Anomalies in the Kinetics of Substitution in $[Os(NH_3)_5H_2O]^{3+}$

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The ^{57}Fe Mössbauer spectrum of $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ consists of a quadrupole doublet, showing that, in being formed in the reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6{}^{3-}$, the bridging ligand has undergone a rotation of 180°, consistent with there being an induction period in the reaction profile for its appearance. In harmony with the foregoing, $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$, the product of the analogous reaction, shows a single absorption peak, its appearance following a first-order reaction. Though an induction period is observed in the formation of $[Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$, the Mössbauer spectrum of the potassium salt shows a single absorption peak. Our present more detailed study of the kinetics of substitution by $Fe(CN)_6{}^{4-}$ and $Co(CN)_6{}^{3-}$ in $[Os(NH_3)_5H_2O]^{3+}$ in unacidified solution shows that a catalyst for the reaction of the former is generated by the residual O_2 in a controlled-atmosphere box. The kinetic behavior of the reaction system with catalyst deliberately generated is described in this paper. Catalysis depends on labilization to substitution attending the oxidation of an Os(III) species to the Os(IV) state.

Introduction

In an earlier communication,[1] we reported anomalous kinetic effects in the substitution in $[Ru(NH_3)_5H_2O]^{3+}$ and $[Os(NH_3)_5H_2O]^{3+}$ by a number of hexacyano complexes. Each cation reacts with $Fe(CN)_6{}^{3-}$ to form two major inner-sphere products. These reactions are by parallel paths, there being no significant interconversion in this early reaction phase. As followed by the change in light absorption with time, the appearance of one of the products obeys simple first-order kinetics, while that of the second shows an induction period, following which first order behavior is also observed. The effect referred to is much less prominent when the aqueous reaction medium is acidified (e.g. 1.5×10^{-2} M H^+). Because the formation of one of the products is a strictly first-order reaction, that of the other must also be a first-order process and the anomaly is ascribed to a secondary reaction of one of the two immediate products of substitution, it changing to a species showing stronger absorption at the wavelength of measurement than does the early product of substitution.

Our study[1] of the reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6{}^{3-}$ led to the conclusion that $[Ru^{III}(NH_3)_5(Fe^{III}(CN)_6)]$ is the product of the path obeying normal kinetics, while $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ is the product of the other. For the corresponding $[Os(NH_3)_5H_2O]^{3+}$ system, we inferred that $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ is the product of the path following normal kinetics, while $[Os^{III}(NH_3)_5(Fe^{III}(CN)_6)]^*$, the formation of which shows an induction period, is the product arising from the other. Later observations[2] made in the course of studying the reaction of $[Os(NH_3)_6]^{3+}$ with $Fe(CN)_6{}^{3-}$ led to the conclusion that $[Os^{III}(NH_3)_5(Fe^{III}(CN)_6)]^*$ is the more stable isomer of the initial product of substitution, which we formulate as $[Os^{III}(NH_3)_5NCFe^{III}(CN)_5]$, of normal structure. The extinction coefficient of the more stable form at λ_{max} 826 nm is 6.7×10^3 M^{-1} cm^{-1}, while that of the species first produced, λ_{max} 606 nm, is 7.0×10^2 M^{-1} cm^{-1}, and ϵ is very low at the wavelength of measurement, ca. 820 nm. We suggested that the secondary reactions leading to the kinetic anomalies, i.e. the apparent induction periods, involve a "flip" of the bridging CN^- in the inner-sphere products.

Apart from our work, nothing seems to have been done on the reactions of either cation with $Fe(CN)_6{}^{3-}$, and encountering the kinetic anomalies referred to was therefore not altogether surprising. More surprising was the finding[1] that the substitution reactions of $[Os(NH_3)_5H_2O]^{3+}$, also with the nonoxidizing nucleophiles $Ru(CN)_6{}^{4-}$, $Fe(CN)_6{}^{4-}$, $Os(CN)_6{}^{4-}$, and $Co(CN)_6{}^{3-}$ show induction periods, which were very pronounced in water but less so on acidification, and tacitly, at least, we attributed these anomalies to the same cause, a "flip" of the bridging CN^- after formation of the inner-sphere product. In contrast to the reactions with $Fe(CN)_6{}^{3-}$, dual products are not formed, and thus isomerization of the initial product of substitution is not demanded by the kinetic data for these systems.

In this paper we report additional observations on the effects outlined, which help to clarify the chemistry. They include the results of applying ^{57}Fe Mössbauer spectroscopy to selected compounds recovered from reaction solutions, and further kinetic studies on the reactions of $Fe(CN)_6{}^{4-}$ and $Co(CN)_6{}^{3-}$ with $[Os(NH_3)_5H_2O]^{3+}$.

Experimental Section

Preparations. $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was prepared from OsO_4 according to the literature procedure.[3] The aquation rate for $[Os(NH_3)_5(CF_3SO_3)]^{2+}$ is 8.8×10^{-4} s^{-1} at 25 °C.[3] To avoid initial effects arising from the conversion of the triflate complex to the aquo, the solutions of $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ were prepared 2 h before mixing with the nucleophiles and, during this interval, were stored in a controlled-atmosphere box (CAB) in a capped container. A sample of $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was also purchased from Aldrich Inc.

$[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was prepared as described in the literature.[4] The rate constant for the aquation of $[Ru(NH_3)_5(CF_3SO_3)]^{2+}$

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is 1.9×10^{-2} s^{-1};[4] in all experiments we kept the ruthenium solutions 20 min before adding the nucleophiles.

