Stability of Pentaammineosmium(II) in Aqueous Solution

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The reduction of $Os(NH_3)_5(OTf)_3$ in D_2O or H_2O over zinc amalgam gives rise to a species that retains the ability to form $(NH_3)_5Os^{II}$ adducts with the π-acidic ligands acetone, *N,N*-dimethyluracil (DMU), and acetonitrile for periods of hours in the absence of reducing agent. The η^2-DMU complex was shown not to be in equilibrium with free DMU, in contrast to a previous report. Kinetic trapping studies are described that demonstrate the following: (1) an "active" source of $(NH_3)_5Os^{II}$ other than the aquo complex is formed and decomposes by a first-order process with a half-life of about 3 h at room temperature in D_2O; (2) the rate of the decomposition process increases markedly at lower pH; and (3) the decomposition rate in H_2O is about twice that in D_2O. No direct spectroscopic or electrochemical evidence of species having osmium–hydrogen bonds was observed at neutral pH.

Pentaammineosmium(II) is an extraordinarily versatile metal center for the binding and manipulation of π-acidic ligands.[1] We are interested in the π-complexation of $(NH_3)_5Os^{2+}$ with molecules of biochemical significance, but its chemistry in aqueous solution has received very little attention. We have recently found it possible to prepare π-complexes of $(NH_3)_5Os^{2+}$ with nucleic acid bases in high yields in aqueous solution, by an experimental protocol related to that of Zhang and Shepherd,[2] in which $(NH_3)_5Os^{3+}$ is reduced by zinc amalgam in the presence of the π-accepting base.[3] Desiring a system in which the reducing agent and ligand are not present in the same reaction mixture, we found that the zinc amalgam could be removed before addition of the nucleobase to give the desired η^2-Os adducts with little or no loss in yield. This was surprising, since the low formal potential of the $(NH_3)_5(H_2O)Os^{II/III}$ redox couple (−0.73 V vs NHE)[4] suggested to us and others[5] that $Os(NH_3)_5(OH_2)^{2+}$ would be unstable in aqueous solution. Gulens and Page have noted that $(NH_3)_5Os^{2+}$ decomposes rapidly in 1 M aqueous acid but shows some stability on an electrochemical time scale at pH 7.[4]

Here we report the results of kinetic trapping studies that demonstrate the following: (1) an "active" source of $(NH_3)_5Os^{II}$ other than the aquo complex is formed in aqueous solution and decomposes by a first-order process with a half-life of hours at room temperature; and (2) the rate of the decomposition process increases markedly at lower pH and is greater in H_2O than in D_2O.

Results

Consistent with previous reactions in methanol,[6] when a stirred mixture of $Os(NH_3)_5(OTf)_3$ and zinc amalgam in 1 M aqueous HCl was filtered and immediately treated with $NaBPh_4$ to precipitate the cationic metal components, $[Os(NH_3)_5(\eta^2\text{-}H_2)](BPh_4)_2$ was isolated in 72% yield. The osmium byproducts, presumably paramagnetic Os(III) and Os(IV) compounds, were not characterized. In contrast, $NaBPh_4$ precipitation of an identical mixture prepared in neutral H_2O showed less than a 2% yield of the dihydrogen adduct. This led us to explore the competence of the reduced aqueous osmium species in binding π-acidic ligands in the absence of reducing agent.

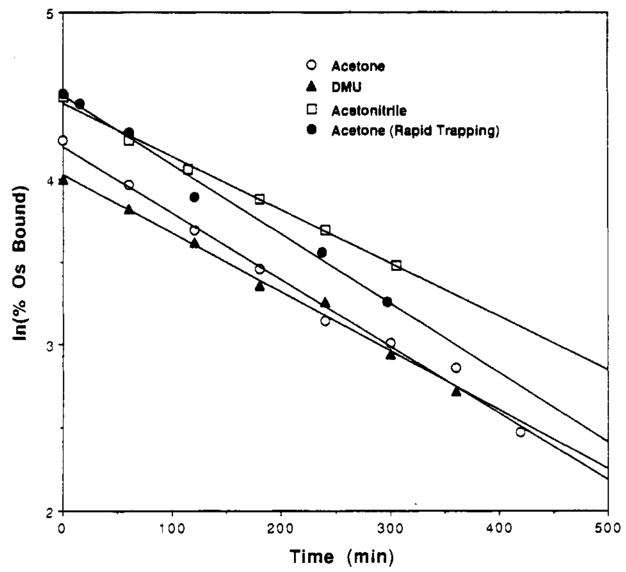

Figure 1. Os(II) decomposition kinetics in D_2O (22 ± 1 °C; $[Os]_{tot}$ = 0.013 ± 0.002 M) with trapping by acetone (open circles), DMU (triangles), acetonitrile (squares), and a large excess of acetone (closed circles).

