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Contribution from the Department of Chemistry,
University of Guelph, Guelph N1G 2W1, Ontario, Canada

Kinetics of the Chromium(II) Reduction of *m*- and *p*-Acetylbenzonitrile Complexes of Pentaamminecobalt(III). Observation of a Chromium(III) Intermediate

ROBERT J. BALAHURA* and W. L. PURCELL

Received October 14, 1974		AIC40711K

The kinetics of the Cr(II) reduction of the pentaamminecobalt(III) complexes of *m*- and *p*-acetylbenzonitrile have been studied. In both cases, the rate law for reduction is $-d \ln [\text{complex}]/dt = k_{obsd}[Cr(II)]$. The kinetic parameters for the reaction are $k(25°) = 0.28 \pm 0.035$ and $(6 \pm 2) \times 10^3$ M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 3.2 \pm 0.7$ and -2.0 ± 1.5 kcal mol^{-1}, and $\Delta S^{\ddagger} = -50 \pm 2$ and -48 ± 5 eu for the meta and para complexes, respectively. An inner-sphere mechanism for the reduction of the para complex is indicated by the observation of a Cr(III) intermediate which rapidly aquates to give $Cr(OH_2)_6^{3+}$. The rate law for the aquation of the intermediate is $-d \ln [\text{intermediate}]/dt = (k' + k''[H^+]^{-1})[Cr(II)] + k'''[H^+]^{-1}$. At 25° the values for the rate constants are 420 ± 150 M^{-1} sec^{-1}, 6.8 ± 6.6 sec^{-1}, and 0.91 ± 0.13 M sec^{-1} for k', k'', and k''', respectively. The rate differences for the reduction process are explained by considering the conjugation of the carbonyl group with the aromatic ring and the various mechanisms available for transfer of the electron from reductant to oxidant.

Introduction

It has been pointed out that when attempting to assess the mechanistic details of the reduction kinetics of pentaamminecobalt(III) complexes $(NH_3)_5CoXR$, several potential advantages exist if X is a nitrile linkage, $-N{\equiv}C-$, vs. the corresponding carboxylato linkage, $-O-C(=O)-$.[1] In a recent study Taube and Zanella[2a] reported the observation of a carbonyl-bonded Cr(III) intermediate in the Cr(II) reduction of the *p*-formylbenzoato complex of pentaamminecobalt(III). In this study the interpretation of the results is complicated by the observation of a first-order hydrogen ion term in the rate law for reduction, as well as possible hydration of the remote formyl group. A similar Cr(III) intermediate has been reported in the Cr(II) reduction of the *p*-formylcinnamato complex of pentaamminecobalt(III).[2b] Here again a strong first-order hydrogen ion term is present in the reduction rate expression. We wish to report a study of the Cr(II) reduction of the *m*- and *p*-acetylbenzonitrile complexes of pentaamminecobalt(III), the MAB and PAB complexes, respectively. We were interested primarily in seeing if similar intermediates were produced with either or both of the nitrile complexes and what effects the position of ring substitution has on the rate of electron transfer. This system is potentially simpler than the carboxylato systems mentioned above since it has been shown that hydration does not occur for the remote acetyl group. We also expected that the rate law would be independent of hydrogen ion concentration.[1]

Experimental Section

Reagents. All reagent solutions were prepared in water doubly distilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate stock solutions were prepared using G. F. Smith anhydrous reagent grade $LiClO_4$ and filtered through a 0.5-μ Millipore filter. The solutions were standardized by charging an aliquot onto an ion-exchange column of Amberlite IR-120(H) cation-exchange resin and titrating the $HClO_4$ liberated from the column with standard NaOH to a Bromothymol Blue end point.

Perchloric acid stock solutions were prepared from G. F. Smith double-vacuum-distilled 70% $HClO_4$. The solutions were standardized with standard base.

Chromium(II) perchlorate solutions were prepared by reduction of solutions of G. F. Smith chromium(III) perchlorate with zinc amalgam. Chromium(II) concentrations were determined every few days by a titration procedure described previously.[3] Solutions were stored under an atmosphere of high-purity argon.