$K_4Os(CN)_6$ was prepared from K_4OsCl_6 as described in the literature.[5] Sodium hexacyanoferrate(II) decahydrate (Strem), potassium ferricyanide (Sigma), potassium hexacyanoruthenate(II) trihydrate (Aldrich), and potassium hexacyanocobaltate were used as received.

Unless otherwise specified, the temperature for all the kinetic measurements was 20.0 °C, the reaction medium was water, and the materials used to prepare the reaction mixtures were kept in the CAB, under an atmosphere of N_2, and thus were deoxygenated to the level obtainable by the equipment ($O_2 \leq 5$ ppm).

The measurements were made outside the CAB, but as demonstrated by experiments with other O_2-sensitive solutions, leakage of O_2 into the cell is not a significant factor even for slow reactions. This conclusion is supported also by internal evidence: in many instances, over much of the reaction course, the appearance of color is zero order in the concentration of $[Os(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$. As shown below, catalyst is generated by O_2, and were O_2 leakage a serious complication, such simple kinetic behavior would not obtain.

The samples for the ^{57}Fe Mössbauer spectra, $K[Ru^{III}(NH_3)_5(Fe^{II}(CN)_6)]$, $K[Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]$, $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]\cdot 6H_2O$, and $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]\cdot 2H_2O$, were isolated from the reaction mixtures after the completion of substitution (8, 4, 1, and 15 h, respectively, after mixing), by addition of ethanol to the aqueous solutions in a 1/1 ratio and refrigeration to induce precipitation. The colored solids were filtered off washed with ethanol and diethyl ether, and vacuum-dried.[1] Anal. Calcd for $C_6H_{19}N_{11}O_2FeRu$: C, 16.56; H, 4.37; N, 35.49; Fe, 12.86; Ru, 23.29. Found: C, 16.55; H, 3.90; N, 34.79; Fe, 12.50; Ru, 25.20. Calcd for $C_6H_{27}N_{11}O_6FeOs$: C, 12.12; H, 4.54; N, 25.92; Fe, 9.39; Os, 32.02. Found: C, 11.51; H, 3.99; N, 25.96; Fe, 9.77; Os, 32.20.

Instrumentation. UV−vis spectra and kinetic measurements were recorded with a Hewlett-Packard 8452 A spectrophotometer with a thermostated cell holder. An mgw Lauda RC 20 Brinkmann circulating water bath was used to maintain the temperature in the cell holder. All kinetic measurements were performed in spectrophotometric cells with greased glass stoppers which were kept under Ar during the experiment to avoid air diffusion in the solution. IR spectra were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer.

Iron-57 Mössbauer spectra were recorded using a spectrometer consisting of an MDU-1200 driving unit, a DFG-1200 digital function generator, an MTV-1000 velocity transducer from Wissenschaftliche Electronik GmbH, and an N-5500 multichannel analyzer from EG&G ORTEC. The ^{57}Co(Rh) Mössbauer source (1.5 GBq) was purchased from Amersham International plc. The spectra were computer-fitted to Lorentian lines, and the isomer shift is given relative to α-iron foil at room temperature. The intensities and line widths for the quadrupole doublet were constrained to be equal.

Electrochemical experiments were performed under nitrogen by using a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltamograms were recorded using a gold working electrode, a Pt^0 counter electrode, and a Ag/AgCl reference electrode. The ionic strength was kept constant using LiOTF (0.010 M) as supporting electrolyte. All potentials are reported vs SHE.

Results

From the reaction mixtures we were able to isolate $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]\cdot 6H_2O$ and $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]\cdot 2H_2O$ by addition of ethanol to the aqueous solutions after completion of substitution, the entering nucleophile in each case being $Fe(CN)_6{}^{3-}$.[1] The IR spectra of the two solids in KBr disks showed broad bands which were assigned to the C≡N stretch, at 2045 and 2046 cm^{-1}, respectively. The bands are broad compared to that of $[Ru(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{3-}$, and they are close to that of $K_4Fe(CN)_6$ (2033 cm^{-1}) but well removed from that of $K_3Fe(CN)_6$ (2122 cm^{-1}). The failure to observe a separate CN$^-$ stretching peak in the infrared spectra of the two species, considering that the bands are broadened compared to that of $K_4Fe(CN)_6$, cannot be taken as evidence that substitution or isomerization respectively has not taken place. The nature of the atom attached to CN$^-$ not only affects the shift but also can have a profound effect on intensities.[6] Adding to characterization, the spectra of the solutions of these two solids in water are observed to exhibit a maximum at 320 nm, which is characteristic of $Fe(CN)_6{}^{4-}$, but not at 420 nm, where $Fe(CN)_6{}^{3-}$ has a strong absorption ($\epsilon = 1050$ M^{-1} cm^{1}) at absorbances consistent with their presumed abundances. Moreover, addition of acid to these solutions causes the IT absorption bands (614 nm for $[Os^{IV}Fe^{II}]$ and 935 nm for $[Ru^{IV}Fe^{II}]$) to shift to higher energies, as has been observed[1] for other cases in which $Fe(CN)_6{}^{4-}$ participates in a charge transfer transition, confirming the assignment of the 2+ oxidation state to the iron.

