.2×10^4)
4-Cyanobenzoic acid	1 M $HClO_4$	469 (80), 287 (2.74×10^3), 247 (2.36×10^4)

[a] The complex will be partially dissociated to the phenoxide form under these conditions.

same ultraviolet and visible spectra as those for the compound described above. *Anal.* Found: C, 14.8; H, 3.46; N, 15.0.

$(NH_3)_5Co(3\text{-cyanophenol})(ClO_4)_3$. Aquopentaamminecobalt(III) perchlorate (5 g), 3-cyanophenol (5 g), and Linde 3A molecular sieve (~15 g) were mixed in 50 ml of TMP. The mixture was heated on a steam bath for 50 min, when the initially red solution had turned yellowish brown. The solution was filtered and added to 800 ml of *sec*-butyl alcohol, and stirred for 15 min while the product precipitated. The precipitate was collected by filtration and recrystallized from a minimum of warm water and an equal volume of saturated sodium perchlorate solution. The product was collected by filtration, washed with ethanol, methanol, and ether, and air-dried.

The sample was purified further by ion-exchange chromatography on Rexyn 102 weak acid cation-exchange resin (Fisher Scientific Co.) in the sodium ion form. The sample was eluted with sodium chloride solutions of increasing concentrations from 0.1 to 0.8 M. The latter served to move the desired product down the column and the band of resin containing the product was separated physically and the resin collected on a filter. The resin was washed with water and then with warm 2 M perchloric acid to remove the product from the ion-exchange resin. An equal volume of saturated sodium perchlorate was added to the filtrate containing the product and the solution was cooled. The crystalline product was collected by filtration, washed with ethanol and ether, air dried, and stored in a refrigerator. *Anal.* Calcd for $(NH_3)_5Co(NCC_6H_4OH)(ClO_4)_3$: C, 15.0; H, 3.56; N, 15.0. Found: C, 15.1; H, 3.64; N, 15.1.

$(NH_3)_5Co(\text{benzonitrile})(ClO_4)_3$. This complex was prepared by the same method as used for the 3-cyanophenol complex and was purified by recrystallization twice from aqueous perchloric acid. *Anal.* Calcd for $(NH_3)_5Co(NCC_6H_6)(ClO_4)_3$: C, 15.4; H, 3.66; N, 15.4. Found: C, 15.3; H, 3.71; N, 15.1.

Reagents. All reagent solutions were prepared in water redistilled from alkaline permanganate in an all glass apparatus. Lithium perchlorate solutions were prepared and standardized as described previously.[6]

Chromous perchlorate solutions were prepared from electrolytic grade chromium metal and standardized as described previously.[6] Chromous solutions were stored and handled in an atmosphere of high-purity argon.

Ion-Exchange Separation of Reaction Mixtures. The ion-exchange separations were carried out with columns of Dowex 50W-X12 about 2 in. long and 10 mm in diameter maintained at 5° in a cold bath. The resin purification and elution procedures were as described previously.

Extinction coefficients of chromium(III) products are based on the total chromium concentration determined spectrophotometrically as chromate (ϵ 4815 M^{-1} cm^{-1} at 372 nm) after oxidation with alkaline hydrogen peroxide.

Determination of Ionization Constants. The acid dissociation constants of coordinated 3- and 4-cyanophenol were measured by potentiometric titration of a known weight of complex ($\sim 5 \times 10^{-4}$ M) in 20.0 ml of water with 0.010 M NaOH. Care was taken to exclude carbon dioxide by degassing the solutions with nitrogen and using a nitrogen atmosphere to protect the solution. The titrations were done with a Metrohm 1-ml buret and pH measurements were made on a Beckman Expandomatic pH meter with a 2 pH unit full-scale expansion. All titrations were carried out in a darkened room with the solution further protected from light by aluminum foil. The pK_a values reported are averages calculated as described by Albert and Sergeant.[7]

Kinetic Measurements. The rates of reduction of the cobalt(III) complexes were followed by observing the change in absorbance at the longest wavelength maximum of the cobalt(III) complex. The results were treated in the usual way[6] to obtain the observed rate constant. The kinetic runs were done on a Bausch and Lomb Precision spectrophotometer with the temperature control accessories described previously.[6]

Physical Measurements. The pmr spectra were obtained with a Varian A56/60 spectrometer. Molar extinction coefficients were measured on a Cary 14 spectrophotometer. The infrared spectra were recorded on a Perkin-Elmer 421 grating spectrophotometer.