This issue was addressed by reduction of $Os(NH_3)_5(OTf)_3$ with zinc amalgam in D_2O followed by filtration. The resulting Os(II) solution was allowed to stand under nitrogen. The amount of active Os(II) was determined as a function of time by transfer of aliquots to neat acetone in large excess, which resulted in the rapid formation (see Experimental Section) of the stable adduct $(NH_3)_5Os(\eta^2\text{-acetone})^{2+}$ (**1**).[7] The aliquot taken immediately after by filtration of the reducing agent was designated as t = 0. Following removal of excess acetone in vacuo, the resulting aliquot mixtures were dissolved in D_2O and analyzed by ^1H NMR in the presence of added *N,N*-dimethylacetamide as internal integration standard to determine the amount of **1** formed relative to total osmium concentration. The plot of ln(% Os bound) vs time shown in Figure 1 demonstrates a good linear correlation, providing an observed rate constant for Os(II) decay (averaging two runs: Table I, supplementary material) of $(6.8 \pm 0.5) \times 10^{-5}$ s^{-1}, representing a half-life of approximately 170 min.

The rate of Os(II) decomposition was also determined by a more convenient procedure, in which aliquots were transferred

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(6) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261–2263.

(7) (a) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227. (b) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439–2445.

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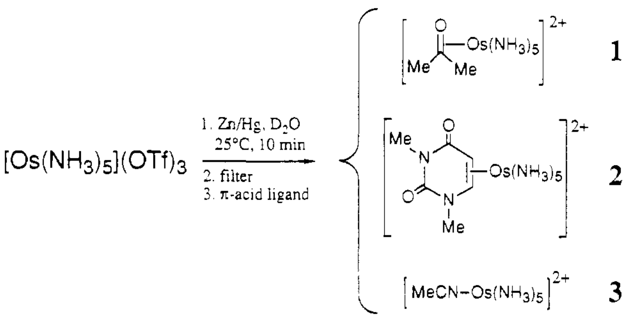
Scheme I. Pentaammineosmium(II) Complexes Used as Kinetic Traps



to D_2O solutions of a 2–3-fold excess of either acetone, *N*,*N*-dimethyluracil (DMU), or acetonitrile as π-accepting trapping ligand (Scheme I) and analyzed directly by ^1H NMR. All three ligands are known to form stable adducts with $(NH_3)_5Os^{2+}$ in high yield,[2,3,7,8] the first two in an η^2 geometry. Although the use of lower concentrations of ligand results in slower trapping rates (vide infra), the corresponding plots [ln(% Os bound) vs time] were also linear; Figure 1 shows representative examples. Each of the three π-acidic ligands gave identical slopes within experimental error; averaging these values provided an observed rate constant for Os(II) decay of $(6.2 \pm 0.8) \times 10^{-5}\ s^{-1}$, confirming the value obtained above with rapid acetone trapping. Unless otherwise noted, all additional kinetics experiments discussed below were performed with the more convenient trapping procedure.

The Os(II) decomposition process responds as expected to changes in temperature: first-order rate constants at 40 and 10 °C were found to be $(3.8 \pm 0.7) \times 10^{-4}$ and $(2.2 \pm 0.8) \times 10^{-5}\ s^{-1}$, respectively. This has the practical consequence of making Os(II) available in aqueous solution at lower temperatures for very long periods. Control experiments are as follows.

(1) NMR spectra of D_2O solutions of $[Os(NH_3)_5(\eta^2\text{-acetone})](OTf)_2$ (complex **1**)[7] and $[Os(NH_3)_5(\eta^2\text{-DMU})](OTf)_2$ (complex **2**),[3] both from crude D_2O reaction mixtures and after purification from methanol, were unchanged against internal standard over a 48-h period. A solution of **2**, prepared independently in methanol and purified by precipitation as the triflate, was similarly stable in D_2O when stirred over zinc amalgam for 18 h. In addition, purified **2** showed no formation of **1** in D_2O solution in the presence of a large excess of acetone. On the other hand, when $Os(NH_3)_5(OTf)_3$ is reduced and added to a mixture of DMU and acetone, **1** and **2** are both formed (vide infra). These data are inconsistent with thermodynamically-controlled equilibration and instead confirm that **1** and **2** are nonlabile and stable in the absence of air over the course of our kinetics experiments.

(2) The observed rate of Os(II) decomposition was found to be the same with reagents deoxygenated and handled under either nitrogen or argon atmosphere: the former was routinely used for convenience.

(3) Several samples of zinc amalgam in D_2O were stirred for 10 min and filtered into flasks containing the $[(NH_3)_5Os](OTf)_3$ precursor. After 10 min of stirring, a 2-fold excess of DMU was added to each to give *no* observable **2**. These experiments, conducted under conditions closely approximating those of the kinetic runs, confirm that the persistence of Os(II) in solution in the absence of zinc amalgam is not due to finely-divided or colloidal Zn(0) that travels through the filter frit. In addition, samples of H_2O in which Zn/Hg had been stirred and then filtered out contained less than 10 ppm of zinc by atomic absorption analysis, representing a fraction of 1 mol % zinc with respect to osmium.

