

Thermal and Light-Induced Electron Transfer between Iron(II) and Cobalt(III) Mediated by Bridging Pyrazines¹

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Abstract: The first-order, specific rates of reduction of Co(III) by Fe(II) in complexes of the type $[(\text{NH}_3)_{(4 \text{ or } 5)}\text{CoLFe}(\text{CN})_5]$ with L as chelating 2-carboxylatopyrazine, pyrazine, and 2-methylpyrazine are 1.3×10^{-2} , 5.5×10^{-2} , and $30 \times 10^{-2} \text{ s}^{-1}$, respectively, at 25 °C, pH 6–7, $\mu = 0.15 \text{ M}$. For the first two reaction systems ΔH^\ddagger equals 22.7 ± 1.0 and $24.8 \pm 1.4 \text{ kcal/mol}$, respectively, while ΔS^\ddagger is 9.5 ± 3.0 and $18.5 \pm 5.0 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively. Photoinduced electron transfer occurs upon irradiation of the iron(II) to heterocycle charge transfer bands near 620 nm. Within experimental error, the quantum yield is unity for the first two species. The complexes are formed by aqueous reaction of pentacyanoaquaferrate(II) with the appropriate Co(III) ammine incorporating the bridging ligand. Kinetics of formation ($\mu = 0.15 \text{ M}$) are first order in each of the reactants with specific rates of 3.1×10^3 , 7.0×10^3 , and $3.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for the three complexes at 25 °C. ΔH^\ddagger and ΔS^\ddagger for formation of the first two are approximately 17 kcal/mol and $16 \text{ cal mol}^{-1} \text{ K}^{-1}$. pH and ionic strength dependences of the formation and electron transfer steps are discussed.

Introduction

Current investigations of electron transfer dynamics have employed detectable "precursor" complexes in which oxidant and reductant are joined by a common bond system.^{2–10} Although the existence of highly reactive, binuclear redox intermediates was proved some time ago,¹¹ it is only recently that a few slowly reacting complexes have been produced in aqueous solution for direct study.

In this article, we describe three new complexes based on the reducing moiety pentacyanoferrate(II) in conjunction with the oxidants pentaammine- or tetraamminecobalt(III). The bridging groups are the polyfunctional ligands pyrazine, 2-carboxylatopyrazine, and 2-methylpyrazine. The binuclear species are light sensitive, undergoing photoredox decomposition when irradiated in the MLCT band. Measurements of the quantum efficiency of this process at 620 nm are presented herein. Studies of thermal electron transfer kinetics and the rates of formation of the new intermediates are also described.

Experimental Section

Materials. Doubly distilled water was used throughout the experiments. Buffers were made up using commercially available reagent grade phosphate and acetate salts. Lithium perchlorate solutions, employed to maintain ionic strength conditions, were prepared from reagent grade lithium carbonate and perchloric acid. Neutral stock solutions of LiClO_4 were analyzed for lithium by atomic absorption and for perchlorate ion by gravimetric analysis.¹² Metal complexes were obtained as described in the following paragraphs.

$\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$. This salt was prepared as described previously,¹³ washed with methanol, and stored in vacuo in the absence of light. Anal.¹⁴ Calcd for $\text{Na}_3\text{FeC}_5\text{H}_9\text{N}_6\text{O}_3$: C, 18.24; H, 2.78; N, 25.78. Found: C, 18.18; H, 2.84; N, 25.71.

$[\text{Co}(\text{en})_2(2\text{-pyrazinecarboxylate})_2](\text{ClO}_4)_2$. This preparation was identical with that given by Toma.⁶ Anal. Calcd for $\text{CoC}_9\text{H}_{19}\text{N}_6\text{Cl}_2\text{O}_{10}$: C, 21.53; H, 4.01; N, 16.74. Found: C, 21.85; H, 3.97; N, 17.00.

$[\text{Co}(\text{NH}_3)_4(2\text{-pyrazinecarboxylate})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)_2](\text{ClO}_4)_3$ ¹⁵ (1.5 g) was heated together with 0.48 g of sodium 2-pyrazinecarboxylate in ca. 5 mL of water at 85 °C for 40 min. The orange-brown solution was treated with 5 mL of saturated aqueous sodium perchlorate. After evaporating for a few minutes on a steam bath, crystals began to form. Crude product (1.1 g) was collected after cooling to ice temperature for several hours. The material was recrystallized from dilute perchloric acid. Anal. Calcd for $\text{CoC}_5\text{H}_{17}\text{N}_6\text{Cl}_2\text{O}_{11}$: C, 12.85; H, 3.67; N, 17.98. Found: C, 12.82; H, 3.48; N, 17.93.