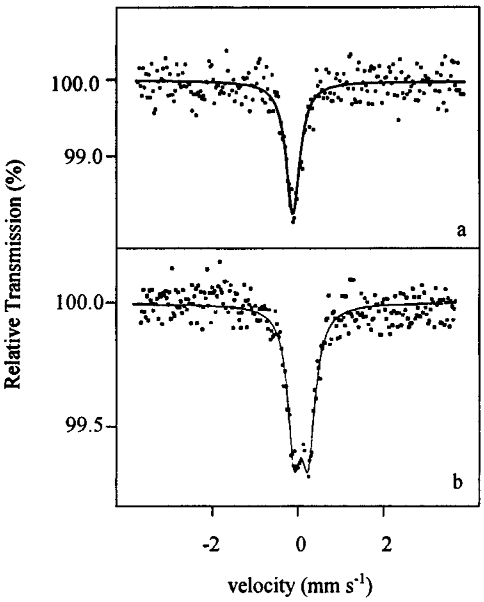

Figure 1. ^{57}Fe Mössbauer spectra of (a) $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]\cdot 6H_2O$ and (b) $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]\cdot 2H_2O$ at room temperature.

The Mössbauer spectra of the binuclear complexes at room temperature are shown in Figures 1and 2, and the Mössbauer parameters for the spectra recorded at room temperature and at 80 K are summarized in Table 1. The ^{57}Fe Mössbauer spectrum of $[Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$ shows that linkage isomerization of the bridging CN$^-$ has not occurred, and the result has led us to reexamine the kinetics of the reaction of $[Os(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6{}^{4-}$.

In Figure 3 is shown the increase in the absorption characteristics of the product $[Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$ as a function of time for reaction solutions treated in three different ways. Trace A was obtained for a sample to which the second reagent, $K_4Fe(CN)_6$, was added at the end of 2 h, whereupon the reaction mixture was transferred to a spectrophotometric cell which was then sealed. The shape of the curve (Figure 3) resembles those observed when the intervention of a bridging CN$^-$ flip is supported by other evidence. Similar shapes have repeatedly been seen for different preparations of $[Os(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ as well as for a sample of this compound purchased from Aldrich Inc. The specific rate for substitution calculated from the trace for experiment A, leaving out the initial phase, is 2.1×10^{-4} s^{-1} (much the same value was obtained by use of the Aldrich sample). Curve B (Figure 3) was obtained for a

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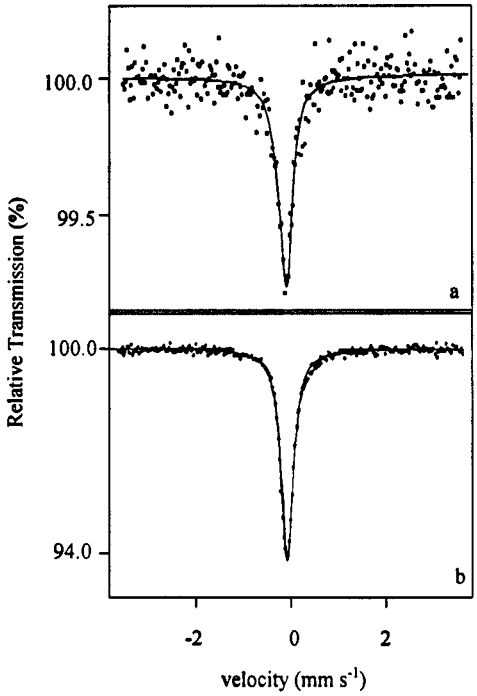

Figure 2. ^{57}Fe Mössbauer spectra of (a) $K[Os^{III}(NH_3)_5Fe^{II}(CN)_6]$ and (b) $K[Ru^{III}(NH_3)_5Fe^{II}(CN)_6]$ at room temperature.

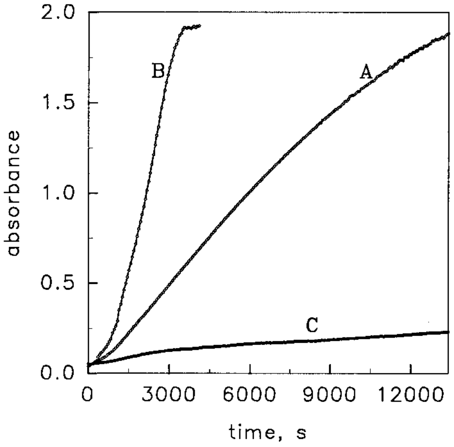

Figure 3. Absorbance vs time traces for $[[Os(NH_3)_5H_2O]^{3+}] = [Fe(CN)_6{}^{4-}] = 1.1 \times 10^{-3}$ M, temperature 20 °C, aquation period 2 h in the CAB, in a capped vial: (A) N_2 as blanketing gas; (B) brief exposure to the air; (C) ascorbic acid (1.0×10^{-4} M) added after the 2 h aquation period.

solution treated as in the case of curve A, but with the difference that the solution of deoxygenated $K_4Fe(CN)_6$ was added after uncapping the cuvette very briefly outside the CAB. An enormous increase in the reaction rate was observed, and following a short induction period, the reaction was zero order over most of its course.

When a solution such as used in experiment A is kept in a stoppered container, and thus not subjected to a changing atmosphere of N_2, for an additional 12 h before $Fe(CN)_6{}^{4-}$ is added, the rate of reaction is only slightly greater than that obtained for an experiment started 2 h after the complex was dissolved; if the solution is kept for 5 days, the initial rate of reaction is very much less than it is for experiment A, but there is now an extended induction period, the reaction accelerating almost over the entire course, as if catalyst were slowly being generated throughout (the reaction profile for this experiment is not shown).

