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Reactions of the Ion Pair $[Os(NH_3)_6]^{3+}\cdot[Fe(CN)_6]^{3-}$

Vassiliki G. Poulopoulou and Henry Taube*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

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In investigating the chemistry of the ion pair $[Os(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{3-}$, because of the rapid formation of the highly colored inner sphere products, we had difficulty in determining the properties of the absorption band associated with the intervalence transition.[1] It has been shown that λ_{max} for the IT transitions in $[Ru(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{4-}$ and $[Ru(NH_3)_6]^{3+}\cdot[Fe(CN)_6]^{4-}$ are similar, 718[1] and 714 nm,[2] respectively, and with this precedent in mind we turned to $Os(NH_3)_6^{3+}$ as a stand-in for $[Os(NH_3)_5H_2O]^{3+}$ in the expectation that substitution would now be very much slower. On preparing an aqueous solution containing equal (5.0×10^{-4} M) concentrations of the reagents we observed the rapid appearance of a blue color with no further change, perceptible by visual observation, after about 10 min at room temperature. Measurements of the properties of the absorption band showed $\lambda_{max} = 614$ nm, $\epsilon = 1.3 \times 10^3$ M^{-1} cm^{-1}, identical within experimental error with the properties of S_i,[3] the species which we concluded[1] has $Fe(CN)_6^{4-}$ ligated to an Os(IV) ammine, the state of protonation of the ammine moiety having been left undetermined.

To determine the amount of NH_3 released in the substitution, a similar mixture was prepared, but with each reagent at higher concentration (2.0×10^{-3} M). After approximately 10 min at room temperature it was passed through an anion exchange resin (Bio-Rad AG1-X2, 200–400 mesh, Cl^- form) which we found removes most of the color, and then through a cation exchange resin (Sephadex SP C-25) which retains the residual color. The colored species remains on the column on elution with 0.10 M NaCl, a composition which readily elutes NH_4^+. Determination of the amount of NH_3[4] in the final solution showed that 0.19 mg of NH_3 had been released in the reaction, to be compared to 0.18 mg expected for replacement of one NH_3 per $Os(NH_3)_6^{3+}$. There is no significant change in pH in the course of the reaction (6.9 initial; 6.8 final) and on this basis we conclude that the stoichiometry for the production of S_i is

$$[Os(NH_3)_6]^{3+}\cdot[Fe(CN)_6]^{3-} = [Os^{IV}(NH_3)_4NH_2(Fe^{II}(CN)_6)]^- + NH_4^+$$ [5]

Os(IV) being stabilized by the loss of a single proton and by the quite nucleophilic ligand $Fe(CN)_6^{4-}$. The earlier work left the state of protonation of the ammine moiety undetermined.

In studies of the reaction kinetics (all done at 20 °C), we used a series of buffers, in which the ionic strength was kept constant, and to retain first order behavior for the rate of collapse of the ion pair, it was kept low. In an experiment performed at pH = 7.0 ((KH_2PO_4 + Na_2HPO_4) + $LiSO_3CF_3$, $\mu = 1.3 \times 10^{-2}$) the rate constant for the first reaction phase, which we take to involve substitution, was determined as 1.1×10^{-2} s^{-1}. This phase produces a species not encountered in our earlier work. The spectrum of the new (n) species, S_n, is shown in Figure 1 (trace b) as recorded in an experiment done at somewhat lower pH to extend the life. An important feature of the spectrum of S_n is that the profile of the lowest energy charge transfer band of $Fe(CN)_6^{3-}$ (maximum at 420 nm), is retained in detail. IT absorption appears at $\lambda_{max} = 606$ nm ($\epsilon = 700$ M^{-1} cm^{-1}) (Figure 1, trace b). Additional results to be introduced presently show that these absorption characteristics are unchanged over a very wide range in pH. We conclude that S_n arises from substitution in the ion pair, without net relocation of electrons, and without structural change apart from that involving replacement of NH_3 by $Fe(CN)_6^{3-}$. We find the same species as the initial product in the $[Os(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{3-}$ system on carrying out the reaction in a solution buffered at pH = 4.7. The connection with the earlier work,[1] all of which was done at lower pH (3.6–1.8), is established by the finding that when a solution containing S_n is treated with acid (e.g, 1.0×10^{-2} M HSO_3CF_3) a rapid transformation takes place yielding a spectrum similar to that reported earlier for these conditions: namely absorption with a

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(1) Poulopoulou, V. G.; Li, Z. W.; Taube, H. *Inorg. Chim. Acta* **1994**, 225, 173.
(2) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, 21, 1562.
(3) On collapse of the ion pair $[Os(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{3-}$ to inner sphere products,[1] new absorption appears in three different regions of the spectrum. We introduced the notation S_l, S_i, S_h to distinguish the species showing absorption in the low, intermediate and high energy regions.
(4) The amount of NH_4^+ was determined by boiling the solution after addition of a known excess of NaOH (10 mL, 0.01 M). Ammonia escapes with the steam, and the excess sodium hydroxide was titrated with a standard HCl solution.
(5) Two bracket pairs are used to represent an ion pair, and one bracket pair is used for an inner sphere form.