$[\text{Co}(\text{NH}_3)_5(\text{pyrazine})](\text{ClO}_4)_3$. Pyrazine (20 g) was heated at 90 °C for 30 min with 1.5 g of $[\text{Co}(\text{NH}_3)_5(\text{Me}_2\text{SO})](\text{ClO}_4)_3$ ¹⁶ and enough added dimethyl sulfoxide to give a homogeneous solution. After cooling to room temperature, the pyrazine was extracted with ether. The remaining syrupy layer was treated at 0 °C with ca. 2 mL of concentrated perchloric acid, added dropwise. The precipitate which formed in this step was collected by filtration after several hours storage at 0 °C. The crude product (1.1 g after drying) was recrystallized several times by dissolution in a minimum amount of 60 °C 0.01 M perchloric acid and cooling slowly to ice-bath temperature. After washing with ethanol and ether and drying in vacuo, the yield was 0.5 g of yellow-orange needles. We encountered difficulties in our first preparations of this complex, owing to the presence of unreacted starting material. Good microanalytical results were obtained from a sample that had been precipitated quickly from a small volume of water by adding several milliliters of ethanol containing a few drops of concentrated perchloric acid. Anal. Calcd for $\text{CoC}_4\text{H}_{19}\text{N}_7\text{Cl}_3\text{O}_{12}$: Co, 11.27; C, 9.19; H, 3.66; N, 18.76. Found: Co, 11.36; C, 9.17; H, 3.27; N, 18.62. The ¹H NMR spectrum of the salt in D_2O solution featured multiplets of 9.0 and 8.7 ppm confirming the presence of N-coordinated pyrazine. The visible spectrum consisted of a single peak for which λ_{max} was 473 nm ($\epsilon_{\text{max}} 53.9 \text{ M}^{-1} \text{ cm}^{-1}$) and a strong end absorption masking the region below 350 nm.

$[\text{Co}(\text{NH}_3)_5(\text{Mepyz})](\text{ClO}_4)_3$. This compound was prepared from the Me_2SO complex in a manner analogous to the preparation of the pyrazine derivative. It was isolated as the iodide salt and recrystallized as the perchlorate as described by Dockal and Gould.¹⁷ Anal. Calcd for $\text{CoC}_5\text{H}_{21}\text{N}_7\text{Cl}_3\text{O}_{12}$: Co, 10.98; C, 11.19; H, 3.95; N, 18.28. Found: Co, 10.24; C, 11.11; H, 4.14; N, 18.25.

$[\text{Cr}(\text{urea})_6]\text{Cl}_3$. This compound was prepared in dim light, according to published methods.¹⁸ It was stored in darkness, in vacuo. The compound in aqueous solution gave absorption peaks at 442 and 625 nm with extinction coefficients 46.5 and $38.3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, in good agreement with known values (46.9 and $38.4 \text{ M}^{-1} \text{ cm}^{-1}$). Chromium in the complex was determined spectrophotometrically as chromate ion after H_2O_2 oxidation in basic solution.¹² The percent chromium found (10.06%) agreed well with the theoretical value of 10.02%.

Data Analysis. Reaction conditions were adjusted to yield pseudo-first-order rate processes in every case. Kinetics runs normally were made in triplicate and were reproducible within $\pm 5\%$. For each run, approximately 20 absorbance values were taken over 3 half-lives. These were fit by computer to the equation $A(t) = B \exp(-k_{\text{obsd}}t) + C$, where A is the absorbance, B is a proportionality constant, and C is the final absorbance. k_{obsd} , A , B , and C were refined in the calculation, performed on the University of Missouri's IBM 370/168 computer employing an iterative least-squares program. In the few cases where the rates of formation and decay of the intermediates were not widely (at least 20-fold) dissimilar, a program option fitting at least 50 points spaced throughout the growth and decay curve was used.

In this procedure the measured absorbance vs. time curve was fitted to the integrated equation for consecutive, first-order reactions given by Benson.^{19,20} The three parameters optimized in the computation were the specific rates of growth and decay and the molar absorptivity of the intermediate. Calcplot plots of the computed curves superimposed on the experimentally determined absorbance values showed excellent agreement. The limits of error computed in the regression analysis were never more than $\pm 3\%$.

Solutions of $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}(\text{aq})$. Care was taken to perform kinetics measurements on fresh solutions of pentacyanoaquaferate(II) ion. Approximately 0.2 mmol of sodium pentacyanoammineferate(II) was dissolved in 1 L of water (pH 8) and immediately a 5.00-mL sample was diluted in reduced light at pH 8–9 to 50.0 mL with a solution of appropriate ionic strength, deaerated by bubbling with N_2 . Syringe transfer technique was used to load the stopped-flow apparatus. Kinetics runs were made within 0.5 h of dissolution. Although good first-order plots with reproducible values of k_{obsd} were obtained, the total absorbance increase due to complex formation tended to decrease in consecutive runs. Control of pH was accomplished by adding buffers to the solutions of Co(III) oxidant. The acetate and hydrogen phosphate buffer solutions were made up to known ionic strength according to established procedures.²¹ At constant ionic strength and pH, the presence or absence of buffers was seen not to affect the results. The pH was measured after mixing reactant solutions.

Instrumentation. Cary Models 12 and 14 spectrophotometers, a Durrum D-150 stopped-flow instrument, and an Orion Model 801 pH meter were employed. Temperature control of ± 0.3 K was maintained in the spectrophotometer cuvettes. For intermediate-rate kinetics runs the stopped-flow instrument was connected to a Houston Instruments XY recorder with time base.

