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Reactions of Chromium(II) with Chloro- and Iodoacetonitrile and Their Pentaamminecobalt(III) Complexes

W. C. Kupferschmidt and R. B. Jordan*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received April 8, 1983

Abstract: The products and kinetics of the reaction of chromium(II) with XCH_2CN, and $(NH_3)_5CoNCCH_2X^{3+}$, where X = I or Cl, have been studied. For X = I, the free nitrile yields 25% $(H_2O)_5CrCH_2CN^{2+}$ while the cobalt(III) complex yields >95% of the novel dimer $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. The differences in yields are attributed to reaction of Cr^{2+} at the nitrile nitrogen of the $NCCH_2$ intermediate from the free nitrile. The rate constant (25 °C, 0.50 M $LiClO_4$–$HClO_4$), ΔH^* (kcal mol^{-1}) and ΔS^* (cal mol^{-1} deg^{-1}) for ICH_2CN are 9.17 M^{-1} s^{-1}, 5.44 ± 0.74, and −35.8 ± 2.5 respectively, and for $(NH_3)_5CoNCCH_2I^{3+}$, 45.2 M^{-1} s^{-1}, 3.80 ± 0.55, and −38.2 ± 1.9, respectively. For X = Cl the reactions are slower and kinetics are complicated by competing reactions. The $(H_2O)_5CrCH_2CN^{2+}$ product is very stable to aquation, but unusually reactive toward chromium(II)-catalyzed aquation ($k = 1.73 \times 10^{-2} + (5.62 \times 10^{-4})[H^+]^{-1}$, 25 °C, 0.50 M $LiClO_4$–$HClO_4$). The mercury(II) derivative $[(NH_3)_5CoNCCH_2HHg(OH_2)](ClO_4)_4$ has been isolated and characterized.

Since the first identification of an aquoorganochromium(III) species by Anet and Leblanc[1] a great number of such complexes have been prepared and studied.[2-5] Although these species have been made in a variety of ways,[6-10] one of the simplest procedures involves the reaction of an alkyl halide (RX) with chromium(II):

$$RX + 2Cr(OH_2)_6^{2+} \rightarrow (H_2O)_5CrR^{2+} + (H_2O)_5CrX^{2+} \qquad (1)$$

In this study the reactions of chromium(II) with chloro- and iodoacetonitrile have been investigated. In addition, the reactions of chromium(II) with the $(NH_3)_5Co^{3+}$ complexes of these ligands have been studied. The analysis of the products and their reactivity provides a more detailed picture of the factors affecting the product distribution of reaction 1 and of the reactivity of aquoorganochromium(III) complexes.

Experimental Section

Materials. (Trifluoromethanesulfonato)pentaamminecobalt(III) trifluoromethanesulfonate (**1**) was prepared as described previously.[11] Chloroacetonitrile (Aldrich) was distilled before use. Iodoacetonitrile was prepared from chloroacetonitrile by the method of Merbach and Bünzli.[12] Reagent grade sulfolane (tetramethylene sulfone or thiolane 1,1-dioxide) (Aldrich) was dried over freshly heated (120 °C) Davison 4-Å molecular sieves.

Mercury(II) perchlorate solutions were prepared by dissolving a weighed amount of yellow mercuric oxide in a known volume of excess perchloric acid of known concentration.

Cobalt was determined as $Co(SCN)_4^{2-}$ (extinction coefficient 1786 M^{-1} cm^{-1} at 622 nm) in 50% (by volume) acetone containing 2.5 mL of 50% NH_4SCN in 50 mL of final solution.

Other reagents and analytical methods have been described previously.[13]

$[(NH_3)_5CoNCCH_2I](ClO_4)_3$. A solution of 20 mL of sulfolane and 6 g of iodoacetonitrile was dried over molecular sieves for 6 h. The molecular sieves were removed by filtration, 40 mL of sulfolane, 6 g of **1**, and 5 drrops of CF_3SO_3H were added, and the solution was allowed to stand for 20 h at room temperature, and then at 40 °C overnight. The warm solution was added slowly to 500 mL of ether while stirring. The ether was decanted from the resulting oil, which was washed three times with ether and air dried. The residue was dissolved in 80 mL of 0.02 M HCl at 40 °C, filtered, and concentrated perchloric acid was added dropwise to precipitate the product, which was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried. Anal. Calcd for $[(NH_3)_5CoNCCH_2I](ClO_4)_3$: C, 3.94; H, 2.81; N, 13.79. Found: C, 3.83; H, 2.81; N, 13.71. The electronic spectrum has a maximum at 468 nm with an extinction coefficient of 66.7 M^{-1} cm^{-1}. The infrared spectrum, in a Nujol mull, shows a C≡N stretch at 2300 cm^{-1} compared to 2243 cm^{-1} for pure liquid ICH_2CN. In the NMR spectrum the $-CH_2-$ protons appear at τ 5.81 and the trans and cis NH_3 protons are at τ 6.53 and 6.13, respectively.