(4) A solution of $[(NH_3)_5Os](OTf)_3$ in H_2O was stirred with zinc amalgam for 10 min in the standard fashion, filtered, and evaporated to dryness. Elemental analysis of the resulting solid revealed the presence of mercury at a concentration of only 5 ppm. This rules out the formation of species containing an Os–Hg bond, as has been observed for Rh in the reduction of $[Rh(en)_2]^{3+}$ at a mercury electrode.[9]

(5) The observed rate of Os(II) decomposition was found to be independent of the time of reduction of the Os(III) precursor. Thus, stirring $Os(NH_3)_5(OTf)_3$ over zinc amalgam in D_2O for 3 h instead of 10 min, followed by filtration and analysis of aliquots by the acetone trap assay, gives rise to a decomposition rate ($7.2 \times 10^{-5}\ s^{-1}$) similar to that discussed above. Interestingly, the yield of complex **1** at the start of this assay was greatly diminished (23% compared to 69%), suggesting that Os(II) decomposition also occurs in the presence of reducing agent. It appears that $(NH_3)_5Os^{2+}$, once decomposed, cannot be completely regenerated with zinc amalgam.

(6) NMR spectra of **1**[7] and **2**[10] are unaffected by the presence of their respective Os(III) analogues, due to linkage isomerization that accompanies the redox process. Therefore, the NMR method of assay cannot be compromised by the presence of Os(III) byproducts. Conversely, resonances for the acetonitrile adduct **3** are completely suppressed by rapid electron transfer in the presence of trace amounts of $[(NH_3)_5Os(CH_3CN)]^{3+}$. The observation of clean quantitative NMR spectra for reactions involving acetonitrile indicate that reduction of $Os(NH_3)_5(OTf)_3$ with zinc amalgam proceeds completely to the Os(II) state.

The reduction of $Os(NH_3)_5(OTf)_3$ *in the presence* of 1 equiv of DMU at osmium concentrations similar to those used in the kinetics experiments above provides complex **2** in excellent yield (70%–90%) within 10 min. However, when the Os(III) precursor is reduced *in the absence* of π-acidic ligand and is then exposed to DMU, formation of **2** is more sluggish. This was first observed in our initial use of DMU as a trap for the kinetics experiments discussed above. When the resulting aliquots were analyzed by NMR less than 1 h after their preparation, the data showed more scatter and a greater apparent Os(II) decay rate than is depicted in Figure 1. In addition, the observed ratios of bound to free DMU in the NMR samples were found to increase with time. Data in Figure 1 were therefore obtained with quenched aliquots that were allowed to stand until a stable ratio of bound to free ligand was observed (4 h for **2**; 2 h for **1** and **3**) by NMR, with the consistent results described above.

The unexpectedly slow formation of an Os(II)–DMU adduct prompted us to quantitate the rate of binding of DMU, acetone, and acetonitrile, by monitoring separate sealed NMR samples of freshly-generated $(NH_3)_5Os^{II}$ in D_2O at similar concentrations in the presence of 2.5–3.0 equiv of each ligand. Figure 2 shows the percentage yields of **1**–**3** (with respect to total osmium) for each sample. Note that the formation of the DMU complex **2** occurs more slowly than the formation of the acetonitrile adduct **3**, requiring approximately 90 and 30 min to go to completion, respectively. The relative rates of acetone and DMU binding are not so clearly differentiated in Figure 2, so an internal competition experiment was performed: a freshly-prepared D_2O solution of $(NH_3)_5Os^{2+}$ was treated with a mixture of 1.7 equiv of DMU and 1.5 equiv of acetone, and the formation of the resulting η^2 adducts was monitored by NMR. After 1 h, **1** and **2** were present in 48% and 27% yields, respectively, relative to total osmium, demonstrating more rapid binding of acetone. Since decomposition of the Os(II) precursor occurs at a significant rate with respect to that of DMU complexation, the final yield of **2** is lower than those of **1** and **3**.

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(9) Gulens, J.; Konrad, D.; Anson, F. C. *J. Electrochem. Soc.* **1974**, *121*, 1421–1429. (b) Gulens, J.; Anson, F. C. *Inorg. Chem.* **1973**, *12*, 2568–2574.