Actinometry. Incident radiation entering the stopped-flow cuvette (I_0) was determined by measuring absorbance changes due to photolysis of hexaureachromium(III) ion. The contribution of the photolysis products to the measured absorbance of 620 nm was found as follows.

Aqueous, unbuffered solutions of $\text{Cr}(\text{urea})_6^{3+}$, usually ca. 10^{-3} M, were irradiated in spectrophotometer cells of various path lengths with visible light from a focused 200-W tungsten source or, in some cases, a sodium lamp. Appropriate filters (nitromethane or commercial infrared and ultraviolet cutoff filters) were employed to screen out nonvisible components. Irradiation times were approximately 30–60 min, giving ca. 10% photolysis. After irradiation, the unreacted $\text{Cr}(\text{urea})_6^{3+}$ was precipitated by adding a large excess of solid sodium perchlorate as described by Wegner and Adamson.²² Control experiments showed that the amount of hexaureachromium(III) remaining in solution was negligible. After the rapid precipitation step, the absorbance of the filtrate was measured at 620 nm. Subsequently, the solution was treated with basic hydrogen peroxide and analyzed spectrophotometrically for chromium as chromate ion ($\epsilon_{\text{max}} 4815 \text{ M}^{-1} \text{ cm}^{-1}$ at 375 nm).¹² Six such measurements yielded values of the molar absorptivity of the partially aquated chromium(III) product(s) ranging from 25.8 to 27.8 $\text{M}^{-1} \text{ cm}^{-1}$ with an average value of 26.7 $\text{M}^{-1} \text{ cm}^{-1}$. The quantity $(\Delta A/\Delta[\text{Cr}])$, which under the experimental conditions is the change in molar absorptivity at 620 nm per mol/L of hexaurea complex photolyzed, could then be calculated as 19.8 $\text{M}^{-1} \text{ cm}^{-1}$. This result agreed well with the measured difference in absorbance of the original solution before and after irradiation, divided by the concentration of Cr(III) found in the filtrate. Using the filtered sodium lamp as the photolysis source, a nearly identical result was obtained. Variations in the path length of cells (1.00–10.0 cm), twofold changes in concentration, and the rate or lack of stirring were shown not to affect the results within experimental error. However, $(\Delta A/\Delta[\text{Cr}])$ was found to be sensitive to the photolysis time, being somewhat larger at short times, falling to the values given above after ca. 15 min, then to lower values after approximately 1–2 h. This was ascribed to the increasing importance of secondary photolysis.

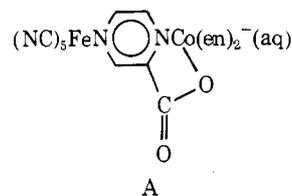
I_0 in the 2.0-cm path length stopped-flow cuvette was measured by following the absorbance change at 620 nm when a 1.0×10^{-3} M solution of hexaureachromium(III) was photolyzed in the cell. The light source used was the standard Osram tungsten lamp and Durrum monochromator adjusted to 5.0-mm slit width. The optical dispersion was 3 nm/mm. To compensate for the inner-filter effect of the chromophore produced by photolysis, I_0 was computed using²³

$$I_0 = \frac{\Delta[\text{Cr}]}{\Delta t \phi (1 - 10^{-A_0})} \left[1 + \frac{26.7\mu}{2(46.4)} - \frac{\Delta A (10^{-A_0})}{2(1 - 10^{-A_0})} \right] \quad (1)$$

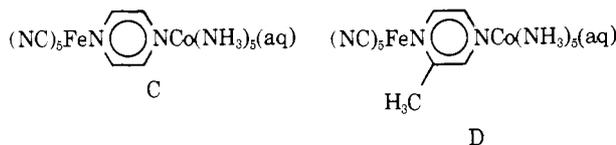
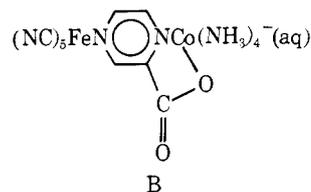
In eq 1 $\Delta[\text{Cr}]/\Delta t$ is the change in concentration of hexaureachromium(III) per unit time, ϕ is the photoaquation quantum yield (0.101), A_0 is the initial absorbance (usually 0.1 or less), and μ equals $[\text{Cr}]/[\text{Cr}_0]$. The major source of error was the difficulty in measuring the small values of the absorbance change. Normally this was accomplished by expanding the output of the photomultiplier circuitry on the X-Y recorder. Typical values of $[\text{Cr}_0]$, $\Delta[\text{Cr}]$, ΔA , and Δt were approximately 1.0×10^{-3} M, 1.7×10^{-4} M, 9×10^{-3} , and 1600 s, respectively. I_0 was found near 4×10^{15} quanta/ $\text{cm}^2 \cdot \text{s}$ but varied from week to week in the range $2\text{--}6 \times 10^{15}$ quanta/ $\text{cm}^2 \cdot \text{s}$. For the quantum yield determinations I_0 was determined before and after photoelectron transfer measurements.