Cobalt(III) Complexes. The preparation, purification, and characterization of the PAB complex has been described elsewhere.[4] The MAB complex was prepared and purified in an analogous fashion. The complex was identified as the nitrile-bonded $[(NH_3)_5CoNCC_6H_4COCH_3](ClO_4)_3$.

Anal. Calcd for $C_9H_{22}N_6Cl_3O_{13}Co$: C, 18.40; H, 3.77; N, 14.30. Found: C, 18.40; H, 4.06; N, 14.40.

Infrared spectrum: CN stretch, 2235 cm^{-1} (free ligand), 2300 cm^{-1} (complex); CO stretch, 1690 cm^{-1} (free ligand), 1685 cm^{-1} (complex).

Visible spectrum: λ_{max} 468 nm; molar extinction coefficient 75.9 M^{-1} cm^{-1}.

NMR spectrum: methyl protons, τ 7.40; trans ammines, τ 6.75; cis ammines, τ 6.15; aromatic protons, τ 1.82 (center of multiplet).

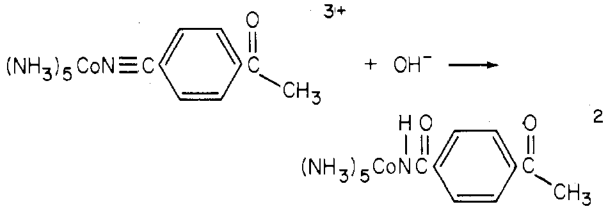
Kinetic Measurements. Solutions for kinetic studies were deoxygenated using high-purity argon. Due to the facile base hydrolysis of cobalt(III) nitrile complexes,[4,5] these solutions were prepared just prior to use in acidic solution.

The rates of reduction of the cobalt(III) complexes were measured by observing the change in absorbance due to the disappearance of the complex at both 280 and 470 nm. Kinetic runs for the MAB complex system were performed on a Beckman Acta CIII spectrophotometer equipped with a Thermistemp Model 73 temperature controller from Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. Kinetic runs for the PAB complex were carried out on a Durrum Model D-110 stopped-flow spectrophotometer.

Treatment of Kinetic Data. All kinetic runs were carried out under pseudo-first-order conditions using an excess of Cr(II) reductant. Under these conditions the rate of reduction of the MAB complex was obtained from plots of log ($A_t - A_\infty$) vs. time where A_t is the absorbance at time t and A_∞ is the absorbance after reaction is complete. The reaction of Cr(II) with the PAB complex can be treated as a two-step series reaction with pseudo-first-order rate constants k_1 and k_2 for the reduction of the cobalt(III) complex and the aquation of the Cr(III) intermediate, respectively (see Results). After correction of the experimentally determined absorbancies for background Cr(II) contributions, A_t is described by the expression given by Nordmeyer[6] (eq 2). Unknown parameters in eq 2 were determined with a nonlinear least-squares program[7] based on an algorithm developed by Marquardt.[8] Error limits reported in the text are ±1σ determined by least-squares analysis.

Results

It is important to establish the mode of coordination of the complexes in order to interpret the kinetic data. Physical evidence has been presented previously[4] to indicate that the complexes are bonded to cobalt(III) via the nitrile nitrogen. The best criterion for proof of nitrile bonding is the fact that both complexes undergo facile base hydrolysis to form a coordinated carboxamide



If the complex were bonded via the carbonyl oxygen this reaction would not occur under mild conditions.[4]

Hydration. The possibility of hydration of the carbonyl group to the *gem*-diol exists for both the MAB and PAB complexes. However, no evidence for the existence of hydrate was encountered in the kinetic studies reported herein. This conclusion was further confirmed with the PAB complex by a study of the NMR spectrum of the chloride salt in D_2O and D_2O–DCl.

Products. The products of the reaction of Cr(II) with the complexes of both MAB and PAB were determined by the reaction of 1:1 mole ratios of Cr(II) and complex. The reaction mixtures were then separated by cation-exchange chromatography, and in each case only one Cr(III) product was observed. The Cr(III) band was eluted and characterized by its visible spectrum, and the chromium concentration was determined as chromate. In each case, the product isolated was $Cr(OH_2)_6^{3+}$.