(10) Cyclic voltammetry of complex **2** reveals anodic and cathodic components of the II/III redox couple that are separated by approximately 1.0 V in the same manner as for complex **1**, characteristic of redox-mediated linkage isomerization.[7] A full description of the electrochemistry of **2** and related complexes will be reported separately.[3]

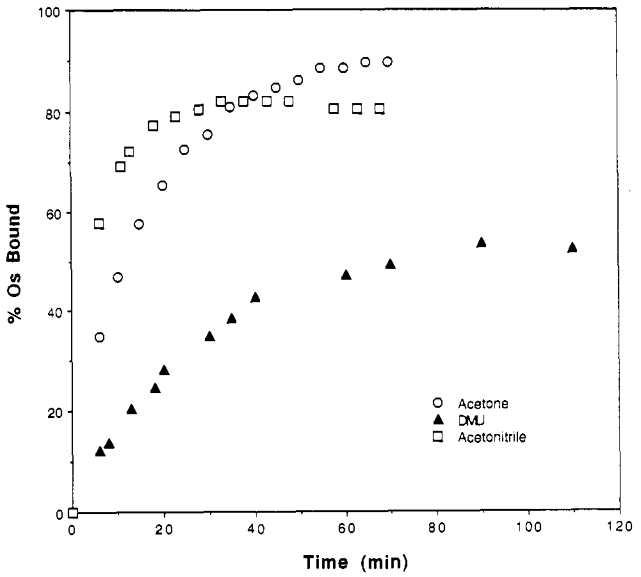

Figure 2. Formation of Os(II) adducts in D_2O as a function of time, with the following initial concentrations. **1**: [Os] = 0.0122 M, [acetone] = 0.0320 M. **2**: [Os] = 0.0122 M, [DMU] = 0.0311 M. **3**: [Os] = 0.0128 M, [MeCN] = 0.0379 M.

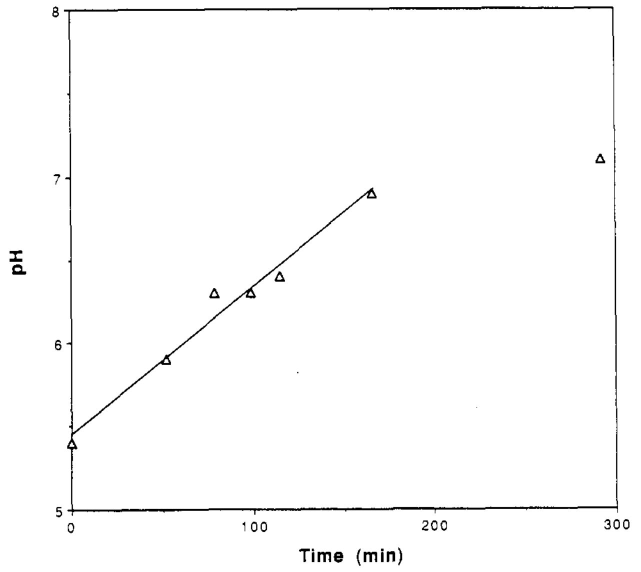

Figure 3. pH of a reduced $(NH_3)_5Os(OTf)_3$ solution (0.013 M in D_2O) following removal of Zn/Hg, at room temperature vs time.

The rate of oxidation of Os(II) by protons has been reported to be sensitive to pH.[4] The pH profile of an Os(II) reaction mixture in the absence of trapping ligand is shown in Figure 3. The pH of a 0.013 M solution of $(NH_3)_5Os(OTf)_3$ in D_2O was measured as 3.5, consistent with the acidic nature of an aquo ligand bound to Os^{3+}.[11] The pH of the mixture rose to a stable value of 5.1 in 10 min of stirring over zinc amalgam. After the reducing agent was removed by filtration (defined as $t = 0$), the pH of the solution increased over a period of 3 h to a value of 6.9. The plot of pH vs time (Figure 3) appears roughly linear in this range, showing a slope of approximately 1.5×10^{-4} s^{-1}, similar that of the Os(II) "decay" rate [ln(% Os bound) vs time] measured by the trapping experiments described above. After an additional 2 h, the pH of the reaction mixture was 7.1. Thus, the end of the Os(II) decomposition process coincides with the end of pH change of the reaction mixture.[12]

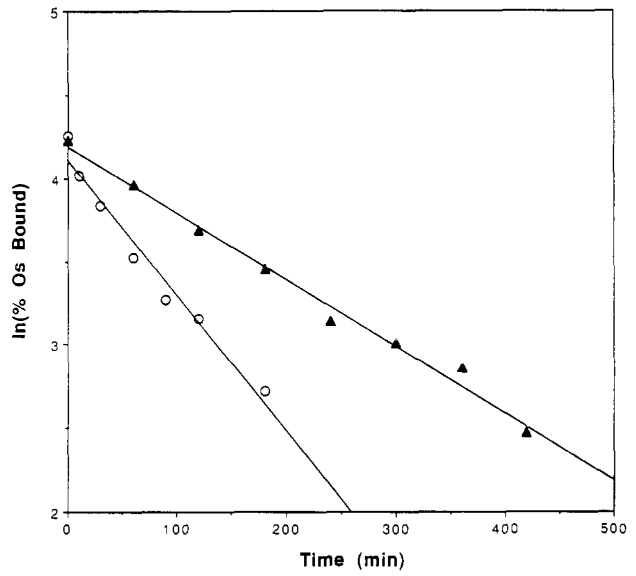

Figure 4. Examples of Os^{II} decomposition kinetics in H_2O (circles) and D_2O (triangles) with trapping by acetone (method B, Experimental Section; 22 ± 1 °C; $[Os]_{tot} = 0.013 \pm 0.001$ M).