$[(NH_3)_5CoNCCH_2Cl](ClO_4)_3$. This compound was prepared by a method analogous to that for the iodoacetonitrile complex. The reaction solution was allowed to stand overnight and the product was recovered by addition to ether and recrystallized as described for the iodoacetonitrile complex. Anal. Calcd for $[(NH_3)_5CoNCCH_2Cl](ClO_4)_3$: C, 4.64; H, 3.31; N 16.23. Found: C, 4.54; H, 3.34; N, 15.93. The electronic spectrum has maxima at 467 and 333 nm with extinction coefficients of 62.4 and 56.8 M^{-1} cm^{-1}, respectively. The C≡N stretch is observed at 2323 cm^{-1}, compared to 2259 cm^{-1} in pure liquid $ClCH_2CN$. The NMR spectrum shows the $-CH_2-$ protons at τ 4.95 and the trans and cis NH_3 protons at τ 6.61 and 6.18, respectively.

Instrumentation. Proton NMR, infrared, and electronic spectra were measured as described previously.[11] Carbon-13 spectra were recorded on a Bruker WH-200 spectrometer. The electronic spectra were measured in 0.5 M $HClO_4$ to supress ligand hydrolysis. The equipment and techniques for the kinetic measurements and product analysis have been described previously.[13] Unless otherwise indicated, kinetic studies were run in 0.50 M $LiClO_4$–$HClO_4$.

Results

Cr(II) + ICH_2CN. The stoichiometry of the reaction was determined by oxidation of excess chromium(II) with iron(III) and determination of excess iron(III) iodometrically. The results showed that 2.09 ± 0.01 mol of chromium(II) react per mol of ICH_2CN, as expected from eq 1.

The reaction products were separated by ion-exchange chromatography at 5 °C on Dowex 50W-X2 (H^+) cation exchange resin. The first product to elute was identified as $(H_2O)_5CrI^{2+}$ from its electronic spectrum and hydrolytic instability.[14] The second product eluted just after the first, and is red and stable for weeks at 5 °C. The electronic spectrum of this species, shown in Figure 1, has maxima at 527, 409, 262, and 209 nm with extinction coefficients at 40.3, 102, 4.43 × 10^3, and 6.46 × 10^3 M^{-1} cm^{-1}, respectively. The band maxima are characteristic of an aquoorganochromium(III) species, and the complex is formulated as $(H_2O)_5Cr$–CH_2CN^{2+}. The extinction coefficients

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[1] Anet, F. A. L.; Leblanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649.
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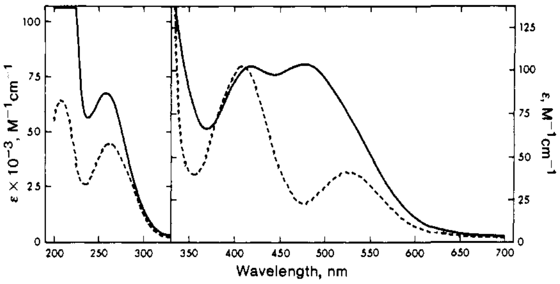


Figure 1. Electronic spectra of $(H_2O)_5CrCH_2CN^{2+}$ (---) and $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$ (—) at 25 °C in 0.50 M $HClO_4$.

reported here are about 35% higher than those of Funke and Espenson.[15] It seems possible that their sample was contaminated with $Cr(OH_2)_6{}^{3+}$.

The quantitative yield of $(H_2O)_5CrCH_2CN^{2+}$ was determined in 0.10 M $HClO_4$ with the chromium(II) (9.28×10^{-2} M) in 25% stoichiometric excess and 50% deficiency over ICH_2CN. In both cases the yield of $(H_2O)_5CrCH_2CN^{2+}$ was 25%, based on the deficient reagent.

The remaining organic product was identified by showing that the distillate from the reaction solution has a ^{13}C NMR spectrum identical with that of aqueous acetonitrile under the same conditions.

The kinetics of formation of $(H_2O)_5CrCH_2CN^{2+}$ from chromium(II) and ICH_2CN was followed at 528 nm and the rate law is given by

$$\frac{d[(H_2O)_5CrCH_2CN^{2+}]}{dt} = k_1[ICH_2CN][Cr^{2+}] \qquad (2)$$

The rate constants at 15.3, 25.0, and 35.0 °C were 6.76 ± 0.23, 9.17 ± 0.41, and 13.3 ± 0.7 M^{-1} s^{-1}, respectively.[17] The activation enthalpy and entropy are 5.44 ± 0.74 kcal mol^{-1} and −35.8 ± 2.5 cal mol^{-1} deg^{-1}, respectively.[17]

Cr(II) + $ClCH_2CN$. Since this system has several kinetically competitive processes, as described below, quantative ion-exchange product studies were not undertaken. A distinct band corresponding to $(H_2O)_5CrCH_2CN^{2+}$ could not be separated from $(H_2O)_5CrCl^{2+}$, but spectrophotometric analyses of later fractions of $(H_2O)_5CrCl^{2+}$ indicated that some $(H_2O)CrCH_2CN^{+2}$ was formed. The absorbance in the 410–430-nm region during the reaction was consistent with conversion of 5–10% of the ligand to $(H_2O)_5CrCH_2CN^{2+}$. The yield of the latter is substantially less than that obtained with iodoacetonitrile.