The MAB System. Due to the solubility properties of the perchlorate salt of this complex, the reduction kinetics was studied at an ionic strength of 0.5 instead of the more usual 1.0. Ionic strength was controlled with $HClO_4$ and $LiClO_4$. The results obtained at both 470 and 280 nm were identical within experimental error. The rate of reduction was independent of H^+ concentration in the range 0.05–0.4 *M* $HClO_4$. The disappearance of complex obeys the rate law

$$\frac{-\mathrm{d}\ln[\text{cobalt(III) complex}]}{\mathrm{d}t} = k_{\text{obsd}}[\text{Cr(II)}] \qquad (1)$$

The rate data are given in Table I. The enthalpy and entropy of activation were determined from studies at 25, 35, 40, and 45°. Table II presents a summary of rate parameters for this as well as the PAB system.

The PAB System. This complex proved to be more insoluble than its meta isomer, precluding the possibility of ionic strength control for studies at 470 nm. However, a few studies were performed at this wavelength without ionic strength control. These studies indicated a very rapid rate of reduction (a rate constant of approximately 5000 M^{-1} sec^{-1}) with essentially no acid dependence.

Table I. Kinetic Data for the Reduction of the *m*-Acetylbenzonitrile Complex of Pentaamminecobalt(III) by Chromium(II)

Temp, °C	10^3[Co-(III)], *M*	10^3[Cr-(II)], *M*	[H$^+$], *M*	k_{red}, M^{-1} sec^{-1}	λ, nm
25.0	0.33	20	0.40	0.380	280
25.3	0.33	10	0.050	0.217	280
25.3	0.11	20	0.050	0.284	280
25.3	0.11	20	0.10	0.256	280
25.3	0.33	30	0.050	0.265	280
25.3	0.33	40	0.050	0.286	280
25.3	0.33	40	0.050	0.275	280
25.6	0.11	19	0.050	0.357	280
35.0	1.0	40	0.10	0.385	470
35.0	1.0	50	0.10	0.364	470
35.2	0.33	10	0.023	0.320	280
35.2	0.33	20	0.050	0.315	470
39.5	1.0	10	0.10	0.385	470
39.5	1.0	10	0.10	0.350	470
39.5	1.0	20	0.10	0.310	470
39.5	1.0	20	0.10	0.350	470
39.5	1.0	40	0.10	0.412	470
39.5	1.0	40	0.10	0.372	470
44.6	1.0	10	0.10	0.428	470
44.6	1.0	30	0.10	0.470	470
44.6	1.0	40	0.10	0.445	470

Table II. Summary of Kinetic Parameters for the Chromium(II) Reduction of *m*- and *p*-Acetylbenzonitrilepentaamminecobalt(III)

Complex	$k(25°)$, M^{-1} sec^{-1} (ionic strength 0.5)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
m-Acetylbenzonitrile	0.28 ± 0.035	3.2 ± 0.7	−50 ± 2
p-Acetylbenzonitrile	(6 ± 2) × 10^3 [a]	−2.0 ± 1.5	−48 ± 5

[a] The large error limits are due mainly to the large number of experimental runs performed at low acid concentrations where the second reaction becomes fast enough to interfere with the accurate determination of rate constants for the first reaction. Such experiments were necessary in order to determine the rate law for the second reaction. The rate constants for the first reaction determined from these experiments, however, were included in our tables and calculations in order to represent honestly our experimental results.