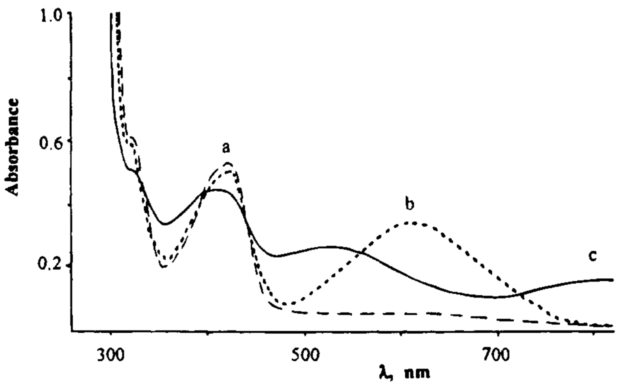

Figure 1. Charge transfer absorption of the new species $[Os^{III}(NH_3)_5\cdot Fe^{III}(CN)_6]$ (S_n): (a) after mixing the two solutions $[Os(NH_3)_6^{3+}] = [Fe(CN)_6^{3-}] = 5.0 \times 10^{-4}$ M, pH 4.1, total buffer concentration 3.5×10^{-3} M ($NaHC_6H_7O_7$ + HCl), ionic strength 1.3×10^{-2}; (b) at the end of substitution (first phase); (c) addition of 1.0×10^{-2} M HSO_3CF_3.

maximum at ca. 820 nm which we had assigned to an anomalous[6] form of $[Os^{III}(NH_3)_5Fe^{III}(CN)_6]$, S_l, absorption at shorter wavelengths which we assigned to a protonated form of S_i (see Figure 1, trace c), and, at still higher energy, S_h, which was unassigned.

In a slower reaction, governed by a rate constant of 1.4×10^{-3} s^{-1}, (pH = 7.0), S_n transforms to S_i ($[Os^{IV}(NH_3)_4NH_2(Fe^{II}(CN)_6)]^-$).[1] This is followed by a third reaction phase which over the whole range of pH is slower than the previous one. We find from our present work that the over-all stoichiometry at this stage conforms to

$$3[Os^{III}(NH_3)_6]^{3+}\cdot[Fe^{III}(CN)_6]^{3-} = [Os^{VI}(NH_3)_4N(Fe^{II}(CN)_6)]^- + 2[Os^{III}(NH_3)_5Fe^{II}(CN)_6]^- + 3NH_4^+ \quad (1)$$

i.e., the Os(IV) coordinated to $Fe(CN)_6^{4-}$ in S_i eventually disproportionates to Os(VI) and Os(III).

The amount of $[Os^{III}(NH_3)_5Fe^{II}(CN)_6]^-$ produced as measured by monitoring the charge transfer band at 628 nm (1.6×10^3 M^{-1} cm^{-1})[1,7] after 24 h was found to correspond within 3% to that expected on the basis of this stoichiometry. The $[Os^{VI}(NH_3)_4N(Fe^{II}(CN)_6)]^-$ was also identified spectrophotometrically. The spectrum of the final product solution shows a prominent peak at 430 nm. When $Fe(CN)_6^{4-}$ in equal concentration is added to a solution containing $[Os^{VI}(NH_3)_4N]^{3+}$ [8] the same value of λ_{max} is obtained. The value of ϵ is measured as 2.8×10^3 M^{-1} cm^{-1}, which agrees within 10% with that calculated for the product solution on the basis of eq 1. The band at 430 nm is apparently charge transfer in origin and arises on mixing the two components, equilibrium being reached after about 1 min (5.0×10^{-4} M).

The rate of the first reaction phase was measured over a wide range in pH, and the results are summarized in Figure 2. At pH 7.0 and below, manual mixing procedures sufficed but in the more alkaline media, a stopped flow device was used (Hitech Scientific SFA-II Rapid Kinetics Accessory). To determine the rate of reaction in the substitution phase, as free as possible from complications arising in the second phase, the data were treated by the Guggenheim method.