Kinetic observations with >20-fold excess of chromium(II) showed biphasic behavior. The reaction could be studied most favorably by monitoring the formation of $(H_2O)_5CrCl^{2+}$ at 609 nm. The observations are consistent with the following reactions:

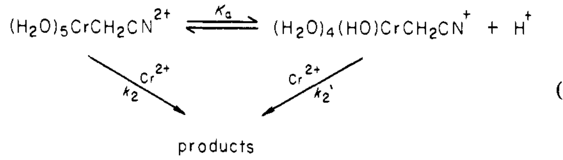
$$2Cr^{2+} + ClCH_2CN \xrightarrow{k_1} (H_2O)_5CrCl^{2+} + \text{other products}$$

$$Cr^{2+} + (H_2O)_5CrCl^{2+} \xrightarrow{k_1'} Cr^{2+} + Cr(OH_2)_6{}^{3+} + Cl^- \qquad (3)$$

where k_1' is the rate constant for chromium(II)-catalyzed aquation of $(H_2O)_5CrCl^{2+}$. This assignment of the second reaction is consistent with a previous kinetic study[18] and with experiments done during this work which gave[19] $k_1' = ((2.29 \pm 0.05) \times 10^{-4})[Cr^{2+}]/[H^+]$. The biphasic kinetic data were fitted by nonlinear least squares to an A → B → C scheme, and k_1 was determined while k_1' was held fixed at the appropriate value.[16] The rate law was found to be analogous to eq 2 with $k_1 = 1.07 \pm 0.07 \times 10^{-2}$ M^{-1} s^{-1} at 25 °C.

The formation of the organochromium species in this system is competitive with its chromium(II)-catalyzed aquation described in the next section. Thus direct observation of the formation of $(H_2O)_5CrCH_2CN^{2+}$ in the 409-nm region is complicated by aquation of both the organo and chloro complexes, and such studies were not pursued.

Cr^{2+} + $(H_2O)_5CrCH_2CN^{2+}$. The organochromium species was prepared from ICH_2CN and chromium(II) and separated by ion-exchange chromatography. The decrease in absorbance at 409 nm was observed, and the rate law[16] is consistent with the following reaction scheme:



(4)

If $[H^+] >> K_a$, then

$$\frac{-d[(H_2O)_5CrCH_2CN^{2+}]}{dt} = \left[k_2 + \frac{k_2'/K_a}{[H^+]}\right][Cr^{2+}][(H_2O)_5CrCH_2CN^{2+}] \qquad (5)$$

A least-squares fit of the data gave $k_2 = 1.73 \pm 0.07 \times 10^{-2}$ M^{-1} s^{-1} and $k_2'/K_a = 5.62 \pm 0.70 \times 10^{-4}$ s^{-1} at 25 °C.

The product of the reaction was identified as $Cr(OH_2)_6{}^{3+}$ by its electronic spectrum.

Cr^{2+} + $(NH_3)_5CoNCCH_2I^{3+}$. The stoichiometry of this reaction was studied in a manner analogous to that described for iodoacetonitrile. It was found that 2.03 ± 0.02 mol of chromium(II) reacts per mol of $(NH_3)_5CoNCCH_2I^{3+}$, consistent with the observation that no cobalt(II) is formed during the reaction.

Ion-exchange studies at 5 °C on Dowex 50W-X2 revealed a green chromium(III) product, which was shown to be $(H_2O)_5CrI^{2+}$ from its electronic spectrum,[14] and a red species, which would not elute from Dowex 50W-X2 even with 0.5 M $HClO_4$ and 1.0 M $NaClO_4$. The red species could be separated and eluted on Sephadex SP-C25 cation exchange resin, and subsequent product analyses used this resin.

Product analysis was done by allowing the reaction to proceed to completion and then oxidizing the excess chromium(II) with air, diluting the solution, and letting it stand for 30 min to allow $(H_2O)_5CrI^{2+}$ to aquate to $Cr(OH_2)_6{}^{3+}$ and I^-.[14] The solution was charged onto a Sephadex resin column and eluted with increasing concentrations of $NaClO_4$ and $HClO_4$. In a typical experiment with a 20% excess of Cr(II), the initial eluent contained 99.8% of the expected amount of I^-, and the first product to elute was $Cr(OH_2)_6{}^{3+}$ in 117% of the expected amount.[20] The final red band was found to contain 95% of the original cobalt[21] and an equimolar amount of chromium.