At 280 nm complex concentrations were reduced and the ionic strength was controlled to 0.5. The stopped-flow traces at this wavelength, however, indicated the existence of two reactions. Traces showed a rapid rise in absorbance on a time scale roughly equivalent to that observed at 470 nm followed by a slower absorbance decrease. Similar behavior was reported by Taube and Zanella[2a] in the uv region for the *p*-formylbenzoatopentaamminecobalt(III) reaction with Cr(II) and is consistent with the formation of a Cr(III) carbonyl-bonded intermediate (the rise in absorbance) followed by the aquation of this intermediate to $Cr(OH_2)_6^{3+}$ (the decrease in absorbance). Under the pseudo-first-order conditions employed in these studies, such a reaction sequence can be treated as an

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

system where A corresponds to the PAB–Co$^{\text{III}}$ complex, B to the Cr(III) intermediate, and C to the final products. The absorbance, $A_{\lambda,t}$, of a solution containing A, B, and C at any time t and at wavelength λ is given[6] by

$$A_{\lambda,t} = A_{\lambda,\infty} + [\mathrm{A}]_0\left[\epsilon_{\mathrm{A},\lambda}e^{-k_1t} + \epsilon_{\mathrm{B},\lambda}\frac{k_1}{k_2-k_1}\times (e^{-k_1t}-e^{-k_2t}) + \epsilon_{\mathrm{C},\lambda}\frac{1}{k_1-k_2}(k_2e^{-k_1t}-k_1e^{-k_2t})\right] \qquad (2)$$

where $[\mathrm{A}]_0$ is the concentration of A at time $t = 0$, and $\epsilon_{\mathrm{A},\lambda}$, $\epsilon_{\mathrm{B},\lambda}$, and $\epsilon_{\mathrm{C},\lambda}$ are the molar extinction coefficients for species A, B, and C, respectively, at wavelength λ. Equation 2 applies for a cell of unit path length containing only A at $t = 0$.

Utilizing eq 2 in a nonlinear least-squares program (see

Table III. Kinetic Data for the Reduction of the *p*-Acetylbenzonitrile Complex of Pentaamminecobalt(III) by Chromium(II)

Temp, °C	10^3[Co(III)], M	10^3[Cr(II)], M	[H$^+$], M	k_{red}, M^{-1} sec^{-1}	k_2, sec^{-1}
15.0	0.054	5.0	0.020	6,500	20.3
15.0	0.048	10	0.020	5,310	26.7
15.0	0.044	10	0.050	6,630	13.4
15.0	0.034	20	0.050	7,850	17.9
15.0	0.051	30	0.10	9,600	16.7
15.0	0.051	40	0.20	10,600	20.8
15.2	0.050	30	0.10	7,330	
15.2	0.050	40	0.10	9,880	
25.2	0.058	4.4	0.05	4,650	20.0
25.2	0.058	4.4	0.05	4,990	18.5
25.2	0.058	8.7	0.015	8,180	67.4
25.2	0.058	8.7	0.015	4,740	41.6
25.2	0.058	8.7	0.020	5,520	50.6
25.2	0.058	8.7	0.020	5,370	51.4
25.2	0.058	8.7	0.025	5,750	42.6
25.2	0.058	8.7	0.050	6,490	20.3
25.2	0.058	8.7	0.050	6,690	20.6
25.2	0.058	8.7	0.22	7,170	9.27
25.2	0.058	10	0.20	3,960	5.10
25.2	0.058	22	0.010	6,040	132
25.2	0.058	22	0.010	6,040	141
25.2	0.058	22	0.025	4,270	57.5
25.2	0.058	22	0.025	5,710	80.7
25.2	0.058	22	0.050	7,650	26.6
25.2	0.058	30	0.014	2,150	64.6
25.2	0.058	30	0.20	4,500	20.5
25.2	0.058	30	0.20	3,800	15.1
25.2	0.058	37	0.017	10,500	65.7
25.2	0.058	37	0.050	8,000	34.4
25.2	0.058	37	0.050	7,270	37.8
25.2	0.058	50	0.023	8,560	73.5
25.2	0.058	50	0.20	6,000	40.3
25.2	0.058	50	0.20	3,640	24.9
34.5	0.038	5.0	0.020	5,220	87.0
34.5	0.11	5.0	0.10	7,060	17.5
34.5	0.13	10	0.020	7,170	78.1
34.5	0.065	10	0.050	6,800	33.3
34.5	0.061	20	0.050	7,250	42.2
34.5	0.098	20	0.20	6,300	22.1
34.5	0.085	30	0.025	8,730	80.8
34.4	0.13	40	0.050	6,220	76.5

Experimental Section) values for k_1, the rate constant for reduction, were obtained which proved to be independent of H$^+$ concentration in the range 0.01–0.22 M HClO$_4$. The rate law for the reduction process is identical with that given by eq 1. The kinetic data are given in Table III. The enthalpy and entropy of activation were determined from studies at 15, 25, and 35°. The rate parameters are summarized in Table II along with those for the MAB system.