Table 1. ^{57}Fe Mössbauer Parameters for the Recorded Spectra[a]

compound	δ^b (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	T (K)
$K[Os^{III}(NH_3)_5Fe^{II}(CN)_6]$	−0.06	0.00	0.37	298
	0.06	0.00	0.35	80
$K[Ru^{III}(NH_3)_5Fe^{II}(CN)_6]$	−0.07	0.00	0.32	298
	0.01	0.00	0.46	80
$[Os^{IV}(NH_3)_4NH_2Fe^{II}(CN)_6H]$	−0.15	0.00	0.41	298
$[Ru^{IV}(NH_3)_4NH_2Fe^{II}(CN)_6H]$	+0.20	0.35	0.40	298
	+0.32	0.37	0.40	80

[a] Relative area 100%. [b] Relative to α-iron foil.

Table 2. Summary of Kinetic Experiments Covering the Zero-Order Reaction Phase

expt	oxidizing reagent	[Cat] (M)	$[[Os(NH_3)_5H_2O]^{3+}]$ (M)	$[Fe(CN)_6{}^{4-}]$ (M)	$k_1{}^a$ (s^{-1})
D	$S_2O_8{}^{2-}$	5.0×10^{-5}	1.0×10^{-3}	9.0×10^{-4}	5.9×10^{-3}
E	$S_2O_8{}^{2-}$	5.0×10^{-5}	1.0×10^{-3}	1.0×10^{-3}	6.8×10^{-3}
F	$S_2O_8{}^{2-}$	2.5×10^{-5}	1.0×10^{-3}	1.0×10^{-3}	7.3×10^{-3}
G	$S_2O_8{}^{2-}$	5.0×10^{-5}	6.0×10^{-4}	6.0×10^{-4}	6.0×10^{-3}
H	$Fe(CN)_6{}^{3-}$	1.0×10^{-4}	1.0×10^{-3}	9.0×10^{-4}	6.8×10^{-3}
I	$Fe(CN)_6{}^{3-}$	1.0×10^{-4}	5.0×10^{-4}	1.0×10^{-3}	1.6×10^{-3}
J	Ce(IV)	1.0×10^{-4}	1.0×10^{-3}	1.0×10^{-3}	4.5×10^{-4}

[a] k_1 is obtained by dividing the slope (converted to M s^{-1}) by the concentration of the catalyst (M^c).

When the reaction solution during the 2 h storage is kept under an atmosphere of high-purity H_2, the rate of reaction is much less than that calculated from experiment A (5.0×10^{-6} s^{-1} as compared to 2.1×10^{-4} s^{-1}). We conclude that, under the conditions of our experiments, the major source (not necessarily the sole source) of the catalyst is residual O_2 in the atmosphere of the CAB. This conclusion is supported by an experiment in which the gas to liquid volume ratio in the capped container during the 2 h interval was increased by a factor of 3, which resulted in a substantial decrease in the time for completion of the reaction.

In experiment C (Figure 3), ascorbic acid (1.0×10^{-4} M) was added to the reaction solution after the 2 h interval. The reaction was now very slow, obeying first-order kinetics over its entire course. The specific rate observed was 2.7×10^{-6} s^{-1}. In a duplicate experiment, except that $K_4Fe(CN)_6$ was replaced by $K_4Os(CN)_6$, the specific rate of reaction was measured as 2.6×10^{-6} s^{-1}.

To generate the catalyst in known concentration, O_2 is not the most convenient choice. The results of a series of experiments in which a variety of oxidizing agents was used and reactant concentrations were changed are summarized in Table 2. The spectrophotometric trace for experiment D is shown in Figure 4. As in the case of trace B (Figure 3), the reaction is zero order over much of its course, toward the end showing a dependence on the concentration of $[Os(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$ which can be treated as first order. In all of the experiments of this series, similar traces are obtained, though the concentration regime in which the kinetics change from zero to first order can alter. In the zero order reaction phase, k_1 (s^{-1}) is obtained by dividing the slope, converted to M s^{-1}, by the concentration of catalyst M^c.

There proved to be a conspicuous complication in the use of Ce(IV) ($Ce(NH_4)_2(NO_3)_6$) as oxidant. A deep red color (λ_{max} = 430 nm) develops on mixing which is not observed in the other cases. This absorption is charge transfer in origin; it is characteristic of $[Os^{VI}(NH_3)_4N(Fe^{II}(CN)_6)]^-$ and is intense ($\epsilon = 2.8 \times 10^3$ M^{-1} cm^{-1}).[2] Apparently, most of the Ce(IV) was consumed in generating Os(VI), despite the large excess of $[Os(NH_3)_5H_2O]^{3+}$.

A limitation on the kinetic experiments is that the solutions are not independently buffered—the reagents $[Os(NH_3)_5H_2O]^{3+}$

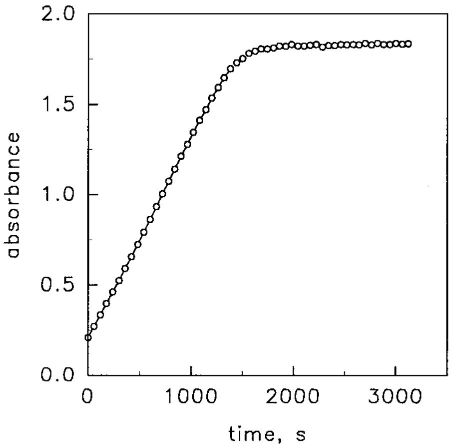

Figure 4. Absorbance vs time trace for $[[Os(NH_3)_5H_2O]^{3+}] = [Fe(CN)_6{}^{4-}] = 1.0 \times 10^{-3}$ M, temperature 20 °C, aquation period 2 h in the CAB, in a capped vial. $[S_2O_8{}^{2-}] = 5.0 \times 10^{-5}$ M was added to the $[Os(NH_3)_5H_2O]^{3+}$ solution after the aquation period.