Results

All of the complexes have been characterized by CHN analysis and by their infrared and pmr spectra. These results have been given in a previous publication[8] except for the terephthalonitrile which has characteristic infrared absorptions due to free and coordinated C≡N stretching vibrations at 2235 and 2290 cm^{-1}. The pmr of this complex shows resonance due to 12 cis NH_3 protons at τ 6.63 and that due to three trans NH_3 protons at τ 6.78 with the aromatic protons at τ 1.78. The characteristics of the electronic absorption spectra of all the compounds are recorded in Table I.

Proton Dissociation from Coordinated Cyanophenol. Potentiometric titrations have been used to measure the pK_a for the general reaction

$$(NH_3)_5CoN{\equiv}CC_6H_4OH^{3+} \rightleftharpoons (NH_3)_5CoN{\equiv}CC_6H_4O^{2+} + H^+$$

The calculated average pK_a values are 6.52 ± 0.1 for the 4-cyanophenol complex and 7.25 ± 0.1 for the 3-cyanophenol complex, compared to 7.97 and 8.57 for the free ligand.[9]

The titration curves for both complexes showed deviations from calculated curves in the high pH region beyond the equivalence point with the observed pH lower than the calculated value. The problem was more apparent with the 3-cyanophenol complex and resulted in some blurring of the end point. These observations are attributed to the hydrolysis of the nitrile to the corresponding carboxamide,[8] perhaps by higher localized concentrations of NaOH during the titration. Consistent pK_a values were obtained for points to within 15% of the equivalence point, but the possibility of some hydrolysis has led to the assignment of rather large uncertainties to the pK_a values.

It was also observed that the 4-cyanophenol complex is very susceptible to photolysis in solutions above pH ~6.2. The photolysis is evidenced by a deepening yellow color and a rise in pH of the solution. The

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(6) R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **93**, 625 (1971).

(7) A. Albert and E. P. Sergeant, "Ionization Constants of Acid and Bases," Wiley, New York, N. Y., 1962.

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

(9) P. D. Bolton and L. G. Hepler, *Quart. Rev., Chem. Soc.*, **25**, 521 (1971).

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

Ligand	Temp, °C	10^3 [Co(III)], *M*	10^2 [Cr(II)], *M*	[H$^+$], *M*	k_{obsd}, M^{-1} sec^{-1}
Terephthalonitrile	15.0	0.44	1.56	0.867	0.673
	15.0	0.71	1.73	0.131	0.670
	24.8	1.13	1.70	0.123	0.925
	24.8	1.08	3.20	0.246	0.922
	24.8	0.42	1.60	0.867	0.922
	24.8	0.49	1.60	0.867	0.904
	34.8	1.27	1.66	0.243	1.30
	34.8	1.08	3.20	0.246	1.27
	34.8	0.49	1.62	0.867	1.34
4-Cyanophenol	24.8	1.65	3.87	0.050	0.0290
	24.8	1.75	6.46	0.124	0.0318
	24.8	1.55	4.85	0.132	0.0301
	24.8	1.30	6.46	0.132	0.0287
	24.8	1.20	4.85	0.219	0.0294
	24.8	1.60	3.87	0.710	0.0288
	24.8	1.75	3.23	0.723	0.0280
	34.8	1.45	6.46	0.132	0.0577
	34.8	1.48	6.20	0.134	0.0570
	34.8	1.44	6.20	0.614	0.0581
	44.8	1.79	5.40	0.132	0.102
	44.8	1.87	2.70	0.134	0.102
3-Cyanophenol	25.0	1.50	4.10	0.05	0.0438
	25.0	1.07	4.30	0.30	0.0427
	25.0	1.17	2.00	0.30	0.0396
	25.0	1.22	3.40	0.35	0.0404
	25.0	1.03	3.40	0.35	0.0420
	35.0	1.24	3.20	0.05	0.0689
	35.0	1.10	1.90	0.30	0.0688
	35.0	1.20	2.00	0.30	0.0730
	35.0	1.21	4.20	0.30	0.0702
	35.0	1.46	3.10	0.35	0.0710
	45.0	1.07	3.20	0.05	0.124
	45.0	1.19	2.00	0.30	0.112
	45.0	1.26	4.40	0.30	0.131
Benzonitrile	25.0	1.55	7.63	1.00	0.0425
	25.0	1.55	3.98	1.00	0.0430
	25.0	1.55	3.80	1.00	0.0428