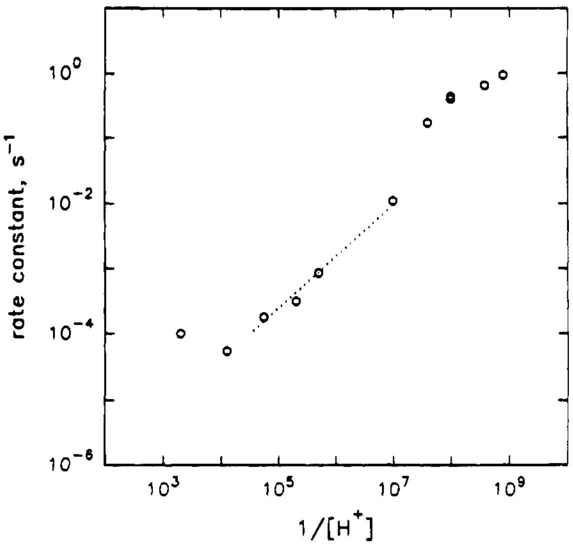

Figure 2. Kinetic data for the substitution reaction in the pH range 3.3–8.9, by using different buffer solutions. Total buffer concentration 3.5×10^{-3} M, ionic strength 1.3×10^{-2}, and $[Os(NH_3)_6^{3+}] = [Fe(CN)_6^{3-}] = 5.0 \times 10^{-4}$ M. Buffers used: $KHC_8H_4O_4$ + HCl, pH 3.3; $NaHC_6H_7O_7$ + HCl, pH 4.1; $NaC_2H_3O_2$ + $HC_2H_3O_2$, pH 4.7; $KHC_8H_4O_4$ + NaOH, pH 5.3 and 5.7; KH_2PO_4 + Na_2HPO_4, pH 7.0; $(HOCH_2)_3CNH_2$ + HCl, pH 7.6 and 8.0; $Na_2B_4O_7$ + HCl, pH 8.0, 8.6, and 8.9.

The result we emphasize in this survey of the kinetics of substitution is that this rate is inverse in [H$^+$] over a range of at least 2 orders of magnitude. As to the extremes in pH, it seems definite that, within the range covered by our study, the reaction rate reaches a limit at low pH, and perhaps passes through a minimum (i.e. there may be a term in the rate law first order in [H$^+$]). At low pH, there is frequent interference by precipitation, a complication which we have as yet found no means to control. At high pH the reaction rate reaches a plateau, which implies complete deprotonation in the ion pair. We interpret the inverse first order dependence of the rate of substitution on [H$^+$], in the middle pH range, to the establishment of the equilibrium

$$[Os(NH_3)_6]^{3+}\cdot[Fe(CN)_6]^{3-} = [Os^{IV}(NH_3)_5NH_2]^{3+}\cdot[Fe^{II}(CN)_6]^{4-} + H^+ \quad (2)$$

the rate of reaction being proportional to the concentration of the deprotonated form. Deprotonation is promoted by the conversion of Os(III) to Os(IV).

Electron transfer from Os to Fe within the ion pair, as postulated, has at least two important consequences: (a) it enormously enhances the rate at which substitution, as already demonstrated in our earlier work, can take place; (b) it catalyzes proton exchange between $Os(NH_3)_6^{3+}$ and D_2O. The latter effect is demonstrated by the experiments now to be described.

Solutions in D_2O of $Os(NH_3)_6(O_3SCF_3)_3$ (1.5×10^{-3} M) in 5×10^{-4} M HCl were prepared, containing a known concentration of *tert*-butyl alcohol as an internal standard. In the absence of $Fe(CN)_6^{3-}$, no change in the ratio of the NMR peaks attributable to HOD and to *tert*-butyl alcohol was observed even

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(6) Induction periods were observed[1] in all reactions of $[Os(NH_3)_5H_2O]^{3+}$ with hexacyano complexes, even with $Ru(CN)_6^{4-}$, $Fe(CN)_6^{4-}$, and $Co(CN)_6^{3-}$. In the reaction with $Fe(CN)_6^{3-}$, an induction period was observed in the formation of S_l, which we concluded is an $[Os^{III}(NH_3)_5Fe^{III}(CN)_6]$ species, but not in the formation of S_i. We attributed the induction periods to linkage isomerization of the bridging CN$^-$.

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after 20 h.[9] With $Fe(CN)_6^{3-}$ present at the same concentration as Os(III), by the time the first measurement was made (3.5 min), the ratio was observed to be 12% greater than in the blank experiment and, within experimental error, that expected for complete exchange of ammine protons (11%). The same result was obtained with $Fe(CN)_6^{3-}$ at a succession of lower concentrations, extending to 1.2×10^{-6} M, $[Os(NH_3)_6^{3+}]$ remaining at 1.5×10^{-3} M. If, as we assume, reaction 2 is responsible for catalysis of the exchange, the specific rate for the forward reaction is at least 1.2×10^4 s^{-1} if all of the ammine protons exchange each time Os(IV) is formed and 18 times greater, if each act leads to the exchange of only a single proton.

The original objective was achieved on two occasions out of fifteen attempts, the failures being due to early precipitation of solids. In mixing equal concentrations of $Os(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$ (5.0×10^{-4} M) at pH = 5.3, (total buffer concentration 6.9×10^{-3} M ($KHC_8H_4O_4$ + NaOH)), in the clearer example, a well-defined maximum was observed at 560 nm ($\epsilon = 40 \pm 5$ M^{-1} cm^{-1}) which we ascribe to the ion pair. The value of λ_{max} for $[Os(NH_3)_5H_2O]^{3+}\cdot[Fe(CN)_6]^{3-}$, arrived at by intercomparisons,[1] is 580 nm.

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(9) The rate of proton exchange between a number of hexammine complexes of tripositive metal ions has been shown to be inverse in $[H^+]$. From the measurement[10] of the rate exchange for $Os(NH_3)_6^{3+}$ at pH 4.75, k_{ex} in 5×10^{-4} M HCl is calculated as 4×10^{-6} s^{-1}, the comparison with $k_{ex} > 10^4$ s^{-1} signifying a powerful catalytic effect for a trace of oxidant.

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