($pK_a = 5.2$)[7] and $Fe(CN)_6{}^{4-}$ (pK_a for $[HFe(CN)_6]^{3-} = 4.2$)[8] do provide some buffer action, but they are at low concentration.

Two experiments were done in buffered solutions ($HOAc/^-OAc$, total concentration 0.010 M) at pH 4.6, which is the initial pH of the solutions of experiments D−H. In one experiment, the concentration of the catalyst generated by the atmosphere of the CAB was minimized by use of H_2 as blanketing gas during the 2 h period ($[[Os(NH_3)_5H_2O]^{3+}] = [Fe(CN)_6{}^{4-}] = 1.0 \times 10^{-3}$ M), the specific rate of the reaction being measured as 1.5×10^{-5} s^{-1}. In a second experiment, but now generating the catalyst by adding $S_2O_8{}^{2-}$ to the 5.0×10^{-5} M level, again first-order kinetics was observed and the specific rate was measured as 7.0×10^{-4} s^{-1}.

The catalytic effect is enormously attenuated when the reaction solutions are acidified, as was already suggested by our earlier work.[1] Thus with $[Os(NH_3)_5H_2O]^{3+}$, $Fe(CN)_6{}^{4-}$, and $S_2O_8{}^{2-}$ at the concentrations stipulated immediately above but with the reaction medium 1.5×10^{-2} M HO_3SCF_3, the specific rate of the reaction, strictly first order, was measured as 1.0×10^{-5} s^{-1}.

Experiments with $Co(CN)_6{}^{3-}$, which, among the nucleophiles studied in this and earlier work, cannot undergo a change in oxidation state in the relevant potential range, provide useful information. Induction periods were reported for unacidified solutions in the earlier work,[1] which were eliminated on acidification, but no experiments were done with oxidizing agent added in known amount. Two experiments were performed with the concentrations of $[Os(NH_3)_5H_2O]^{3+}$ and $S_2O_8{}^{2-}$ the same as in the above experiment, but with $Co(CN)_6{}^{3-}$ replacing $Fe(CN)_6{}^{4-}$. Substitution was accelerated, and the reaction profile was observed to be zero order over much of its course ($k_1 = 6.5 \times 10^{-4}$ s^{-1}), but instead of entering a first-order phase as shown in Figure 4, there was an apparent acceleration toward the end, behavior which was duplicated in a second experiment. Extraneous absorption was noted in the visible region of the spectrum, but not at the wavelength, 312 nm, at which the reaction was monitored. In one experiment, acid (1.5×10^{-2} M HO_3SCF_3) was added to the $[Os(NH_3)_5H_2O]^{3+}/Co(CN)_6{}^{3-}$ mixture after the 2 h period. The aquation took place in an open vial in the CAB, so that catalyst was generated from the residual O_2. The reaction proved to be first order with a rate identical (2.1×10^{-6} s^{-1}) to the one measured for an experiment in which acid was added to the Os(III) solution before the aquation, and the vial was kept in the CAB capped. This value is slightly less than that observed with $Fe(CN)_6{}^{4-}$ and $Os(CN)_6{}^{4-}$ as entering nucleophiles, for what we take to be the uncatalyzed reaction.

For the electrochemical measurements, it is necessary to avoid high concentrations of supporting electrolyte because the stability of the ion pairs decreases sharply with ionic strength, but supporting electrolyte is needed to obtain useful signals in cyclovoltammetry, and low concentrations of the electroactive components must be used to avoid the formation of precipitates. A workable compromise was found with the concentrations of $[Os(NH_3)_5H_2O](O_3SCF_3)_3$ and $Na_4Fe(CN)_6$ each at 2.5×10^{-4} and LiO_3SCF_3 at 0.010 M. In measurements at a sweep rate of 100 mV/s, at room temperature the values of $E_{1/2}$ (vs SHE) observed are 0.39, 0.44, and 0.68 V for $Na_4Fe(CN)_6$, $[Os(NH_3)_5H_2O]^{3+}$,$[Fe(CN)_6]^{4-}$, and $[Os(NH_3)_5Fe(CN)_6]^-$ respectively. Under the conditions of these experiments, collapse of ion pairs to inner-sphere products is first order in ion pair concentration for >90% reaction. The amplitudes of the signal are the same within 10%, and the peak to peak separations are 150, 170, and 165 mV, respectively.

Discussion

^{57}Fe Mössbauer spectroscopy is a powerful tool for diagnosing the orientation of the bridging cyano group.[9] If the bridging CN^- coordinates to Fe(II) by the carbon end, the electron distribution around the Fe(II) atom, t^6_{2g}, has octahedral symmetry and so the electric field gradient is absent, thus giving a single-line absorption. On the other hand, if the bridging CN^- links Fe(II) by the nitrogen, the symmetry of the t_{2g} electron distribution is lowered and consequently a quadrupole doublet will be observed.

Among the four binuclear complexes measured, only $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ shows a quadrupole splitting (0.35 mm/s at room temperature), demonstrating that the CN^- bridge is attached to Fe(II) by nitrogen. The hyperfine interactions have been measured for a series of Fe(II)-substituted pentacyanides;[10] $K_2[Fe(CN)_5NO]$ has the highest quadrupole splitting of 1.76 mm/s, while $Na_4[Fe(CN)_5NH_3]$ has the lowest of 0.6 mm/s. The nitrosyl ion is a very weak σ donor and a very strong π acid, while NH_3 acts simply as a σ donor. When CN^- is ligated through C, it is a weaker π acid than NO^+, and when bonded through N, it is much weaker and is a moderately good σ donor (thus compare the ligand properties of CH_3NC and CH_3CN). It is not surprising therefore that the quadrupole splitting for $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ is closer to the latter and much smaller than the former. Cyanide linkage isomerization has been found to occur in the solid state for the polymeric complex of approximate composition $Fe_3[Cr(CN)_6]_2$, at room temperature in an inert atmosphere in a few days or at 50 °C in about 3h.[11] While the linkage isomerization, in solution, in our system is considerably more rapid than that reported for the solid, it must be kept in mind that the electronic structure, πd^4 for Ru(IV), is unprecedented in earlier studies.