latter presumably is due to production of ammonia. To avoid this problem all titrations were done in a darkened room.

Chromium(II) Reductions. All the reactions were followed under pseudo-first-order conditions, with chromium(II) and hydrogen ion in large excess over the cobalt(III) complex. The results are consistent with the rate law

$$\frac{-\mathrm{d}\ln[\text{cobalt(III) complex}]}{\mathrm{d}t} = k_{\text{obsd}}[\mathrm{Cr}^{2+}]$$

The kinetic data for all the complexes are given in Table II.

Terephthalonitrile Complex. The rate constant at 25° and activation parameters, derived from the data in Table II, are given in Table III. The product analysis was carried out by air oxidizing the reaction solution at the completion of the reaction and subjecting it to ion exchange on Dowex 50W-X12 cation-exchange resin. Quantitative analyses of the ultraviolet spectrum of the eluent, with water as the eluate, showed that essentially all of the terephthalonitrile was present as the free ligand. The ligand is easily characterized by its ultraviolet spectrum, in water, with maxima at 235 nm (ε 1.80 × 10^3 M^{-1} cm^{-1}), 246 (2.85 × 10^4), 282 (1.80 × 10^3), and 291 (1.77 × 10^3). In a typical experiment a reaction mixture, which contained 0.027 *M* chromium(II), 1.4 × 10^{-3} *M* cobalt(III), and 0.182 *M* hydrogen ion, yielded 96% of the terephthalonitrile as free ligand in the product solution.

Several kinetic runs were performed in which the spectrum was scanned over the 300–700-nm region. Good isosbestic behavior was observed with no indication of any intermediate species.

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

Nitrile	*k* (25°), M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	σ_m or σ_p^- of remote group[a]
Terephthalonitrile	0.92	5.5 ± 0.3	−40 ± 2	0.91
4-Cyanophenol	2.96 × 10^{-2}	11.1 ± 1.0	−28 ± 3	−0.11
3-Cyanophenol	4.17 × 10^{-2}	9.4 ± 1.0	−34 ± 3	0.12
4-Cyanobenzoic acid[b]	0.28			0.73
Benzonitrile	4.27 × 10^{-2}			

[a] Values from P. R. Wells, *Chem. Rev.*, **63**, 171 (1963). [b] Detailed results on this system and its linkage isomer will be published elsewhere.

4-Cyanophenol Complex. The kinetic parameters for this system are summarized in Table III. Over the range of concentrations studied no hydrogen ion dependence of the rate could be observed.

The product analyses for free 4-cyanophenol was carried out as in the terephthalonitrile system. In water, free 4-cyanophenol has a maximum at 246 nm (ε 1.7 × 10^4 M^{-1} cm^{-1}) with shoulders at 270 and 280 nm. The results of the product analyses under various conditions are given in Table IV, and indicate that ~10% of the ligand is not released during the reaction.

Elution of the chromium(III) product from the ion-exchange column indicated a product with ion-exchange properties characteristic of a dipositive ion. This product was green and showed absorption maxima in the electronic spectrum at 610 nm (ε 16.0 M^{-1} cm^{-1}), 428 (20.2), and 246 (1.92 × 10^{-3}), with shoulders at about 270 and 280 nm. The latter three features are also found with free 4-cyanophenol. The spectrum and ion-exchange properties indicate that this product is the phenol complex $(H_2O)_5CrOC_6H_4CN^{2+}$.