When a freshly-prepared Os(II) solution in D_2O (0.013 M, initial pH 5.1) was acidified with 0.0013 M DCl to pH 3.0, the rate of subsequent Os(II) decomposition was $(5.7 \pm 0.8) \times 10^{-4}$ s^{-1}, as measured by the acetone trapping assay, a 10-fold increase. The spectroscopic yield of **1** at the first data point (t_0) was 30%, compared to 69% under the standard conditions (pH 5.1). The increase in decomposition rate was not due to chloride ion, since the rate under standard (nonacidified) conditions was unaffected by the presence of 0.013 M NaCl, representing a 10-fold greater concentration of chloride than was present in the DCl experiment.

Rendering a fresh Os(II) solution more basic with NaOD to an initial pH of 7.5 resulted in relatively little change in the measured decomposition rate (8.5×10^{-5} s^{-1} vs 6.8×10^{-5} s^{-1}). The overall yield of the acetone complex **1** was reduced slightly (a t_0 yield of 62% vs 69% at pH 5.1), and an uncharacterized gray precipitate was observed to increase gradually throughout the reaction.

Cyclic voltammetry of the Os(III) precursor, $Os(NH_3)_5(OTf)_3$, showed a quasi-reversible redox wave in unbuffered H_2O (pH 4.1) at approximately −0.77 V vs NHE at a glassy carbon electrode, consistent with measurements made by Gulens and Page.[4] The cathodic current was larger than the anodic current, due to catalytic proton reduction via the Os(II) form, similar to that previously observed for $[(NH_3)_5OsCl]^{2+}$.[4] $(NH_3)_5Os(OTf)_3$ was then reduced with zinc amalgam in H_2O, and the mixture was filtered. The solution showed an onset of Zn^{2+} stripping current at −0.65 V vs NHE, but did not show oxidizing current at more positive values. This is inconsistent with long-lived $[(NH_3)_5Os(OH_2)]^{2+}$, $[(NH_3)_5Os(OH)]^{+}$, and $[(NH_3)_5Os(OTf)]^{+}$ intermediates, each of which have highly negative Os(II/III) redox potentials.[4]

The rate of decomposition of $(NH_3)_5Os^{II}$ in H_2O instead of D_2O was measured by acetone trapping with both quenching techniques discussed above. The observed first-order decomposition rate was found to be $(1.4 \pm 0.1) \times 10^{-4}$ s^{-1}, approximately 2.2 times the rate in D_2O under otherwise identical conditions, as shown in Figure 4. The pH of the Os(II) reaction mixture immediately after the reducing agent was filtered out was 6.1, compared with 5.1 for the D_2O reaction mixture.[13] Since the rate of Os(II) decomposition in D_2O was found to increase in

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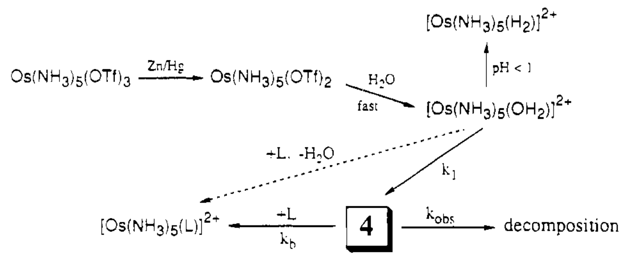
(11) The measured pH of 3.5 translates to a pK_a of 5.1 for $(NH_3)_5Os(OTf)_3$, identical to the value determined previously by electrochemical methods.[4a]

(12) Attempts to measure the rate of decay of Os(II) generated and trapped in citrate and citrate–phosphate buffers failed, giving low yields of **2**, even upon immediate treatment of the filtered reaction mixture with acetone.

(13) pH values recorded in D_2O are usually considered to overestimate the true acidity by 0.40 pH unit.[17] Thus, the H_2O reaction mixture is approximately 0.6 pH unit more basic than the D_2O solution.

Scheme II. General Exchange and Decomposition Pathways of Os(II) in Water



more acidic (pH 3.0) but not in more basic (pH 7.5) solution (vide supra), the faster reaction in H_2O is not due to a pH difference and probably reflects a true isotope effect.