The above results, as well as the electronic spectrum (Figure 1), and Hg(II) derivative discussed later, indicate that the red species is a cobalt(III)–chromium(III) dimer, $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$. Therefore the dominant (>95%) reaction is

$$(NH_3)_5CoNCCH_2I^{3+} + 2Cr^{2+} \xrightarrow{k_3} (NH_3)_5CoNCCH_2Cr^{5+} + Cr(OH_2)_5I^{2+} \qquad (6)$$

Observation of the reaction at 477 and 650 nm showed that the rate is first order in each reactant and independent of hydrogen ion concentration The rate constants are 35.5 ± 1.1, 45.2 ± 1.6, and 60.5 ± 0.7 M^{-1} sec^{-1}[17] at 15.3, 25.0, and 34.4 °C, respectively. The activation enthalpy and entropy are 3.80 ± 0.55 kcal mol^{-1}

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[15] Funke, L. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 897.

[16] Detailed results are given in the supplementary material.

[17] Errors quoted are 95% confidence limits.

[18] Adin, A.; Sykes, A. G. *J. Chem. Soc. A* **1966**, 1518.

[19] The catalysed aquation was monitored as 428 nm with $[Cr^{2+}] = 4.33 \times 10^{-2}$ M, $[H^+]$ in the range of 0.05–0.28 M, at 25 °C, and $\mu = 0.50$ ($LiClO_4$–$HClO_4$).

[20] The excess $Cr(OH_2)_6{}^{3+}$ arises from the air oxidation of Cr(II), which produces some of it, as well as the chromium(III) hydroxy dimer.

[21] A minor trailing yellow edge was observed with the $Cr(OH_2)_6{}^{3+}$, and cobalt analysis indicated that it contained 5% of the initial cobalt(III). The color and ion-exchange properties are consistent with $(NH_3)_5CoNCCH_3{}^{3+}$.

and −38.2 ± 1.9 cal mol^{-1} deg^{-1}, respectively.[17]

The electronic spectrum of the cobalt(III)–chromium(III) dimer, shown in Figure 1, has maxima at 477, 417, and 256 nm with extinction coefficients at 103, 102, and 6.80×10^3 M^{-1} cm^{-1}, respectively. The maxima at 417 and 256 nm are in regions typical of organochromium species, while the 477-nm peak is expected for a pentaamminecobalt(III) chromophore.

Cr^{2+} + $(NH_3)_5CoNCCH_2Cl^{3+}$. The products for this system were determined by methods analogous to those for the iodoacetonitrile complex. The study is complicated by several competitive reactions. Therefore the reaction was allowed to proceed for 3 to 4 half-times before aeration, and the amounts of products found were corrected for the amount of unreacted cobalt(III). The product distribution was essentially independent of $[H^+]$ in the range 0.108–0.188 M. The cobalt products identified were 54.3 ± 1% cobalt(II) and 45.8 ± 1% $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, and $(H_2O)_5CrCl^{2+}$ was identified as the dipositive chromium(III) product. The substantial amount of cobalt(II) produced makes the products significantly different from those from the reaction of the iodoacetonitrile complex. There appear to be two major reaction pathways:

$$\begin{aligned} &Cr^{2+} + (NH_3)_5CoNCCH_2Cl^{3+} \\ &\quad \xrightarrow{54\%} Co^{2+} + 5NH_4^+ + Cr^{3+} + NCCH_2Cl \\ &\quad \xrightarrow{46\%} (NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} + CrCl^{2+} \qquad (7) \end{aligned}$$

The slowness of the reaction and the multiplicity of products make a kinetic study difficult. The main problems are competitive reactions of $NCCH_2Cl$, $(H_2O)_5CrCl^{2+}$, and $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ with excess chromium(II). These reactions were studied independently, as reported elsewhere in this work, and the results were used to analyze the absorbance–time data for the chromium(II)–$(NH_3)_5CoNCCH_2Cl^{3+}$ system. At 609 nm the data were fitted to the sum of three exponential terms, while at 417 nm four exponential terms were required.[22] For the net disappearance of oxidant the rate is first order in cobalt(III) and chromium(II) and independent of $[H^+]$, with a rate constant of $8.9 \pm 0.7 \times 10^{-2}$ M^{-1} s^{-1}, although the value is somewhat approximate because of the complexity of the system.

Cr^{2+} + $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. When the cobalt(III)–chromium(III) dimer reacts with excess chromium(II), there is a monophasic decrease in absorbance at 417 and 477 nm, with an isosbestic point at 575 nm. The final product spectrum is consistent with $Cr(OH_2)_6^{3+}$, and tests for cobalt(II) were positive. Therefore the net reaction is

$$\begin{aligned} &Cr^{2+} + (NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} \rightarrow \\ &\qquad Co^{2+} + 5NH_4^+ + 2Cr^{3+} + NCCH_3 \qquad (8) \end{aligned}$$

The rate is first order in each reactant and independent of $[H^+]$ with a second-order rate constant of $2.39 \pm 0.10 \times 10^{-3}$ M^{-1} s^{-1} (25 °C).[16]