The Chromium(III) Intermediate. The analysis of eq 2 yielded values of k_2, the rate constant for aquation, and $\epsilon_{B,\lambda}$ as well as k_1, the rate constant for reduction. An analysis of k_2 under varying conditions (HClO$_4$ concentrations from 0.01 to 0.22 M and Cr(II) concentrations from 0.0044 to 0.05 M) yielded a rate law for decay of

$$-\frac{d \ln [\text{intermediate}]}{dt} = (k' + k''[\text{H}^+]^{-1})[\text{Cr(II)}] + k'''[\text{H}^+]^{-1} \tag{3}$$

At 25.2° the values obtained for k', k'', and k''' were 420 ± 150 M^{-1} sec^{-1}, 6.8 ± 6.6 sec^{-1}, and 0.91 ± 0.13 M sec^{-1}, respectively. It should be pointed out that, based upon the 25.2° data alone, the necessity of the k'' term in the rate law is marginal. However, the importance of this term is large enough at 15° to necessitate its inclusion (k'' at 15° equals 10 ± 5 sec^{-1}). Temperature studies were not conclusive enough to allow calculation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the k' and k'' processes. However, for the k''' process, values of 12.8 ± 1.8 kcal mol^{-1} for $\Delta H^\ddagger$ and −16 ± 6 eu for $\Delta S^\ddagger$ were obtained. Values of $\epsilon_{B,\lambda}$ were obtained at various wavelengths in the uv region permitting the construction of the spectrum of the intermediate. The intermediate shows a maximum at 278 nm with a molar extinction coefficient of approximately 24,000 M^{-1} cm^{-1} (see Figure 1).

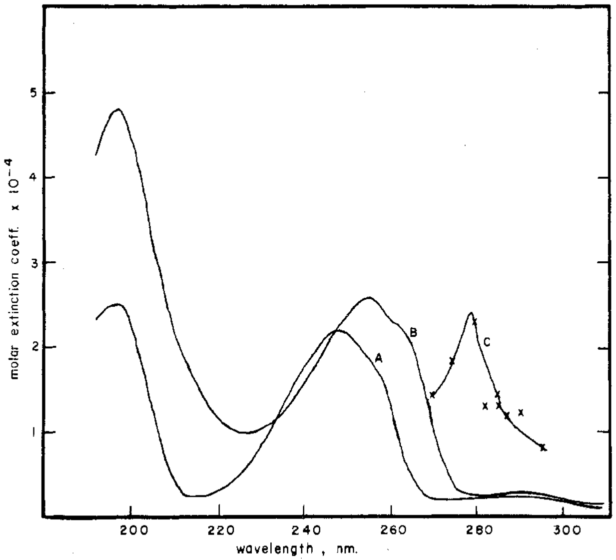
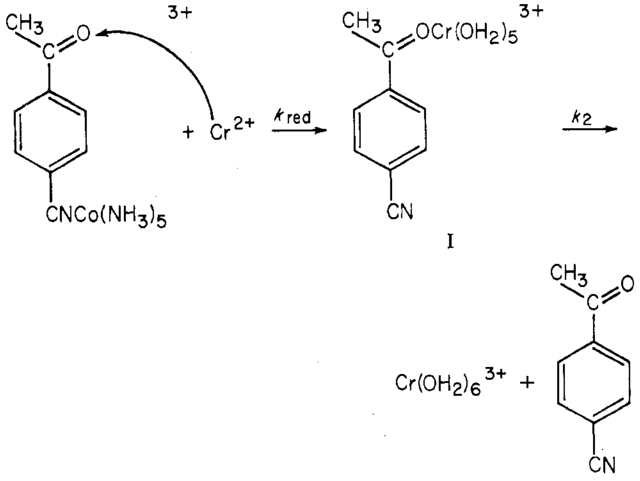


Figure 1. Electronic spectra in aqueous solution: A, PAB ligand; B, pentaamminecobalt(III) complex with PAB (nitrile bonded); C, chromium(III) intermediate I. ×'s denote experimentally determined molar extinction coefficients.