Results

In the reaction of the aqueous pentacyanoferate(II) ion, $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$, with the complex ion pentaammine(pyrazine)cobalt(III) a transient blue color is observed. Visually, the intermediate resembles the rather stable species A which has been characterized by Toma.⁶ Although A is decomposed by



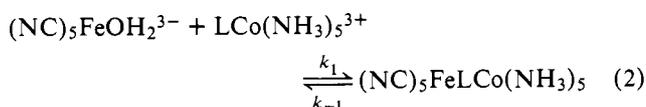
visible light, it is relatively unreactive at room temperature in darkness. By allowing pentacyanoaquaferate(II) ion to react with the appropriate cobalt(III) complexes, we have produced intermediates B–D in solution. Formation and decomposition



of B–D were monitored by stopped-flow spectrophotometry. Within experimental error, values of λ_{max} and ϵ_{max} of the intermediates were 630 ± 20 nm and $9.5 \times 1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 0.1 mm slit width.

Kinetics of Formation. The rates of formation of the intermediates were studied under pseudo-first-order conditions in which large excesses of the Co(III) complexes ($5.0\text{--}30 \times 10^{-4}$ M) were employed. Pentacyanoaquaferate(II) ion ($5\text{--}10 \times 10^{-6}$ M) was generated in solution by aquation of the pentacyanoammineferate(II) ion. The reactions showed no deviation from first-order kinetics over at least 3 half-lives.²⁴

Plots of k_{obsd} vs. $[\text{Co(III)}]$ were essentially linear, although at high concentrations of Co(III) k_{obsd} tended to fall slightly below the expected values. The results for complexes B and D are shown in Figure 1. We note that for D a nonzero ordinate intercept ($11 \pm 1 \text{ s}^{-1}$) was obtained. The results are consistent with complex formation as expressed in eq 2.



Under conditions of excess Co(III),

$$k_{\text{obsd}} = k_1[\text{Co(III)}] + k_{-1}$$

Table I. k_1 , Specific Rates of Formation of Precursor Complexes Containing $\text{Fe}(\text{CN})_5^{3-}$ (25 °C)

Oxidant	$10^{-3} k_1$, $\text{M}^{-1} \text{s}^{-1}$	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/ mol·K
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} 3^{+a}$	7.0 ± 0.3	17.4 ± 1.4	16 ± 5
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} 2^{+a}$	3.1 ± 0.1	17.4 ± 1.5	16 ± 5
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \text{CH}_3 3^{+a}$	3.7 ± 0.4		
$(\text{en})_2\text{CoN} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} 2^{+b}$	2.6 ± 0.2	15.3 ± 0.5	8 ± 2
$(\text{NH}_3)_5\text{CoOC} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} 2^{+c}$	1.5 ± 0.2		
$(\text{NH}_3)_5\text{CoOC} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} 2^{+c}$	1.9 ± 0.1		
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} 3^{+d}$	5.5 ± 0.3		

^a $\mu = 0.15 \text{ M}$, this work. ^b $\mu = 0.2 \text{ M}$, ref 6. ^c $\mu = 0.1 \text{ M}$, ref 8. ^d $\mu = 0.1 \text{ M}$, ref 5.

Table II. Dependence of Formation and Decomposition Rates on pH and Ionic Strength at 25 °C^a

Run	Complex	pH	μ , M	$10^{-3} k_1$, $\text{M}^{-1} \text{s}^{-1}$	$10^2 k_2$, s^{-1}
1	B	8.4	0.15	3.27	1.42
2	B	7.16	0.15	3.27	1.43
3	B	6.11	0.15	3.27	1.43
4	B	4.86	0.15	2.66	1.47
5	B	2.50	0.15	1.27	1.37
6	B	7.2	0.008	16.0	1.60
7	B	7.2	0.55	1.04	1.18
8	C	6.5	0.15	7.03	5.73
9	C	4.5	0.15	6.90	5.26
10	C	2.45	0.15	3.42	5.32
11	C	1.40	0.15	0.40	2.84
12	C	0.77	0.15	0.12	1.23
13	C	6.5	0.008	21.2	5.75
14	C	6.5	0.67	2.03	5.44

^a Although the values of k_1 and k_2 were relatively precise, their accuracy is estimated as $\pm 5\%$.

From the data in Figure 1, the association constant for formation of D, $K_{\text{eq}} = k_1/k_{-1}$, can be computed to be $(3.7 \times 10^3)/11 = 330 \pm 30 \text{ M}^{-1}$. The association quotient for D evidently is greatly diminished by steric repulsion between the pentacyanoferrate(II) moiety and the methyl group on pyrazine. Measurements of k_{-1} for B and C are impossible because of the rapid electron transfer reactions. However, these specific rates are probably near that for A ($3.15 \times 10^{-4} \text{ s}^{-1}$).⁶ We estimate that K_{eq} for B and C is near 10^7 M^{-1} . The results generated at $\mu = 0.15 \text{ M}$ are summarized in Table I. Included are the activation parameters obtained by varying the temperature in the range 11.0–31.0 °C. The pH and ionic strength dependences both for the formation reactions of B and C and