Hg^{2+} + $(H_2O)_5CrCH_2CN^{2+}$. The kinetics of the reaction

$$(H_2O)_5CrCH_2CN^{2+} + Hg^{2+} \rightarrow Cr(OH_2)_6^{3+} + HgCH_2CN^+ \qquad (9)$$

were studied previously by Funke and Espenson.[15] The reaction is first order in each reactant, independent of $[H^+]$ (0.04–0.50 M), and the rate constant found in this study (8.7 ± 0.4 M^{-1} s^{-1}, 25 °C, 1.00 M $LiClO_4$–$HClO_4$)[16] is in reasonable agreement with the earlier value of 9.8 ± 0.3 M^{-1} s^{-1} at 25 °C in 1 M $HClO_4$. The correspondence between these rate constants indicates that the reactive species prepared here is the same as that prepared by Funke and Espenson, despite the differences in extinction coefficients noted above.

Hg^{2+} + $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. Spectrophotometric observation of this reaction in 0.08 M $HClO_4$ over 150 min showed the disappearance of the maximum at 417 nm and a small decrease in absorbance at 477 nm with a shift in the peak position to 471 nm. The products from the reaction of 5.5×10^{-3} M $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ and 2.1×10^{-2} M $Hg(ClO_4)_2$ in 0.10 M $HClO_4$ solution for 3.5 h were separated on Sephadex SP-C25 resin and found to be $Cr(OH_2)_6^{3+}$, and a more strongly retained yellow fraction which eluted with 1.0 M $HClO_4$. The product contains cobalt and mercury (dithizone test),[23] and each mol of reactant produces 0.99 mol of $Cr(OH_2)_6^{3+}$ and 0.96 mol of the yellow product. Therefore the reaction is formulated as

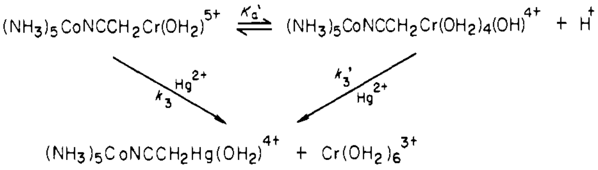
$$\begin{aligned} &Hg^{2+} + (NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} \rightarrow \\ &\qquad (NH_3)_5CoNCCH_2Hg^{4+} + Cr(OH_2)_6^{3+} \qquad (10) \end{aligned}$$

The organomercury complex can be isolated as the perchlorate salt by addition of sodium perchlorate to a product solution analogous to that used for the ion-exchange study. The solid can be conveniently prepared, without any ion-exchange separation, by addition of $Hg(ClO_4)_2$ and sodium perchlorate to a product solution from the chromium(II)–$(NH_3)_5CoNCCH_2I^{3+}$ reaction.

The solid was characterized as $[(NH_3)_5CoNCCH_2Hg(OH_2)](ClO_4)_4$ by Co, C, H, and N analysis[24] and by its infrared and proton NMR spectra. The infrared spectrum shows a C≡N stretch at 2269 cm^{-1}, and the NMR spectrum has the expected cis-NH_3 (τ 6.28), trans-NH_3 (τ 6.72), and CH_2 (τ 7.49) resonances. The organomercury bond is confirmed by observation of a ^{199}Hg–^1H coupling constant of 312 Hz in Me_2SO-d_6 and 361 Hz in D_2O. The electronic spectrum has maxima at 471 and 335 nm, with extinction coefficients of 75.6 and 67.6 M^{-1} cm^{-1}, respectively.

The isolation and characterization of the organomercury derivative provide important information for the characterization of its cobalt(III)–chromium(III) parent, which was not obtained as a solid. It is especially noteworthy that the nitrile function has remained intact. Previous experience[25] led us to suspect that the nitrile in the dimer would be highly activated toward hydrolysis to the carboxamide. This is clearly not the case.

The kinetics of reaction 10 were studied at 417 nm at 25 °C in 1.00 M $LiClO_4$–$HClO_4$.[16] The rate law is consistent with the following reaction scheme:



(11)

If $[H^+] > K_a'$, then

$$\frac{-d[(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}]}{dt} = \left[k_3 + \frac{k_3'K_a'}{[H^+]}\right][Hg^{2+}][(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}] \qquad (12)$$

A least-squares fit of the data[16] to this rate law gives k_3 = $3.49 \pm 0.19 \times 10^{-2}$ M^{-1} s^{-1} and $k_3'K_a'$ = $5.8 \pm 1.8 \times 10^{-4}$ s^{-1}.

Discussion

The reaction of organic halides with chromium(II) has been suggested to proceed by halogen atom transfer to chromium(II), followed by reaction of the organic radical with chromium(II) to produce the organochromium(III) product.[7,26–29]

$$R\text{-}X + Cr^{2+} \rightarrow R\cdot + CrX^{3+}$$

$$R\cdot + Cr^{2+} \rightarrow \text{products} \qquad (13)$$

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[22] At 609 nm $(H_2O)_5CrCl^{2+}$ is the main chromophore and the three rate constants are for the rates of disappearance of oxidant, reaction of Cr^{2+} + $NCCH_2Cl$, and Cr^{2+} + $(H_2O)_5CrCl^{2+}$. At 417 nm the organochromium species also absorb and the rate for the reaction of Cr^{2+} + $(NH_3)_5CoNCCH_2Cr^{5+}$ must be added.