Discussion

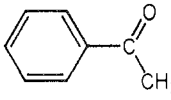
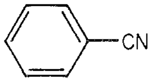
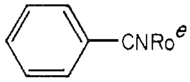
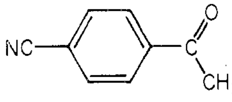
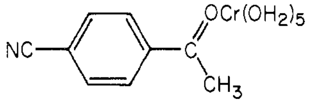
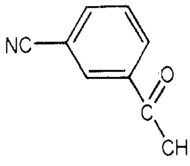
The kinetic data for the reduction of the PAB complex are consistent with a "remote" attack mechanism as shown below



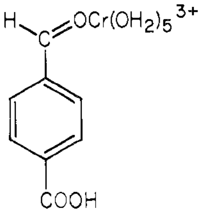
I

Intermediate I seems reasonable on the basis of the stopped-flow results described previously. The results obtained here are similar to those obtained for the chromium(II) reduction of *p*-formylbenzoatopentaamminecobalt(III)[2a] and *p*-formylcinnamatopentaamminecobalt(III),[2b] where the intermediates II and III were observed spectroscopically. In the latter systems the reduction is complicated by a first-order hydrogen ion term in the rate law. The electronic spectra of the PAB ligand, its Co(III) nitrile-bonded complex, and I may be compared in Figure 1. The band at 248 nm for the ligand is shifted to approximately 278 nm for I. This band is attributed to the transition from a predominantly ring π orbital to the lowest unoccupied π^* orbital on the carbonyl group and for this reason has been called an intramolecular charge-transfer band.[9] Other authors have referred to this as a K band.[10] It is well documented that the K band in acetophenone and various substituted acetophenones exhibit a pronounced

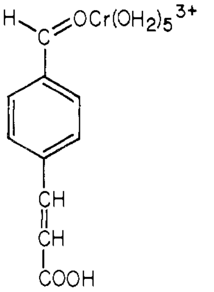
Table IV. K Band Positions and Intensities in Various Solvents

Compd	Solvent	λ_{max}, nm (ε)	
		Cyano K band	Carbonyl K band
	Heptane		238 (12,600)[a]
	Alcohol		242 (11,800)[a]
	Water		245 (11,500)[a]
	H_2SO_4		295 (20,900)[a]
	Cyclohexane	222[b]	
	Methanol	222 (10,600)[c]	
	Water	222 (11,500)[d]	
	3 *M* H_2SO_4	222 (12,000)[d]	
	Concd H_2SO_4	232 (8400)[d]	
	Water	233 (22,000)[f]	
	Concd H_2SO_4		284 (21,000)[d,g]
	Water		~278 (24,000)[d]
	Concd H_2SO_4	224 (20,000)[d]	278 (15,000)[d,g]

[a] Reference 9. [b] C. Leandri and D. Spinelli, *Boll. Sci. Fac. Chim. Ind. Bologna*, 15, 90 (1957). [c] Sadtler Research Laboratories spectra collection, No. 602. [d] This work. [e] Ro ≡ $(NH_3)_5Co$. [f] Reference 1. [g] See Figures 1 and 2 for electronic spectra of the ligands and complexes in water.