$[M^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$ (M = Ru, Os) and $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ give a single-line absorption, indicating that the bridging cyano group coordinates to Fe(II) by carbon.

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The small values of isomer shift (δ) for $Fe(CN)_6^{4-}$ salts of different metal ions such as K^+, Mg^{2+}, Cu^{2+}, Ag^+, and Al^{3+} (-0.047,[12,13] -0.097,[13,14] -0.098,[13,14] -0.122,[13,15] and -0.157 mm s^{-1},[13,14] respectively, relative to α-iron foil at room temperature) have been attributed to the strong π-bonding interactions in the anion.[13,14] This is also true for $[M^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$ (M = Ru, Os) and $[Os^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ (-0.06, -0.07, and -0.15 mm s^{-1}, respectively relative to α-iron foil at room temperature). The present observation suggests that the interaction between two metal atoms through the CN^- bridge is not large and that the Os(IV) atom attracts more t_{2g} electrons than does Os(III) through the CN^- group. The larger value of isomer shift for $[Ru^{IV}(NH_3)_4(NH_2)(Fe^{II}(CN)_6H)]$ (+0.20 mm s^{-1} relative to α-iron foil at room temperature) supports the conclusion that the bridging cyanide has rotated by 180° (as already mentioned the N-terminal of the CN^- group has less π-acceptor capability than the C-terminal), which is reached on the basis of the observed quadrupole splitting, and is also consistent with the kinetic evidence which shows that the immediate product of the substitution undergoes a structural change.

Because of the similarity of the reaction profiles for the substitution on $[Os(NH_3)_5H_2O]^{3+}$ by nonoxidizing nucleophiles ($Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Co(CN)_6^{3-}$, and $Os(CN)_6^{4-}$), with the anomalous profiles observed in the reactions with $Fe(CN)_6^{3-}$, we had assumed[1] that linkage isomerization also took place in these systems. However, the Mössbauer spectrum for the K^+ salt of $[Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$, as mentioned above, is symmetric (Figure 2a) and we conclude that linkage isomerization does not occur, at least when the nucleophile is $Fe(CN)_6^{4-}$. An induction period is not observed in the reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6^{4-}$, and as expected, the Mössbauer spectrum of the K^+ salt of $[Ru^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-$ (Figure 2b) shows a single peak.

In turning to the kinetic data, we note that the rate for experiment A (leaving out the induction period), 2.1×10^{-4} s^{-1}, is much too high to correspond to the intrinsic rate of substitution (see below) and we conclude that we are observing a catalytic process. Reaction in experiment B is complete in 3.5×10^3 s, while in experiment A, it is only 90% complete in approximately 11×10^3 s. We attribute the induction period in experiment B, in which a small amount of O_2 was admitted to the reaction vessel, after which monitoring of the reaction was promptly begun, to build-up of the catalyst. Unacidified aqueous solutions of $[Os(NH_3)_5H_2O]^{3+}$ in air develop color rather rapidly, and this process is inhibited by acid. It is likely, therefore, that $[Os(NH_3)_5OH]^{2+}$ reacts with O_2 more rapidly than does $[Os(NH_3)_5H_2O]^{3+}$. On taking account of the initial pH of the completed reaction mixture, ca. 4.6, and the pK_a for the aquo ion, 5.2,[7] and on the assumption that the hydroxo complex is reactant, k for the reaction of the hydroxo complex with O_2 is calculated to be ca. 12 M^{-1} s^{-1}.

Though from general laboratory experience there had been hints that unacidified solutions containing $[Os(NH_3)_5H_2O]^{3+}$ undergo change—slow darkening—the marked sensitivity to O_2 as indicated by the present studies came as a surprise. If it is assumed that, on the time scale of our studies, Os(IV) is the product of the reaction, that O_2 reacts by a 2 e^- change, and that the O_2 content of the blanketing N_2 is at the upper limit of 5 ppm, the Os(IV) content of the reaction solution at the end of the 2 h period can be as high as 1×10^{-5} M, a value that seems reasonable in relation to the results obtained when Os(IV) is generated by addition of $S_2O_8^{2-}$.

The salient features of results obtained in the experiments in which a catalyst is generated deliberately can be accounted for by a mechanism consisting of two steps.

$$[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-} \xrightarrow{k_1} [Os^{III}(NH_3)_5(Fe^{III}(CN)_6)] + H_2O \quad (1)$$

$$[Os^{III}(NH_3)_5(Fe^{III}(CN)_6)] + [Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-} \xrightarrow{k_2} [Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^- \text{ (final product)} + [Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-} \quad (2)$$

In earlier work[1] it was shown that immediately upon mixing of $[Os(NH_3)_5H_2O]^{3+}$ with $Fe(CN)_6^{3-}$ there is a partial depletion of the latter, implying that the ion pair exists in two forms [III],[III] and [IV],[II]. At the prevailing pH, ca. 3.7, the former is undoubtedly $[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-}$, but the state of protonation of the latter is in doubt and will be dealt with later. As used in the presentation of the mechanism, the formulation $[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-}$ is to be taken to represent the equilibrium mixture of the two forms. At the steady state the equation governing the course of the reaction is

$$d[[Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^-]/dt = \frac{k_1k_2[\text{Cat}][[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}]}{k_1 + k_2[[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}]}$$

where [Cat] is given by the concentration of oxidizing agent added, i.e. equal to $[[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-}] + [[Os^{III}(NH_3)_5(Fe^{III}(CN)_6)]]$.