[23] Sandell, E. B. "Colorimetric Determination of Traces of Metals"; Interscience: New York, 1944; pp 320–329.

[24] Anal. Calcd for $[(NH_3)_5CoNCCH_2Hg(OH_2)](ClO_4)_4$: Co, 7.36; C, 3.00; H, 2.39; N, 10.50. Found: Co, 7.31; C, 3.24; H, 2.40; N, 10.66.

[25] Pinnell, D.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6104.

Table I. Summary of Kinetic Results

reaction	k^a(25 °C), M^{-1} s^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal mol deg^{-1}
$Cr^{2+} + ICH_2CN$	9.17	5.44 ± 0.74	−35.8 ± 2.5
$Cr^{2+} + ClCH_2CN$	1.07×10^{-2}		
$Cr^{2+} + (NH_3)_5CoNCCH_2I^{3+}$	45.2	3.80 ± 0.55	−38.2 ± 1.9
$Cr^{2+} + (NH_3)_5CoNCCH_2Cl^{3+}$	8.9×10^{-2}		
$Cr^{2+} + (H_2O)_5CrCH_2CN^{2+}$	$1.73 \times 10^{-2} + (5.62 \times 10^{-4})[H^+]^{-1}$		
$Cr^{2+} + (NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$	2.39×10^{-3}		
$Hg^{2+} + (H_2O)_5CrCH_2CN^{2+}$	8.7		
$Hg^{2+} + (NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$	$3.49 \times 10^{-2} + (5.8 \times 10^{-4})[H^+]^{-1}$ [b]		

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$) unless otherwise noted. [b] Ionic strength 1.00 M ($LiClO_4$-$HClO_4$).

The observation of the CrX^{2+} product in each of the systems studied here is consistent with this mechanism. However, the substantial differences in products when the organic reactant is ICH_2CN and $ClCH_2CN$, or their respective $(NH_3)_5Co^{3+}$ complexes, appears to argue against this mechanism. In fact, these product differences are due to other competing reactions with the more slowly reacting chloro systems. For example, $ClCH_2CN$ reacts with Cr^{2+} with a rate constant of 1.07×10^{-2} M^{-1} s^{-1} but $(H_2O)_5CrCH_2CN^{2+}$ is destroyed by Cr^{2+} with a rate constant of $(1.73 \times 10^{-2} + 5.6 \times 10^{-4}/[H^+])$ M^{-1} s^{-1}. If only 25% of the organochromium species is formed, as in the iodo system, then a maximum of 7% $(H_2O)_5CrCH_2CN^{2+}$ is expected to be found when $ClCH_2CH$ reacts with Cr^{2+}, in agreement with the qualitative observation of 5–10%.

The product difference is more dramatic in the case of the two cobalt(III) complexes in that the chloroacetonitrile complex produces 54% cobalt(II) while the iodoacetonitrile complex gives no detectable cobalt(II). This might seem to imply that the radical intermediate $(NH_3)_5CoNCCH_2\cdot{}^{3+}$ reacts differently depending on its parentage. However, it is more probable that the complicating feature is competing outer-sphere reduction of the more slowly reacting chloroacetonitrile complex. Previous studies[13] have shown that outer-sphere reduction may have a rate constant in the range of 2–4×10^{-2} M^{-1} s^{-1} for this nitrile complex, and this is the major source of cobalt(II), while about 5–10% results from reduction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$.

There is a marked difference in the products from the reaction of ICH_2CN and its $(NH_3)_5Co^{3+}$ complex. The former yields 25% organochromium product while the latter gives >95% organochromium product. The chloroacetonitrile systems are qualitatively similar in that the Co complex yields much more organochromium product. These observations are consistent with the proposition that the $NCCH_2\cdot$ radical may react with chromium(II) at either the terminal carbon or nitrogen atoms, and in fact the latter is the prefered site.

$$NCCH_2\cdot + Cr^{2+} \xrightarrow{75\%} CrNCCH_2{}^{2+} \xrightarrow[\text{fast}]{H^+} CrNCCH_3{}^{3+} \rightarrow Cr^{3+} + NCCH_3$$
$$\xrightarrow[25\%]{} CrCH_2CN^{2+} \qquad (14)$$

With the complex, the $(NH_3)_5Co^{3+}$ blocks reaction at nitrogen so that only the organochromium species is formed. Recent low-temperature ion-exchange experiments[30] have shown that the initial 3+ product of the $Cr^{2+} + ICH_2CN$ reaction is not $Cr(OH_2)_6{}^{3+}$ but a species that aquates to $Cr(OH_2)_6{}^{3+}$ and $NCCH_3$ in a few mintes at room temperature. This species is tentatively identified as the $CrNCCH_3{}^{3+}$ intermediate in the above reaction scheme.