II



III

bathochromic shift as the polarity of the solvent increases[9] (see Table IV). Hence, the K band shift for the PAB ligand when bonded at the carbonyl oxygen to Cr(III) is expected and supports the assigned structure. Similar shifts were observed for the *p*-formylbenzoate and *p*-formylcinnamate ligands. The intermediates II and III have λ_{max} 290 and 305 nm and ϵ_{max} 1.9×10^4 and 3×10^4 M^{-1} cm^{-1}, respectively. The intermediates II and III have decay rates of 24 and 7.6 sec^{-1} at 25° which are independent of hydrogen ion concentration and chromium(II) concentration below $[Cr^{2+}] = 0.02$ *M*. However, for I, the rate of decay depends upon both the chromium(II) and the hydrogen ion concentrations according to eq 3. For the conditions shown in Table III the k''' term constitutes the major contribution to the observed rate, except at very high chromium(II) concentrations. For the decay of II (and presumably III) the lack of dependence on $[H^+]$ has been explained by postulating that the rate of hydration of the intermediate is the actual process being observed. The hydrated intermediate then rapidly aquates. For I it is unlikely that hydration is involved and the more complex behavior is observed. The k''' term suggests a transition state of composition $[(OH_2)_4(OH)CrOC(CH_3)C_6H_4CN^{2+}]$ where it is probably the trans water molecule which is deprotonated. The trans hydroxo group then labilizes the bound PAB. This type of behavior has been observed previously.[11,12] The activation parameters of $\Delta H^{\ddagger} = 12.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16$ eu seem low and not sufficiently negative, respectively, for reactions of a 2+ ion. This may simply be a reflection of the inherent lability of a chromium–keto linkage.

Of the chromium(II)-dependent terms (k' and k''), k' is dominant and likely results from electron transfer by a second remote attack at the nitrile nitrogen in I. The k'' term is not well established as shown by the large error limits.

No intermediate was observed in the reaction of the MAB complex with Cr(II), the final product being $Cr(OH_2)_6^{3+}$. However, an inner-sphere pathway cannot be ruled out on this basis alone since any carbonyl-bonded product would probably aquate rapidly compared to the observed rate of reduction. Assuming that a Cr(III) intermediate of the MAB ligand would aquate similarly to I, we can estimate its half-life using the rate law defined by eq 3. The longest half-life predicted for such an intermediate (at low Cr(II) concentration and a high concentration of $HClO_4$) is on the order of 0.03 sec while the half-lives for reduction are in the range 50–300 sec. Hence, an intermediate, if formed, could not be expected to be observable.

The MAB complex is reduced some 20,000 times more slowly than the PAB complex. Even though conjugation effects are transmitted across para positions more effectively than across meta positions, this cannot account for the large rate difference observed. ESR studies of the radical anions of both the MAB and PAB ligands indicate that the carbonyl groups are locked into the plane of the aromatic ring for lifetimes of 1 μsec or longer.[13] A sensitive probe into the conformation of the carbonyl group with respect to the aromatic ring is the intensity of the carbonyl K band.[14] Thus, in isopentane solution, the molar extinction coefficients of this band for acetophenone, 2-methylacetophenone, and 2,6-dimethylacetophenone are 12,050, 10,700 and 2010 M^{-1} cm^{-1}, respectively,[15] as steric hinderance to coplanarity increases. The

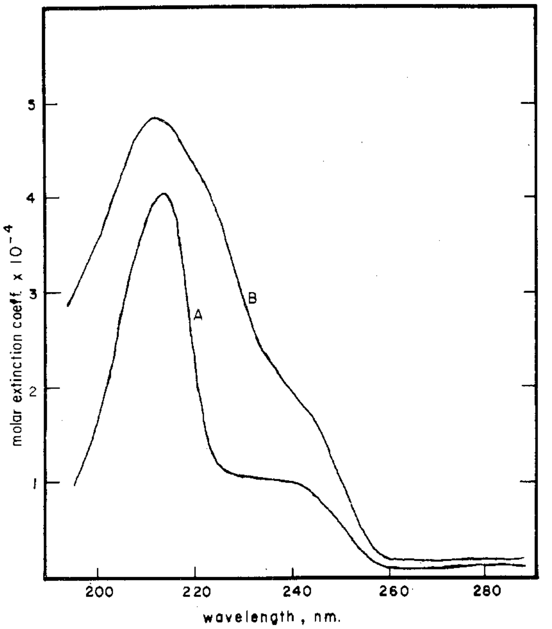


Figure 2. Electronic spectra in aqueous solution: A, MAB ligand; B, pentaamminecobalt(III) complex with MAB (nitrile bonded).