Table IV. Ion-Exchange Analysis for 4-Cyanophenol Released in the Reaction of $(NH_3)_5CoNCC_6H_4OH$ with Cr(II)

Temp, °C	[H$^+$], *M*	10^3 [Co(III)], *M*	10^2 [Cr(II)], *M*	% free phenol recovered
25	0.050	1.28	4.06	89.6
25	0.050	1.65	3.87	85
25	0.050	3.80	1.14	92
25	0.087	11.9	3.75	83
25	0.710	1.6	3.87	91

A reasonably concentrated solution of this phenol complex was prepared by ion-exchange separation, after 90 min, of a reaction solution initially 0.03 *M* in chromium(II), 0.028 *M* in the cobalt(III) complex, and 0.18 *M* in hydrogen ion. The phenol complex was separated from $Cr(OH_2)_6^{3+}$ by elution with a solution of 2.5×10^{-3} *M* $HClO_4$ and 0.125 *M* $NaClO_4$ and finally eluted quickly from the column with a solution of 0.05 *M* $HClO_4$ and 0.25 *M* $NaClO_4$.

In order to investigate the kinetic properties of the phenol complex a sample was kept at 45° in 0.1 *M* $HClO_4$ for 25 hr. Ion-exchange treatment yielded 9% free 4-cyanophenol at the end of this period, indicating that the complex is quite stable hydrolytically.

In a separate experiment to determine if the chromium(III) phenol complex was susceptible to electron transfer catalyzed aquation, a solution containing 0.056 *M* chromium(II), 1.58×10^{-3} *M* $(H_2O)_5CrOC_6H_4CN^{2+}$, and 0.05 *M* hydrogen ion was equilibrated for 3 hr at 24.8. This solution was then air oxidized and subjected to ion exchange. Only 12% of the phenol was recovered as the free ligand indicating that the chromium(III) phenoxide complex is not rapidly aquated by an electron transfer mechanism.

3-Cyanophenol Complex. The kinetic parameters for this system are summarized in Table III. The rate of reduction showed no hydrogen ion dependence over the concentration range studied.

Preliminary product analysis experiments in this system indicated behavior similar to the 4-cyanophenol system, with about 10% ligand transfer. A more extensive study was made of the hydrogen ion and temperature dependence of the amount of ligand transfer to chromium(III). It was hoped that this might indicate the factors affecting ligand transfer. However, as can be seen from Table V no significant trends are observed. It seems that, as with 4-cyanophenol, two reaction paths with similar $\Delta H^{\ddagger}$ values are present, and that the proportion of the reaction proceeding with ligand transfer changes very little, if at all, with temperature.

Table V. Ion-Exchange Analysis for 3-Cyanophenol Released in the Reaction of $(NH_3)_5CoNCC_6H_4OH$ with Cr(II)

Temp, °C	$[H^+]$, *M*	10^3 [Co(III)], *M*	10^2 [Cr(II)], *M*	% free phenol recovered
25.0	0.05	1.14	4.10	88.1
25.0	0.68	1.07	4.00	91.5
35.0	0.05	1.25	3.00	88.2
35.0	0.05	1.23	3.00	88.9
35.0	0.30	1.26	3.20	88.4
35.0	0.30	1.08	4.10	90.5
35.0	0.30	1.10	1.90	90.0
35.0	0.30	1.07	4.30	86.2
35.0	0.30	1.19	4.30	82.3
35.0	0.30	1.17	2.00	80.4
35.0	0.30	1.20	2.00	95.1[a]
35.5	0.68	1.17	2.96	85.7
35.5	0.68	1.27	2.96	93.7
45.0	0.05	1.07	3.20	89.5
45.0	0.30	1.26	4.40	90.2
45.0	0.30	1.19	2.00	89.4
45.0	0.30	1.10	3.20	87.8
45.0	0.68	1.17	8.62	86.2
45.0	0.58	1.15	3.20	87.3

[a] The reaction mixture was ion exchanged 8 days after the reaction was completed. It was stored at room temperature during this time.

Benzonitrile Complex. This complex was studied only to test predictions made from the systems described previously. As a result only very limited kinetic data at 25°, as reported in Table II, have been obtained.