The following experiments provided no direct evidence for the intermediacy of species having osmium–hydrogen bonds. (i) When $Os(NH_3)_5(OTf)_3$ in 1 M aqueous HCl (H_2O) was reduced over zinc amalgam and the mixture was filtered, the expected dihydrogen complex $[(NH_3)_5Os(H_2)]^{2+}$ was readily observed at −8.6 ppm. No such high-field resonance could be detected in nonacidified reaction mixtures; indeed, the NMR spectrum of $(NH_3)_5Os(OTf)_3$ reduced in D_2O shows *only cis and trans ammine resonances which exchange with time.* No electrochemical evidence for the presence of $[(NH_3)_5Os(H_2)]^{2+}$ in the $(NH_3)_5Os^{II}/H_2O$ reaction mixture was observed. (ii) $[(NH_3)_5Os(H_2)](OTf)_2$, prepared and isolated from methanol,[6] was found to be stable in D_2O solution for at least 12 h by NMR and gave none of the complex **1** upon standing in D_2O in the presence of a 3-fold excess of acetone. (iii) The addition of $[Cp_2Fe][PF_6]$ to $[(NH_3)_5Os(H_2)]^{2+}$ in nonaqueous solvents has been found to afford the Os(IV) hydride complex $[(NH_3)_5OsH]^{3+}$.[14] No formation of **1** was observed upon repetition of this experiment using 1 equiv of $[Cp_2Fe][PF_6]$ in a 1:1 H_2O:acetone solution of $[(NH_3)_5Os(H_2)](OTf)_2$. (iv) No evidence of Os dihydrogen or Os hydride species was observed in infrared spectra (KBr pellet) of the material isolated from solutions of $(NH_3)_5Os^{II}$ in H_2O and D_2O by precipitation with $NaBPh_4$. Infrared and electronic spectroscopic data for freshly-generated aqueous solutions of $(NH_3)Os^{2+}$ are presented in the Experimental Section but allow no conclusions regarding the nature of the long-lived Os^{II} intermediate.

Discussion

It has been reported that the reduction of $Os(NH_3)_5(OTf)_3$ in water in the presence of DMU results in an equilibrium distribution of the Os(II) aquo and DMU complexes, with a binding constant for the formation of complex **2** of 23 M^{-1}.[2] However, we have demonstrated here (control reaction 1, above) and elsewhere[3] that free DMU is not in equilibrium with an η^2-bound form, either by itself or in the presence of a zinc amalgam surface. The previous report may reflect instead the irreversible formation of **2** in low yield.

The decomposition of the species acting as a source of Os(II) in aqueous solution appears to be a first-order process, with a half-life of about 3 h at ambient temperature and an initial pH of 5.1. Both the linear increase in pH that accompanies the disappearance of available Os(II) and the increase in decomposition rate with reduced pH are consistent with proton reduction as the dominant Os(II) decomposition pathway.

Scheme II shows a set of transformations consistent with the data obtained thus far. $Os(NH_3)_5(OH_2)^{2+}$ can be expected to be the immediate product of reduction and rapid triflate aquation.[15] Recall that reduction of Os(III) in the presence of 1 equiv of DMU results in rapid formation of complex **2**. This reaction must proceed through the Os(II) aquo complex, since the on-rate of solvent H_2O is expected to be much faster than that of DMU at these concentrations. Thus, the aquo complex is highly substitution-labile.

In contrast, if Os(III) is first reduced in water and then π-acidic ligand is added, the Os(II) complexes take longer to form (30–90 min, depending on the ligand), as demonstrated by individual rate measurements. Thus, the aquo complex $Os(NH_3)_5(OH_2)^{2+}$ cannot persist in the absence of π-acid but is rapidly converted to a species (**4**) that can function as an Os(II) synthon and which decomposes at the slower rate (k_{obs}) measured in the trapping studies described above. The observed isotope effect for Os(II) decomposition (k_{H_2O}/k_{D_2O} = 2.2) also argues against the persistence of the Os(II) aquo complex, since dissociation of D_2O from the coordination sphere of Os(II) would not be expected to be 2.2 times slower than the dissociation of H_2O. The putative species **4** is not electroactive in the aqueous electrochemical "window" and so escapes detection by these means.[4] In the presence of higher concentrations of acid, the dominant species formed is the dihydrogen complex.

The Os(II) dihydrogen complex $[(NH_3)_5Os(H_2)]^{2+}$ and the Os(IV) hydride $[(NH_3)_5OsH]^{3+}$ are each logical candidates for **4**. Taube and co-workers have recently found that the hydride complex can be converted to the Os(II) complex $[(NH_3)_5Os(py)]^{2+}$ by deprotonation in the presence of pyridine.[14] However, the intermediacy of $[Os(NH_3)_5(H_2)]^{2+}$ is ruled out by the observation that an independently-prepared sample is stable to the aqueous decomposition reaction conditions. The identification of **4** as the Os(IV) hydride appears unlikely, since treatment of a D_2O solution of acetone and $[(NH_3)_5Os(H_2)]^{2+}$ with $[Cp_2Fe][PF_6]$, which provides the hydride complex in situ in nonaqueous solvent,[14] affords no acetone complex **1**. In addition, no evidence of a hydride or coordinated dihydrogen moiety has been observed by IR of samples precipitated from aqueous solution.