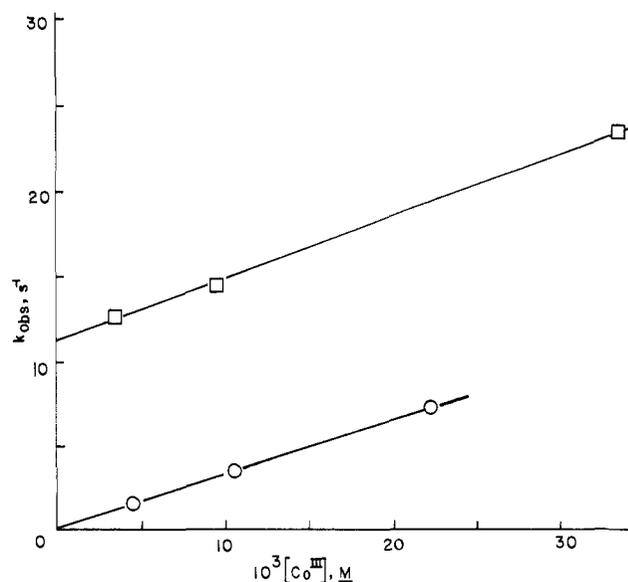
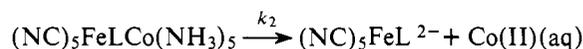


Figure 1. $[\text{Co(III)}]$ dependence of k_{obsd} for formation of complexes B and D (upper line). In the latter case k_1 and k_{-1} are resolved as slope and intercept. $\mu = 0.15 \text{ M}$, 25 °C, pH ~ 6.5 .

for the subsequent electron transfer step are given in Table II.

Kinetics of Intramolecular Electron Transfer. The reaction step following eq 2 is electron transfer:



(3)

The rates of disappearance of the intermediates were studied systematically under conditions of weak illumination at 620 nm. Decomposition was found to be a first-order process over at least 3 half-lives. For intermediates B and C the specific rate of decay was independent of concentration of Co(III) within the entire range $0.5 - 2.0 \times 10^{-3} \text{ M}$. For precursor D, k_2 was found to increase with increasing $[\text{Co(III)}]$. This was consistent with the relatively small value of the formation constant for this intermediate. At the highest concentration of Co(III), $5.0 \times 10^3 \text{ M}$, k_{obsd} for D was 0.184 s^{-1} for the thermal electron transfer step. Using the relationship $k_{\text{obsd}} = k_2 K_{\text{eq}} [\text{Co(III)}] / (1 + K_{\text{eq}} [\text{Co(III)}])$ and the value of K_{eq} (330 M^{-1}) we find that k_2 is 0.3 s^{-1} , if the reaction proceeds purely by an inner-sphere pathway. The results of the kinetics studies at narrow slit width, $\mu = 0.15 \text{ M}$, 11–31 °C, are summarized in Table III, along with results obtained by Haim and co-workers^{5,8} for some related systems.

Photoinduced Electron Transfer. Variations in k_2 with Slit Width. It was noted in our early experiments with these systems and in the experiments of others^{5,25} that the pentacyanoferrate(II) based precursor complexes are light sensitive. In the present work, the complexes normally were generated in a stopped-flow spectrometer whose light source was operated at minimum intensity (0.1 mm slit width).

An increase in the slit width was found to increase markedly the specific rate of disappearance of the complexes. This effect is shown in Figure 2 for complexes B and C. In each case, k_{obsd} is seen to be independent of the slit width at its lowest values, then to increase almost linearly. The curves in Figure 2 are very similar. Their vertical separation reflects the different rates of thermal intramolecular electron transfer in B and C.

Variations ($\pm 20 \text{ nm}$) in the wavelength setting were found not to affect the results. Therefore the increase in k_{obsd} given in Figure 2 was ascribed to an increase in I_0 , the intensity of incident light. The light intensity was measured at 5.0-mm slit

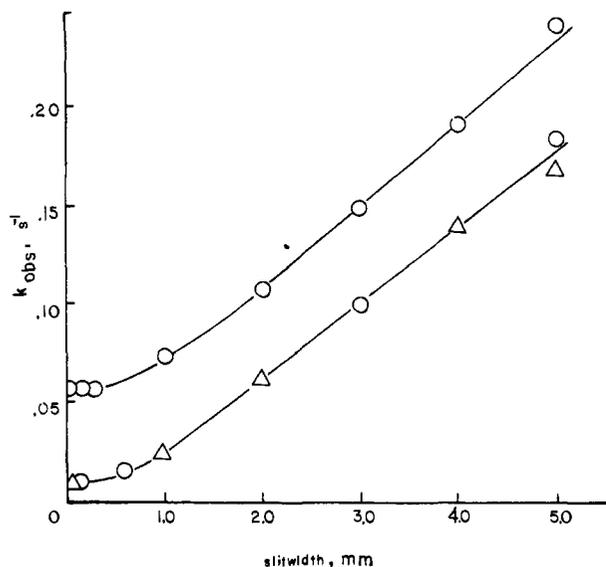


Figure 2. Slit width dependence of k_{obsd} for intramolecular electron transfer. Upper line is for complex C, lower for B. Triangles denote added ascorbic acid (5×10^{-4} M). $\mu = 0.15$ M, 25 ± 0.3 °C.

width, as described in the Experimental Section, by determining the rate of photolysis of hexaureachromium(III) ion in the 2.0 cm stopped-flow cuvette at 620 nm.