In the appropriate concentration range, at the beginning of the reaction the k_2 term in the denominator dominates, so that the rate of reaction is given by k_1[Cat] and the reaction therefore is zero order. When the reagent ion pair is sufficiently depleted, k_1 in the denominator can become the dominant term and the rate law becomes $k_2[\text{Cat}][[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}]$; i.e., it assumes first-order kinetics.

When the reaction rate is zero order, the catalyst at the steady state is mainly in the outer-sphere form; collapse to the inner-sphere form is rate determining so that figures in the last column of Table 2 are the experimental values of k_1. It is clear from the comparison of the data that $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ give similar results (experiments D–H). The low value observed in experiment J is attributable to the side reaction in which Os(VI) is generated by Ce(IV).

A possible complication in studying the reaction in the catalytic mode is that an excess of $Fe(CN)_6^{4-}$ can affect the efficiency of the catalyst by the electron exchange process

$$[Fe(CN)_6]^{4-} + [Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-} = [Fe(CN)_6]^{3-} + [Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-} \quad (3)$$

The outer-sphere affinity of $Fe(CN)_6^{4-}$ for $[Os(NH_3)_5H_2O]^{3+}$ is expected to exceed that of $Fe(CN)_6^{3-}$ so that, when free $Fe(CN)_6^{4-}$ is present, not all of the $Fe(CN)_6^{3-}$ is in contact with $[Os(NH_3)_5H_2O]^{3+}$. We conclude that, in experiment I, which is similar to experiment H except that free $Fe(CN)_6^{4-}$ is present,

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the ratio of $Fe(CN)_6{}^{3-}$ in the ion pair to that free is 0.85/5.95. On taking account of the concentrations of the other species involved in reaction 3, the value of the equilibrium constant is calculated as 7—a lower limit because some of the catalyst is stored as [Os(IV)],[Fe(II)].

The value of the ratio of the two forms of the catalyst, [Os(IV)],[Fe(II)], **1**, and [Os(III)],Fe(III)], **2**, affects the interpretation of the values of k_1 in Table 2, k[**1**] and k[**2**] being equivalent representations, when equilibrium is maintained. Moreover, it should be noted that the ratio will be dependent on the pH as determined by the pK_a values for $[Fe(CN)_6H]^{3-}$ and $[Os(NH_3)_5H_2O]^{3+}$, which in the ion pairs are expected to be slightly different from the values for the free ions.

In principle, the value of k_1 for experiment H, 6.8×10^{-3} s^{-1}, should agree with that measured directly by mixing $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{3-}$ in a 1/1 ratio in unacidified solution, 1.5×10^{-2} s^{-1}.[1] Though the difference is outside experimental error, it is very unlikely that the mechanisms in the two cases are different—the agreement is too close for that to be a reasonable possibility. More likely, the discrepancy is a result of the difference in the two environments. The pH of the solutions in which the dominant species are $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{4-}$, on the one hand, and $[Os(NH_3)_5H_2O]^{3+}$ and $Fe(CN)_6{}^{3-}$, on the other, are ca. 4.6 and ca. 3.7, respectively, and this alone can account for the difference.

In experiment G of Table 2, the concentration of the reactant ion pair is reduced compared to that in experiment E. As required by the mechanism, the first-order kinetic regime is found to account for a larger fraction of the total reaction than it does in experiment E. By treating the last portions of the rate profiles as first order, we calculate the specific rates, k_2, for the electron transfer steps as 40 and 45 M^{-1} s^{-1}, respectively.

Marked changes in the character of the reactions are brought about by changes in environment. The components of the acetate buffer themselves accelerate the rate of substitution, absent oxidizing agent, as shown by the specific rate of 1.5×10^{-5} s^{-1} with 0.01 M buffer, pH 4.6, compared to 2.7×10^{-6} s^{-1}, at the same pH without buffer. Presumably, proton shifts are involved in the activation process also for the intrinsic reaction. For the reaction catalyzed by oxidizing agents, on the addition of buffer, pH remaining unchanged, the kinetics become first order over the entire reaction course, the specific rate 1.5×10^{-5} s^{-1} being 41-fold greater than it is in the absence of the oxidizing agent. When the catalyzed reaction is in the first-order mode, electron transfer rather than substitution is rate determining. The specific rate of 7 M^{-1} s^{-1} for electron transfer calculated for the buffered systems is a factor of 6 slower than it is when the solution is unbuffered, and this is almost enough to account for electron transfer being rate determining, without invoking an accelerating effect of buffer on the rate of substitution.