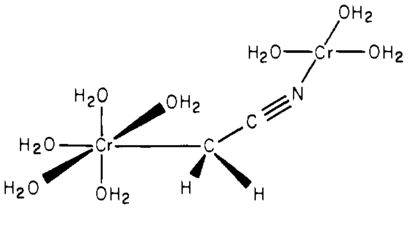
Radical coupling does not account for the lower yields of organochromium product from the free haloacetonitriles, because no succinonitrile product could be found. In addition, the large rate of reaction of chromium(II) with organic radicals (>1×10^7 M^{-1} s^{-1})[8] and the high chromium(II) concentrations make radical coupling a poor competitor.

In summary, first appearances notwithstanding, the product studies are consistent with the halogen abstraction reaction mechanism in eq 13. Aside from competing reactions not involving the haloacetonitrile, the only complicating feature is that the radical intermediate may react with chromium(II) at more than one site.

The kinetic results from this study are summarized in Table I. Iodoacetonitrile reacts about 850 times faster than chloroacetonitrile. This is consistent with the halogen abstraction mechanism and the lower bond energy of C–I bonds compared to C–Cl bonds.[29] A similar kinetic difference has been observed in the reaction of haloacetic acids.[3] The activation parameters for reaction of chromium(II) with ICH_2CO_2H ($\Delta H^‡ = 5.4 \pm 0.7$ kcal mol^{-1}; $\Delta S^‡ = -40.4 \pm 2.9$ cal mol^{-1} deg^{-1})[3] are almost identical with those for iodoacetonitrile.

The iodoacetonitrile complex reacts about 5 times faster than the free ligand. The increased reactivity is almost completely due to a 1.6 kcal mol^{-1} lower $\Delta H^‡$. The almost constant $\Delta S^‡$ indicates that the increased charge in the transition state has little effect on the reactivity, and the increased rate may be attributed to weakening of the C–I bond in $(NH_3)_5CoNCCH_2I^{3+}$.

The reactivity of $(H_2O)_5CrCH_2CN^{2+}$ toward Cr^{2+} was unexpected in view of previous observations that $(H_2O)_5CrCH_2Cl^{2+}$ does not react with Cr^{2+} [31] and that Cr^{2+} does not catalyze the aquation of $(H_2O)_5CrCH_3{}^{2+}$.[32] Such a reaction usually is observed with other ligands. For example, for $(H_2O)_5CrX$ with $X \equiv OH_2$,[33] NH_3[34] and $CH_3CO_2{}^-$,[35] values of k_2 (see eq 5) are $<2 \times 10^{-5}$, 2.4×10^{-5}, and 1.56×10^{-5} M^{-1} s^{-1}, respectively, at 25 °C, while k_2' is 1.1×10^{-4}, 5.9×10^{-5}, and 2.5×10^{-5}, respectively. With $X \equiv CH_2CN^-$, the k_2 of 1.73×10^{-2} is $\sim 10^3$ times larger than any previously observed value, while k_2' is about 5 times larger. This enhanced reactivity, and the failure to observe such reactions with other organochromium complexes, indicates some special role for the $-CH_2CN$ ligand. A reasonable possibility is electron transfer via a bridged-outer-sphere intermediate of the form



This intermediate is similar to that proposed for the reduction of $(NH_3)_5CoNCCH_2CO_2{}^{2+}$ by Cr^{2+}.[13] An analogous intermediate may account for the reaction of $(H_2O)_5CrCH_2CO_2H^{2+}$ with Cr^{2+}, which has a rate constant of 6.8×10^{-3} M^{-1} s^{-1} (20 °C, 0.50 M $HClO_4$).[3] Unfortunately the acid dependence and products of

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the latter reaction were not established.

The reaction of mercury(II) with organochromium(III) complexes is believed to occur by a bimolecular electrophilic substitution of Hg^{2+} on the carbon coordinated to chromium(III).[36] This is consistent with the second-order kinetics and decreasing rate constant with more electron-withdrawing substituents on the organic ligand.[15,37] The reactivity of $(H_2O)_5CrCH_2CN^{2+}$ and $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ fits into this pattern.

An unusual feature of the $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ + Hg^{2+} reaction is the inverse hydrogen ion term in the rate law. Since this is not normally observed[15,37] for these reactions, the simplest explanation seems to involve ionization of a water coordinated to chromium(III), as suggested in eq 11. The presence of the $(NH_3)_5CoNCCH_2^{2+}$ ligand may enhance the acidity of a coordinated water enough to make the inverse hydrogen ion path detectable.