4-Cyanobenzoic Acid Complex (nitrile bonded). The rate law for reduction of this complex contains a dependence on the hydrogen ion concentration and is not well established at the present time. However we are able to report the rate constant for reduction of the protonated form of the complex from a number of runs at high acid concentration ($[H^+] = 0.5\text{–}1.0$), and this is given in Table III for comparative purposes.

Discussion

The results of the three systems studied in detail in this work would appear at first sight to be accounted for by an outer-sphere electron transfer mechanism, since the reactions were found to proceed mainly ($\gtrsim 85\%$) without ligand transfer to chromium(III). However, from a consideration of the rate constants and activation parameters in Table III, it can be seen that the results are not compatible with a simple outer-sphere mechanism. The problem is that an outer-sphere rate constant would not be expected to be greatly affected by substituents in the 3 and 4 positions on the aromatic ring. Since the $CoN{\equiv}C-$ linkage is expected to be linear no interference with the *cis*-amines would be expected. It should be noted however that this probably would not be true for ortho-substituted nitriles.[10] The 30% difference in rate constants between the 3-and 4-cyanophenol complexes seems incompatible with an outer-sphere reaction, and the factor of 30 greater rate constant for the terephthalonitrile complex is certainly outside the limits of change expected for an outer-sphere mechanism. It is also noteworthy that as the rate increases both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ decrease.

A trend in mechanism might be proposed in which case the lower $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for terephthalonitrile would be consistent with an inner-sphere mechanism.[11,12] However, no ligand transfer is observed with terephthalonitrile, but some at least is found with the 3- and 4-cyanophenol complexes. It seems unlikely that the terephthalonitrile chromium(III) complex hydrolyzes during the reduction reaction in view of the hydrolytic stability of the $(NH_3)_5Co(\text{benzonitrile})^{3+}$[13] and the general parallel between hydrolysis rates of the $(H_2O)_5CrX^{3+}$ and $(NH_3)_5CoX^{3+}$ systems. Similarly electron transfer catalyzed hydrolysis of $(H_2O)_5CrNCC_6H_4CN$ seems unlikely since $(H_2O)_5CrX^{3+}\text{–}Cr^{2+}$ electron transfer is generally much slower[11,14] than the corresponding $(NH_3)_5CoX^{3+}$–

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[10] Y. Wang and E. Gould, *J. Amer. Chem. Soc.*, **91**, 4998 (1969). These authors note that 2-substituted pyridines are reduced about 100 times as rapidly as the 3- and 4-substituted analogs *via* an outer-sphere mechanism. However, the rate differences among the 3- and 4-methyl- and 4-ethylpyridines are very slight in agreement with the above statements.

[11] F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

[12] J. K. Hurst and H. Taube, *ibid.*, **90**, 1118 (1968).

[13] The half-life for hydrolysis to $(NH_3)_5CoOH_2^{3+}$ is 400 min, at 50° in 1 *M* $HClO_4$.

[14] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 6.

Cr^{2+} reaction, but the possibility cannot be completely eliminated.

In view of the difficulties outlined above it seemed worthwhile to seek an alternative mechanism to explain the fact that the rate of reduction is quite sensitive to nitrile substituents but yields little ligand transfer product. A possibility, first considered by Taube,[15] is what might be called an outer-sphere ligand reduction mechanism. The essential feature of this mechanism is that the electron is transferred to the nitrile ligand without coordination of a remote group on the ligand to chromium(II). Such a mechanism would be favored by an "easily" reducible ligand[16] with a remote substituent which is not very basic toward chromium(II). In such a system it could be energetically more favorable to use the outer-sphere ligand reduction path than to break a chromium(II)–OH_2 bond and make a bond to the remote substituent.

If this mechanism is operative in the systems studied here then a correlation between nitrile reducibility and electron transfer rate would be expected. Zuman has found that the polarographic half-wave potentials for reduction of aromatic nitriles correlate reasonably well with the Hammett σ_m and σ_p^- [17,18] constants for meta and para substituent, respectively. If a constant effect of the $(NH_3)_5CoN{\equiv}C-$ substituent is assumed,[19] then a correlation of chromium(II) reduction rate and σ_m and σ_p^- should exist. The σ values and rate constants given in Table III are plotted in Figure 1 and show the expected correlation.