At the low concentrations of Fe(II) employed, the total absorbance was always 0.1 or less. Under these conditions, light intensity throughout the cuvette was assumed equal to I_0 . ϕ_{et} , the quantum yield for electron transfer, could then be calculated using²⁶

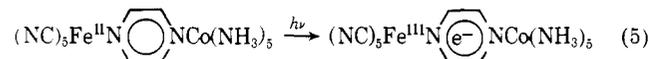
$$\phi_{\text{et}} = k_{h\nu} / (2.303 \times 10^3 I_0 \epsilon) \quad (4)$$

In this equation, ϵ is the extinction coefficient of the precursor complex at 620 nm, 5.0 mm slit width, and $k_{h\nu}$ is $k_{\text{obsd}} - k_{\text{th}}$, where k_{th} is k_{obsd} at low slit width. The results are given in Table IV.

While considering the slit width dependences of these reactions, we should include the following caveat. Our experiments indicate that undetected, light-induced errors may arise in spectrophotometric studies of reaction kinetics. Unless care is taken to maintain low light levels, photoinduced processes can become a major reaction pathway for species of high ϵ , if the quantum yield is appreciable.

Discussion

Spectra. The strong, visible absorption bands ($\lambda_{\text{max}} \sim 630$ nm at pH ~ 7) in the pyrazine-bridged precursor complexes are quite similar to those found for other pentacyanoferrate(II) species which incorporate aromatic, N-heterocycles in the first coordination sphere of iron(II).¹³ The bands are assigned to iron(II) to pyrazine charge-transfer (MLCT) excitation, eq 5. As in the *N*-methylpyrazinium complex of pentacyanoferrate(II), for which λ_{max} is 655 nm, the MLCT bands of the binuclear species show a bathochromic shift with respect to the pyrazine complex (452 nm). The shifts in the precursor complexes are ascribed by analogy to the inductive effect of the Co(III) substituent on the pyrazine ring.



It was noted that λ_{max} decreases gradually to values near 560 nm when the pH is made to fall in stages below ca. 2.5. Hypsochromic shifts of this type have been observed previously in mixed cyano complexes of iron(II).^{13,27,28} The effect is attributed to a stabilization of the iron(II) ground state, caused

Table III. k_{et} , Thermal Electron Transfer in Precursor Complexes Containing $\text{Fe}(\text{CN})_5^{-3}$

Oxidant	$k_{\text{th}}, \text{s}^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{cal/mol}\cdot\text{K}$
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{3+^a}$	0.055 ± 0.005	24.6 ± 1.4	18 ± 5
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{2+}$	0.013 ± 0.001	22.7 ± 1.0	9.5 ± 3.0
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{3+^a}$ CH ₃	~ 0.3		
$(\text{en})_3\text{CoN} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{2+}$	$< 10^{-5}$		
$(\text{NH}_3)_5\text{CoOC} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{2+}$	$< 3 \times 10^{-5}$		
$(\text{NH}_3)_5\text{CoOC} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{2+}$	1.75×10^{-4}		
$(\text{NH}_3)_5\text{CoN} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{N}^{3+^d}$	0.0026		

^a $\mu = 0.15$ M, this work, ^b $\mu = 0.2$ M, ref 6. ^c $\mu = 0.1$ M, ref 8. ^d $\mu = 0.1$ M, ref 5.

Table IV. Quantum Yields of Photoinduced Electron

Complex	$k_{h\nu}, \text{s}^{-1}$	$10^3 \epsilon, \text{M}^{-1} \text{cm}^{-1}$	$10^8 I_0, \text{einstains cm}^{-2} \text{s}^{-1}$	ϕ_{et}
A	4.1×10^{-3}	8.4 ± 1	1.1 ± 0.1	0.020 ± 0.003
B	0.17 ± 0.01	6.1 ± 1	1.4 ± 0.1	0.9 ± 0.15
C	0.18 ± 0.01	6.2 ± 1	1.4 ± 0.1	0.9 ± 0.15

by protonation of the pentacyanoferrate(II) group at cyanide.

Kinetics of Formation. Formation kinetics have been investigated for the aqueous pentacyanoferrate(II) complexes of numerous ligands.^{6,8,29-31} The relative rates depend mainly on the charge types of the attacking ligands and are virtually independent of the ligands' basicities. These observations have led to a general characterization of the substitution process as one in which breakage of the Fe(II)-OH₂ bond is rate determining. At pH ~ 6.5 the second-order rate constants and activation parameters given in Table I for formation of the pyrazine-bridged precursor complexes are very similar to values found for complexation of pentacyanoaquaferrate(II) by various positively charged ligands.

In Table II it is shown that the specific rates of formation decrease when the pH is lowered. Malin and Koch³² have made a similar observation that protonation at cyanide in pentacyanoaquaferrate(II) strongly retards substitution of *N*-methylpyrazinium for the bound water molecule. Part of this effect probably is due to the increase in positive charge carried by iron(II) in the protonated complex. The observed decrease in reactivity is consistent with a strengthening of the iron(II)-oxygen bond.