Addition of acid (1.5×10^{-2} M) also brings about a change in the kinetics of the catalyzed reaction from zero order to first, the specific rate of 1.0×10^{-5} s^{-1} presumably including the contribution of the intrinsic path. The difference of 7.3×10^{-6} then represents the catalytic path when electron transfer, step 2, is rate determining. The specific rate for step 2 then is calculated as 7.3×10^{-2} M^{-1} s^{-1} in acidic solution. Under these conditions, the catalyst will be almost completely in the form $[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6H]^{3-}$ ($Fe(CN)_6{}^{4-}$ may even be doubly protonated)[8] and reaction 2 assumes the form

$$[Os^{III}(NH_3)_5(Fe^{III}(CN)_6)] + [Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6H]^{3-} \rightarrow [Os^{III}(NH_3)_5(Fe^{II}(CN)_6)]^- + [Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-} + H^+$$

or a similar form in which electron transfer is coupled to proton transfer from the outer-sphere complex to the inner sphere. Protonation of $Fe(CN)_6{}^{4-}$ in the outer sphere form apparently adds an additional barrier to electron transfer, suggesting that in 1.5×10^{-2} M H^+ it may be doubly protonated.

For most of the reactions we have dealt with, the pH of the solutions was in the range 3.7−4.6, where the [Os(IV)],[Fe(II)] form of the catalyst is stabilized relative to [Os(III)],[Fe(III)] so that electron transfer based on the Os(IV)/Os(III) couple can contribute to the catalytic cycle. That this is in fact the case is shown by experiments with $Co(CN)_6{}^{3-}$ as the entering nucleophile. While in acidic solution, $[H^+] = 1.5 \times 10^{-2}$ M, catalysis by the oxidizing agent is negligible, it is substantial in unacidified solutions. From the rate of the reaction in the zero-order mode, the specific rate for substitution in the ion pair $[Os^{IV}(NH_3)_5OH],[Co^{III}(CN)_6]$ is calculated as 6.5×10^{-4} s^{-1}, to be compared to substitution in the ion pair $[Os(NH_3)_5H_2O]^{3+},[Co(CN)_6]^{3-}$, 2.1×10^{-6} s^{-1}. The rate of electron transfer in the zero-order mode must exceed the rate of substitution, and thus a lower limit to the specific rate of electron transfer (reaction 4) based on the Os(IV)/Os(III) couple is 6.5 M^{-1} s^{-1}. At the prevailing pH, the osmium(IV) complex will be stabilized by deprotonation and at the very least, coordinated H_2O will be deprotonated. Reaction 5 would account, qualitatively at least, for the effects of acidity if outer-sphere association of $Fe(CN)_6{}^{4-}$ with the Os(IV) moiety lowers the pK_a of $[HFe(CN)_6]^{3-}$, 4.2,[8] sufficiently so that at the prevailing pH, 3.7, the acid is largely dissociated.

$$[Os^{IV}Co^{III}(CN)_6] + [Os(NH_3)_5H_2O]^{3+},[Co(CN)_6]^{3-} = [Os^{III}Co^{III}(CN)_6] + [Os^{IV}],[Co(CN)_6]^{3-} \quad (4)$$

$$[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{3-} = [Os^{IV}(NH_3)_5OH]^{3+},[Fe^{II}(CN)_6]^{4-} + H^+ \quad (5)$$

Important considerations advanced thus far require reaction 2 to be unidirectional, and this requires $E_{1/2}$ for $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ to be substantially greater for the inner-sphere form, relative to that for the ion pair. This requirement is borne out by the electrochemical measurements: 0.68 and 0.44 V, respectively. The data taken at face value would lead to 1×10^4 for the equilibrium constant governing reaction 2. However, for reactions involving large charges, the ionic environment is difficult to define: thus note that the electrochemical measurements again taken at face value, lead to 7 as the equilibrium constant for formation of $[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}$, at odds with the fact that the uncatalyzed reaction is strictly first order to greater than 90% completion. It is to be noted that even if K_2 were as low as 1×10^2, the requirements of the mechanism would be satisfied.

An incidental conclusion from the electrochemical measurements is that particle formation in the solutions (which may be supersaturated) is not a serious complication. The wave forms of the cyclovoltammetric responses for equimolar solutions of $Na_4Fe(CN)_6$, $[Os(NH_3)_5H_2O]^{3+},[Fe(CN)_6]^{4-}$, and $[Os(NH_3)_5Fe(CN)_6]^-$ are almost identical.

With the agreement of rates of substitution in $[Os(NH_3)_5H_2O]^{3+}$ by $Co(CN)_6^{3-}$ in acid, 2.1×10^{-6} s^{-1}, with those obtained with $Fe(CN)_6^{4-}$ and $Os(CN)_6^{4-}$ as nucleophiles, 2.7×10^{-6} and 2.6×10^{-6} s^{-1}, ascorbic acid being present to remove oxidants, it is rather certain that in these experiments we are measuring the intrinsic rates for collapse of the outer sphere to inner-sphere forms. The effect of ascorbic acid in removing catalyst was at first sight surprising, because our earlier work[1] shows that Os(IV) is not reduced by ascorbic acid. But it also showed that $Fe(CN)_6^{3-}$ is reduced rapidly, and with forms **1** and **2** in rapid equilibrium the outcome is explained.

While we seem to have a reasonable understanding of the major features of the reaction with catalyst generated deliberately, the behavior when it is generated by residual oxygen is far from understood. Reasonable interpretations of some of the observations can be offered. The aging of the catalyst—that is, the decrease in efficiency when it is kept for a long time—and the subsequent autocatalytic behavior over much of the course of the reaction can be attributed to condensation of Os(IV), which then is reversed slowly when $Fe(CN)_6^{4-}$ is present. The initial induction period (curve A, Figure 3) can be attributed to the same cause. However the first-order behavior after the induction period is unexplained. In terms of the mechanism, we must postulate that electron transfer, rather than substitution, is rate determining. The residual catalyst is at much lower concentration than it is in the experiments when it is deliberately generated, but the mechanism as written does not allow for a change in rate-determining step on changing the concentration of the catalyst.

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