Thus, the nature of the aqueous Os^{II} synthon is obscure at present. We speculate that some form of osmium hydride, such as $[(NH_3)_5Os^{IV}(OH)(H)]^{2+}$, remains the most likely possibility. Regardless of the exact form of the active species, the preparation of Os(II) complexes of DMU, acetone, and acetonitrile in D_2O solution in substantial yield even hours after removal of the reducing agent demonstrates that a useful form of $(NH_3)_5Os^{II}$ persists for periods much longer than expected in aqueous media in the absence of dioxygen. It is therefore sufficiently stable for preparative chemistry to be conducted in aqueous solution, as we are currently investigating.[3]

Experimental Section

$(NH_3)_5Os(OSO_2CF_3)_3$ was prepared from OsO_4 by literature methods[16] and gave satisfactory combustion analysis (performed at the University of Virginia on a Perkin-Elmer Model 2400 CHN analyzer). Anal. Calcd for $C_3H_{15}F_9N_5O_9S_3Os$: C, 4.99; H, 2.09; N, 9.69. Found: C, 5.11; H, 2.07; N, 9.29. *N,N*-Dimethyluracil was obtained from Aldrich and used as received. Water was purified by deionization followed by distillation; D_2O (99 atom % D) was used as received from Aldrich and Cambridge Isotope Laboratories. All aqueous solutions were deoxygenated by evacuation with magnetic stirring for 1 h, with periodic refilling with dry nitrogen or argon, or were prepared in the glovebox using water degassed in this manner. Zinc amalgam was prepared from 30-mesh granular Zn metal that was washed with 3 M HCl(aq) and then treated with a saturated aqueous $HgCl_2$ solution for 20 min.

All manipulations (synthesis, purification, chromatography, etc.) were conducted in a Vacuum Atmospheres inert-atmosphere glovebox with a N_2 atmosphere containing ≤5 ppm of O_2, using deoxygenated reagents and solvents. Reactions conducted under an argon atmosphere gave results identical to those obtained under nitrogen, so that latter was routinely employed. NMR samples were prepared in the glovebox using screw-cap NMR tubes (Wilmad Glass Co.) with Teflon-coated septa. NMR spectra were acquired at 300 MHz on General Electric QE-300 and

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(14) Li, Z.-W.; Yeh, A.; Taube, H. Manuscript in preparation.

(15) The exchange of bound triflate for solvent water is likely to be rapid on Os(II), as has been demonstrated in methanol: Barrera, J.; Orth, S. D.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 7316–7318.

(16) Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658–7659.

GN-300 instruments; peak positions in D_2O were referenced against residual HDO at 4.75 ppm. Spectra for quantitative integration were acquired with a delay time of greater than 5 s between pulses. Acidities were determined with a Fisher Acumet Model 900 pH meter and a glass electrode with Ag/AgCl reference. The pH values recorded in D_2O are reported as measured; these values are usually considered to be low by 0.40 pH unit.[17] Atomic absorption data were acquired with a Perkin-Elmer Model 372 spectrophotometer using an American Scientific Products Zn element, calibrated with standard solutions prepared from Zn metal dissolved in aqueous HCl. Microanalysis for mercury was performed by Schwarzkopf Analytical, Woodside, NY. Cyclic voltammetry was performed in aqueous solution (0.5 M LiOTf or 0.5 M NaCl) in a one-compartment cell with a glassy carbon disk (3-mm diameter) or Hg pool (about 7-mm diameter) as the working electrode, a Pt wire as auxiliary electrode, and a Ag/AgCl reference electrode, using a Bioanalytical Systems CV27 voltammograph. Potentials were measured against internal $Ru(NH_3)_6^{2+/3+}$ (+0.051 V vs NHE), and are reported vs NHE.

Synthesis of $[Os(NH_3)_5(\eta^2\text{-}H_2)](BPh_4)_2$. $(NH_3)_5Os(OTf)_3$ (46 mg, 0.064 mmol) in 1.7 mL of 1 M HCl in H_2O was reduced to the Os(II) state by stirring over 1.16 g of zinc amalgam for 10 min. The bright yellow solution was filtered into a solution of $NaBPh_4$ (89 mg, 0.26 mmol) in 1.55 mL of H_2O to give a white precipitate. The solid was filtered off, washed with water, and dried in vacuo to afford 42 mg (72%) of the desired complex,[6] which was judged to be pure by quantitative NMR in acetone-d_6 with *N,N*-dimethylacetamide as integration standard. ^1H NMR (acetone-d_6, δ): 7.25–6.75 (m, 20H), 4.41 (br s, 3H, trans NH_3), 3.55 (br s, 12 H, cis NH_3), –8.61 (s, 2H).