It is also shown in Table II that the rates of complex formation decrease markedly as the concentration of lithium perchlorate is increased. This negative salt effect is typical for

reactions of pentacyanoferrate(II) with positively charged complexing agents.^{29,30}

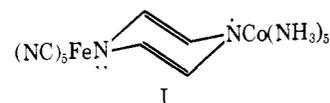
Intramolecular Electron Transfer. In contrast with the above-noted ionic strength effect, we find that the rates of intramolecular electron transfer scarcely are affected by variations in the concentration of inert electrolyte. A similar result was discussed by Fisher, Tom, and Taube,⁹ who studied electron transfer in precursor complexes containing ruthenium(II) as reductant. Thus, the limited data available at this time indicate that for observable precursor complexes, and perhaps for most other electron-transfer intermediates, the principal ionic strength effect arises not during the electron transfer event, but in the process of assembly of the reactive species.

In Table III the results of this study are compared with related work by Toma⁶ and by Haim and co-workers.^{5,8} We note, except for the bis(ethylenediamine) complex in which the driving force is substantially reduced,³³ that the pyrazine-bridged species are significantly more reactive than those bridged by 4,4'-bipyridine or by 3- and 4-pyridinecarboxylate. At least three factors may be considered responsible for this difference. First, the substitution of pyrazine directly into the inner coordination spheres of both Co(III) and Fe(II) permits comparatively close approach of the reducing center to the oxidant. Second, the requirement that electrons be transferred across carbon-carbon single bonds is eliminated in the pyrazine system. This factor may be particularly important because the most likely pathway for electron transfer utilizes the bridging ligand's conjugated low-lying π^* system.

A third condition which is expected to favor intramolecular electron transfer in the pyrazine complexes is the degree of $d\pi-p\pi$ back-donation from iron(II) to the bridging heterocycle. For a series of pentacyanoferrate(II) complexes of simple, aromatic heterocycles, a well-established ordering of oxidation potentials,¹³ Mossbauer isomer shifts,³⁴ NMR chemical shifts,³⁵ rates of substitution, and stability constants²⁹ indicates that increasing $d\pi-p\pi$ interaction is correlated with increasing λ_{\max} (MLCT). As noted previously, the values of λ_{\max} for the pyrazine-bridged precursor complexes are near 630 nm, while those for the species bridged by 4,4'-bipyridine or 3- and 4-pyridinecarboxylates are respectively 505, 370, and 430 nm. This suggests that $d\pi-p\pi$ back-donation from iron(II) to the bridging heterocycle is more extensive in the pyrazine-bridged cases than in the complexes bridged by the pyridine derivatives.

In Table II, runs 8-12 show that the specific rate of intramolecular electron transfer is diminished at low pH. The observation is consistent with the hypsochromic shifts noted when the complexes are protonated at cyanide. The two results demonstrate a stabilization of iron(II) in the protonated form against both thermal and light-induced oxidation.

Photoinduced Electron Transfer. The primary product of irradiation in the MLCT region (eq 5) is a singlet charge-transfer excited state (MLCT*). The fate of MLCT* may be radiationless relaxation to the ground state (1A_1), internal conversion to excited state(s) of lower energy, or chemical reaction. In Table IV, we note for complexes B and C that quenching by reduction of Co(III) occurs after every excitation event. The high quantum efficiencies for B and C are intriguing because of the mismatch in symmetry between the π^* orbitals populated in MLCT* and the Co(III) acceptor orbital (probably d_{z^2}). Attempts to visualize the mechanism are complicated by the possibility that electron transfer may take place directly from MLCT* or from some subsequent, partially relaxed state. In the latter case, we suggest that the symmetry restriction could be circumvented by populating a vibrational mode in which the bridging pyrazine radical approaches the configuration of 1,4-dihydropyrazine, e.g., I. This species is similar to one that has been suggested by Natarajan and Endicott.³⁶ Electron transfer from the coordinated nitrogen



radical to Co(III) would not be symmetry restricted. For unit quantum yield, the mechanism would require that the lifetime of MLCT* be long compared with the time scale of molecular vibration (10^{-12} s). Simple arguments based on oscillator strengths predict an emission lifetime for MLCT* of ca. 10^{-9} s.³⁷

The quantum efficiency of photoelectron transfer in A was much smaller than in B or C. This difference reflects the enhanced oxidizing power of tetraammine- or pentaamminecobalt(III) compared with the bis(ethylenediamine)cobalt(III) center. Mechanistically the decrease in ϕ can probably be linked to the relaxation of the first coordination sphere of Co(III) which is part of the activation process.³⁸ Chelation by ethylenediamine should reduce the efficiency of quenching by electron transfer, by limiting this relaxation.

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Matrix Photoionization Studies of Trifluoromethyl Halide Systems. Infrared Spectra of the CF_3^+ , CF_2X^+ , and CF_3X^+ Cations in Solid Argon

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Abstract: Photoionization of CF_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and H}$) samples by argon resonance radiation during condensation with excess argon at 15 K produced new infrared absorptions which were separated into distinct groups by mercury arc photolysis. Bands slightly reduced by photolysis are assigned to the daughter cations CF_3^+ and CF_2X^+ which were photoneutralized by transfer of electrons from halide ions. Absorptions markedly decreased by 340–1000-nm photolysis with the concomitant growth of CF_2X^+ absorptions are assigned to parent cations CF_3X^+ . Bands destroyed by 290–1000-nm photolysis are attributed to parent molecular anions. The cation CF_3^+ exhibits a very high ν_3 fundamental which is consistent with extensive $\pi(\text{p-p})$ bonding in this species.