The observations can also be explained by considering the energy of the empty orbitals on the cobalt(III) rather than those on the ligand. The important factor is the energy matching of the donor and acceptor metal orbitals. Thus for a common reductant the energy of the lowest empty orbital on cobalt(III) measured relative to some common standard should parallel the rates of reduction. Since the T_{2g} level on cobalt(III) will be sensitive to π-bonding effects, the crystal field energy ($10Dq$) cannot be used as a measure of the energy of the lowest empty orbital. However, following the arguments of Bifano and Linck,[20] it follows that the basicity of the nitrile group for a given ligand would also be a relative measure of the energy of the lowest empty orbital on cobalt(III). Therefore one can predict that the most basic compound (the 4-cyanophenol complex) will react slowest and the least basic (1,4-dicyanobenzene complex) will react fastest. Indeed, using simple inductive effects to arrive at the basicity order for the ligands, 1,4-dicyanobenzene < 4-cyanobenzoic acid < benzonitrile < 3-cyanophenol < 4-cyanophenol, one can correctly predict the observed order for the rates of reduction.[21] Attempts to test the above two theories are currently being made.

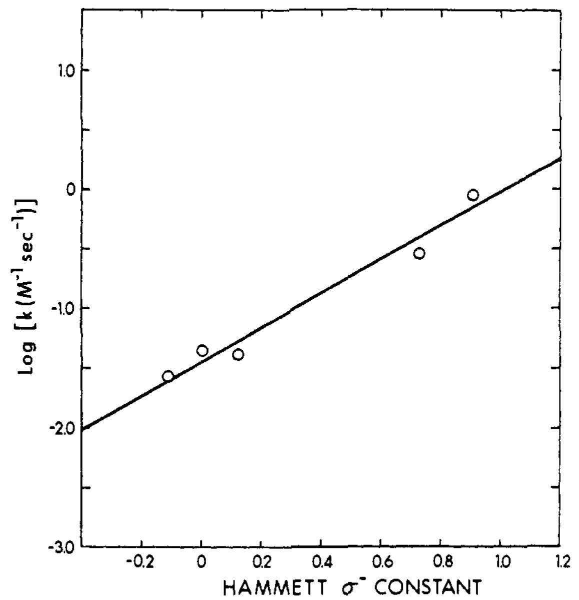

Figure 1. Variation of the logarithm of the rate of reduction by chromium(II) with σ_m or σ_p^- of the remote group for substituted aromatic nitrile complexes of pentaamminecobalt(III), T = 25°.

The product analysis results may be rationalized in terms of dual outer-sphere ligand reduction and inner-sphere ligand transfer mechanisms. The former is favored by more reducible nitrile ligands, while the latter is favored by lower reducibility and more basic remote substituents on the nitrile. The pK_a values for coordinated 3- and 4-cyanophenol measured in this work, and the σ values for OH and O^-, indicate that the –OH is more basic in the 3-cyanophenol complex and therefore it should give more ligand-transfer product on this basis. However, the 3-cyanophenol is also more easily reduced, judging from the σ value, and this factor would favor outer-sphere ligand reduction giving less ligand transfer product. These two factors may compensate in such a way as to make the amount of ligand-transfer with the two cyanophenol systems very similar.

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(15) H. Taube, *Pure Appl. Chem.*, **24**, 289 (1970).

(16) Chromium(II) did not reduce the ligands under the same conditions as the complex reductions were carried out. Also, studies on the terephthalonitrile complex (the most easily reduced ligand) showed that the stoichiometry of the reaction was one Cr(II) per one Co(III).

(17) The σ_p^- is a special constant proposed to take account of enhanced mesomeric effects, and determined from the pK_a of substituted phenols with ρ = 2.26 (see ref 18).

(18) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(19) This seems reasonable since coordination to $(NH_3)_5Co^{3+}$ increases the pK_a by ~1.4 units for both the 3- and 4- cyanophenol compared to the free ligands.

(20) C. Bifano and R. Linck, *J. Amer. Chem. Soc.*, **89**, 3945 (1967).

(21) We are indebted to Dr. R. G. Linck for suggesting this alternate explanation for our data.