The chromium(II) reduction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ presents a special problem in that it is not clear which metal center is reduced first. The fact that the rate constant (2.39×10^{-3} M^{-1} s^{-1}) is less than that for Cr^{2+} + $(H_2O)_5CrCH_2CN$ (1.73×10^{-2} M^{-1} s^{-1}) is consistent with the earlier argument that chromium(II) coordinates at the nitrile nitrogen in the latter system. Then the chromium(III) end of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ would show normal, i.e., very low, reactivity toward chromium(II). The absence of an $[H^+]^{-1}$ term in the rate law for this reaction is consistent also with no reactivity at chromium(III). These observations indicate that the cobalt(III) is reduced first by an outer-sphere mechanism.

$$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} + Cr^{2+} \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + NCCH_2Cr(OH_2)_5^{2+} + Cr(OH_2)_6^{3+} \quad (15)$$

$$(H_2O)_5CrCH_2CN^{2+} + Cr^{2+} \xrightarrow{H^+} Cr^{2+} + Cr(OH_2)_6^{3+} + NCCH_3 \quad (16)$$

The second reaction is much faster than the first (see Table I) so that monophasic kinetics are observed.

An unusual feature of the results is that $(NH_3)_5CoNCCH_2I^{3+}$ reacts essentially quantitatively with chromium(II) to produce the cobalt(III)-organochromium(III) dimer, and no cobalt(II) is detected. This indicates that intramolecular electron transfer within the $(NH_3)_5CoNCCH_2^{3+}$ radical is slow compared to reaction with chromium(II).

$$(NH_3)_5CoNCCH_2^{3+} \xrightarrow[\text{detected}]{\text{not}} Co^{2+} + 5NH_4^+ + NCCH_2^+ \rightarrow \text{products} \quad (17)$$

This seems surprising in view of ESR studies, which show considerable unpaired spin density on nitrogen in the $\cdot CH_2CN$ radical.[38,39] The thermodynamic instability of the carbonium ion $NCCH_2^+$ may explain the apparent absence of intramolecular electron transfer. That the carbonium ion is unstable can be judged from the fact that the ionization potential of $\cdot CH_2CN$ is 61 kcal mol^{-1} higher than that of $\cdot CH_2OH$.[40,41] The latter radical does reduce $Co(NH_3)_6^{3+}$.[42]

It is possible to estimate an upper limit for the rate of reaction 17. If the rate constant for $(NH_3)_5CoNCCH_2^{3+}\cdot$ + Cr^{2+} is $\sim 1 \times 10^7$ M^{-1} s^{-1},[8] then a consideration of our cobalt(II) detectability limits for experiments in which essentially equivalent amounts of $(NH_3)_5CoNCCH_2I^{3+}$ and Cr^{2+} were mixed indicates that reaction 17 has a rate constant $\leq 3.5 \times 10^3$ s^{-1}.

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Registry No. $[(NH_3)_5CoNCCH_2I](ClO_4)_3$, 88157-86-2; $[(NH_3)_5CoNCCH_2Cl](ClO_4)_3$, 88157-88-4; $[(NH_3)_5CoNCCH_2Hg(OH_2)](ClO_4)_4$, 88157-90-8; CH_2CN, 624-75-9; $ClCH_2CN$, 107-14-2; Cr^{2+}, 22541-79-3; $(H_2O)_5CrCH_2CN^{2+}$, 76068-68-3; $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, 88157-91-9; Hg^{2+}, 14302-87-5.

Supplementary Material Available: Tables of appropriate concentrations and rate constants (8 pages). Ordering information is given on any current masthead page.

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Direct Observation of the Intermediates in the Photochemical Reaction of $R_3SiCo(CO)_4$ with R'_3SiH and Establishment of the Mechanism for $R'_3SiCo(CO)_4$ Formation

F. Ruth Anderson and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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Abstract: Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH yields $R'_3SiCo(CO)_4$ and R_3SiH at 298 K in an alkane solvent. The mechanism for this reaction has been established by irradiation at low temperature in alkane media. At 77 K in a rigid alkane medium, irradiation of $R_3SiCo(CO)_4$ (R = Me, Et, Ph) yields dissociative loss of CO to give a 16 e^- complex, $R_3SiCo(CO)_3$, as determined by infrared spectroscopy. If the matrix contains a sufficiently high concentration of R_3SiH (R = Et) the light-induced loss of CO occurs, but the metal carbonyl product is $(R_3Si)(R'_3Si)Co(CO)_3H$. This species can also be formed photochemically at 196 K in fluid solution. The $(Et_3Si)_2Co(CO)_3H$ is sufficiently inert that the Co-hydride resonance in the ^1H NMR can be observed at δ −9.8. Warmup of the $(R_3Si)(R'_3Si)Co(CO)_3H$ to 298 K results in generation of both $R_3SiCo(CO)_4$ and $R'_3SiCo(CO)_4$. The low-temperature photochemistry thus provides direct evidence for both the 16 e^- primary photoproduct and the Co(III) oxidative addition product in the exchange mechanism.

We wish to report spectroscopic detection of intermediates, $R_3SiCo(CO)_3$ and $(R_3Si)(R'_3Si)Co(CO)_3H$, in the photochemical exchange process represented by eq 1.[1] These results establish the mechanism for the exchange process in (1) to be as represented

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