Introduction

The trichloromethyl cation has been produced by secondary hydrogen resonance photolysis of CHCl_3 , proton radiolysis of CCl_4 , and argon resonance photoionization of CCl_4 , and trapped in solid argon for infrared spectroscopic study.^{1–3} The relatively high antisymmetric carbon–chlorine stretching frequency, 1037 cm^{-1} , suggests π bonding between the carbon and chlorines.

¹³C NMR studies of dimethylhalocarbenium ions have shown that fluorine interacts more effectively with the vacant p orbital on carbon than does chlorine.^{4,5} The methyl difluorocarbenium ion has been prepared in superacid media,⁶ but similar attempts to stabilize CF_3^+ failed owing to reaction with F^- to form CF_4 .⁷ In order to learn more about the bonding and stability of these species, the simple trihalomethyl cations CF_2X^+ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) have been prepared for infrared spectroscopic study using the matrix isolation technique. A very recent matrix photoionization investigation of the CFCl_3 , CF_2Cl_2 , and CF_3Cl compounds employed filtered high-pressure mercury arc photolysis of the samples to separate and identify the several molecular ions formed in these experiments, including the CFCl_2^+ and CF_2Cl^+ species.⁸ The present study of CF_3X compounds provides infrared data on CF_3^+ , CF_2X^+ , and the parent cations, and some insight into the bonding and photochemistry of these species.

Experimental Section

The cryogenic equipment, vacuum systems, and matrix photoionization methods have been described previously.^{3,9–11} The CF_3X compounds ($\text{X} = \text{H}, \text{Cl} = \text{Br}, \text{and I}$, Peninsular Chemresearch) were condensed at 77 K and evacuated to remove noncondensables. Carbon-13 enriched fluoroform was synthesized from the reaction of ¹³ CHCl_3 (90% ¹³C, Merck Sharp and Dohme) with $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (Magic Acid, Aldrich) which gave complete fluorination after 4 h. The fluoroform product was distilled from the reaction mixture at -127°C . Samples of $\text{Ar}/\text{CF}_3\text{X} = 200/1, 400/1, \text{and } 800/1$ were deposited on a CsI substrate at 14 K for 20 h with simultaneous irradiation from a windowless argon resonance lamp powered by a microwave discharge.^{11,12} Since a comparable amount of argon from the discharge was condensed with the sample, the $\text{Ar}/\text{CF}_3\text{X}$ ratio in

the matrix was double the sample value. The present experiments employed a 10-mm i.d. open-ended discharge tube. Samples of each reagent were also deposited for 20 h without photoionization to accurately measure the intensities and positions of all precursor absorptions. Infrared spectra were recorded during deposition to monitor product formation and after deposition on expanded wavenumber scales using a Beckman IR-12. Samples were photolyzed with filtered (water, transmits 220–1000 nm; water, Pyrex, transmits 290–1000 nm; and water, Pyrex, Corning 4303, transmits 340–1000 nm) BH-6 high-pressure mercury arc light and additional expanded scale spectra were scanned. The wavenumber accuracy is $\pm 0.5\text{ cm}^{-1}$. Band intensities were measured in absorbance units; comparisons of relative band intensities are accurate to better than 10%.

Results

A series of matrix photoionization experiments was done with each trifluoromethyl halide and fluoroform.

Trifluoromethyl Halides. Figure 1 contrasts infrared spectra for samples of CF_3Cl , CF_3Br , and CF_3I codeposited with simultaneous irradiation from the open argon discharge lamp. All of the spectra exhibited a sharp new feature at 1666.5 cm^{-1} and water impurity lines at 1594, 1610, and 1626 cm^{-1} .¹³ Each precursor gave two new bands in the $1520\text{--}1320\text{ cm}^{-1}$ region which depended on the heavier halogen. In the CF_3Cl experiments, the matrix split bands were dominated by sharp absorptions at 1515 and 1514 cm^{-1} ; these features shifted to 1484 and 1368 cm^{-1} in the CF_3Br run and to 1433 and 1321 cm^{-1} in the CF_3I study. The sharp 1666- and $1320\text{--}1520\text{ cm}^{-1}$ absorptions were slightly reduced by exposure to high-intensity mercury arc light using first 290–1000-nm and then 220–1000-nm filters.

The strongest new product band (labeled P^+) in each experiment also showed a halogen shift from 1299 to 1293 cm^{-1} or 1255 and to 1229 cm^{-1} for the three precursors. The lowest illustrated spectral regions exhibited sharp product bands (also labeled P^+) at 455, 469, and 497 cm^{-1} for the CF_3X precursors. Of particular interest is the chlorine isotopic doublet at 733.5 and 730.0 cm^{-1} in the CF_3Cl experiment. These P^+ absorptions showed substantial reduction upon photolysis with 340–1000-nm BH-6 mercury arc light.