electronic spectra of the PAB and MAB ligands and complexes may be compared in Figures 1 and 2. The K band is well defined for the PAB ligand and complex, appearing at 248 nm with an ϵ of 21,000 M^{-1} cm^{-1} for the ligand and at 255 nm with an ϵ of 26,000 M^{-1} cm^{-1} for the cobalt complex. For reasons which are discussed in the Appendix, we assign the K bands of the MAB ligand and complex to the peak at approximately 236 nm (the shoulders in Figure 2) with ϵ's of approximately 10,000 and 15,000 M^{-1} cm^{-1}, respectively. The lower extinction coefficient of the carbonyl K band in the MAB complex with respect to the PAB complex indicates a lower probability of carbonyl to ring excitation which is most reasonably explained by a lower degree of conjugation. This at least in part accounts for a slower electron-transfer rate. When the acetyl function is replaced by a formyl function, the rate of electron transfer increases,[16] perhaps because the formyl group is less hindered than the acetyl group in achieving coplanarity with the aromatic ring.[17,18]

Another factor contributing to the large rate difference observed between meta and para complexes is the reducibility of the ligands. The PAB ligand is more reducible than the MAB ligand as shown by polarographic half-wave potentials.[13,19] This would favor a radical ion type mechanism for reduction.[20] However, we have not found any evidence of radical formation between Cr(II) and the PAB ligand alone. The ESR spectra[13] of the radicals (generated electrochemically) indicate the presence of significantly more unpaired spin density at the nitrile nitrogen in PAB$^-$ than in MAB$^-$. This would favor a superexchange type mechanism[21] where the ground state and excited states of the precursor complex mix resulting in finite probabilities for the transferring electron and the receptor "hole" existing on the ligand. This mechanism would also be favored if low-lying unoccupied molecular orbitals capable of mixing with filled MO's of the ligand were present in order to produce low-lying excited states.

The lack of radical formation between Cr(II) and the PAB ligand and the fact that the MAB ligand requires a higher potential (~0.3 V higher) to produce the anion radical than the PAB ligand[13] point to an outer-sphere process for reduction of the MAB complex.

The enthalpy of activation for reduction of the PAB complex is approximately zero if not negative as shown in Table II. Low $\Delta H^{\ddagger}$ values have been connected with the contribution of precursor complex formation[22] in the overall electron transfer and this would seem to be a contributing factor for reduction of the PAB complex.

The reduction of the PAB complex has been shown to occur via a remote attack process and is without the complication of a hydrogen ion dependent term. However, the results are consistent with either a radical ion or superexchange mechanism. It appears that the symmetry and energy of the orbitals on the binding group are important with respect to both the reductant and the rest of the organic mediating group. More systematic investigations of these parameters are necessary before an unequivocal choice of mechanism can be made for the "remote" class of electron-transfer reactions.

Acknowledgment. The authors wish to thank the National Research Council of Canada for financial support of this research.

Appendix

The assignment of the intense bands in the ultraviolet spectra as K bands associated with the carbonyl chromophore or K bands for the cyano chromophore is based upon the wavelengths of these bands in various solvents. As shown in Table IV, the position of the cyano K band is not nearly as sensitive to solvent effects as the carbonyl K band. Hence, on the basis of the spectra of the MAB ligand in concentrated H_2SO_4, we assign the carbonyl K band in aqueous solution (Figure 2) to the longer wavelength shoulder at approximately 236 nm while the more intense band in Figure 2 at 212 nm is assigned to the cyano K band.

Registry No. $(MAB)Co(NH_3)_5^{3+}$, 54985-99-8; $(PAB)Co(NH_3)_5^{3+}$, 53739-07-4; Cr(II), 22541-79-3; MAB, 6136-68-1; PAB, 1443-80-7; I, 54985-98-7.

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