Decomposition Kinetics (Representative Procedures). Method A (Rapid Quenching). A solution of $(NH_3)_5Os(OTf)_3$ (144 mg, 0.199 mmol) in 9.7 mL of D_2O was stirred over 1.5 g of zinc amalgam for 10 min and filtered through a 15-mL fritted funnel (porosity M). Immediately, 0.50 mL of this solution was removed by volumetric pipette and added to 1 mL of acetone; this sample was designated as $t = 0$. Similar 0.50-mL aliquots were taken at t = 15, 60, 120, 237, and 297 min. Each sample was allowed to stand for at least 30 min before being evaporated in vacuo to remove excess acetone. The samples were then treated with *N,N*-dimethylacetamide (DMA) in D_2O (12 mg of a 0.64 M stock solution) as integration standard and analyzed by ^1H NMR. To establish that trapping occurs rapidly, a solution of $(NH_3)_5Os(OTf)_3$ was stirred over zinc amalgam in D_2O for 10 min and filtered directly into a large excess of acetone, which immediately produced the characteristic orange color of complex **1**. Aliquots (0.5 mL) were removed (t = 1, 3, 8, 15, and 30 min) and immediately transferred into a large excess (≈3 mL) of acetonitrile. After 30 min, each solution was evaporated in vacuo, the solid was redissolved in D_2O, and the resulting solution was treated with DMA as above. ^1H NMR analysis of each sample showed formation of complex **1** in 93 ± 2% yield and no formation of the acetonitrile complex **3**, demonstrating that acetone trapping is complete in less than 1 min under these conditions.

Method B (in Situ NMR Analysis, DMU Trap Example). A solution of $(NH_3)_5Os(OTf)_3$ (114 mg, 0.158 mmol) in 10.9 mL of D_2O was reduced over Zn/Hg and filtered as above. The reactions in 0.50-mL aliquots were quenched by addition to NMR tubes containing 0.50 mL of a stock solution of 51 mg of DMU (0.364 mmol) in 10.9 mL of D_2O at t = 0, 60, 120, 180, 240, 300, and 360 min. Each sample was examined by ^1H NMR at least 4 h after its generation to ensure complete formation of the desired Os(II) complex. The integrated ratios of free DMU Me signals (3.8, 3.26 ppm) to those of the bound ligand (3.32, 3.09 ppm) were used to establish the percentage of ligand and metal bound as complex **2**, relative to the total amount of osmium present in the sample. Identical results were obtained when DMA was used as internal integration standard. Experiments using acetone and acetonitrile as trapping ligands were performed as above, with the following ^1H NMR chemical shifts: free acetone, 2.21 ppm; bound acetone, 1.55 ppm; free MeCN, 2.05 ppm; bound MeCN, 2.94 ppm. Experiments at 40 and 10 °C were performed by reduction of the Os(III) precursor in the standard fashion, followed by filtration and placement of the reaction flask in a toluene bath of the desired temperature. The flask was swirled for 2–3 min to allow the temperature to equilibrate before the t_0 aliquot was taken. The aliquot solutions were both trapped (acetone in D_2O) and analyzed at room temperature. Experiments in the presence of DCl, NaOD, or NaCl were performed by addition of the indicated additive to a freshly filtered solution of $(NH_3)_5Os^{II}$ prepared as above. The decomposition kinetics parameters for all runs are derived from the data in Table I of the supplementary material.

Formation Kinetics. Representative Procedure (DMU). A solution of $(NH_3)_5Os(OTf)_3$ (56 mg, 0.078 mmol) in 3.20 mL of D_2O was stirred over 1.05 g of zinc amalgam for 10 min and then filtered through a medium-porosity fritted funnel. A 0.5-mL portion of the resulting solution was immediately combined with 0.5 mL of a 0.064 M stock solution of acetone in D_2O in an NMR tube. The sample was then analyzed by ^1H NMR at 5-min intervals, monitoring the appearance of the bound acetone signal of **1** and the disappearance of the resonances of free acetone. Analogous experiments were performed for DMU and acetonitrile, at the concentrations listed in the caption to Figure 2.

DMU/Acetone Competition. The above procedure was employed with $(NH_3)_5Os(OTf)_3$ (90 mg, 0.13 mmol) in 2.7 mL of D_2O, 1.43 g of zinc amalgam, and 0.5-mL portions of D_2O stock solutions of DMU (0.079 M) and acetone (0.069 M).

Spectroscopic Data. Electronic Spectroscopy. A solution of 8 mg of $(NH_3)_5Os(OTf)_3$ in 2.7 mL of H_2O was rapidly reduced by passage through a syringe packed with 0.5 g of zinc amalgam directly into a degassed quartz cell. The UV–vis spectrum of this solution was acquired immediately [λ_{max} (ϵ)]: 202 nm (300); 244 nm (210); 360 nm (27). Over the course of 90 min, the first two bands were observed to increase in intensity by approximately 20% and shift slightly to lower wavelength, while the 360-nm band disappeared.

NMR and IR Spectroscopy. A sample of $(NH_3)_5Os(OTf)_3$ in H_2O was reduced to the Os(II) state in the manner of the kinetics experiments described above. Filtration into a 2-fold excess of $NaBPh_4$ in H_2O gave a white precipitate, which was collected, washed with water, and dreid in vacuo. NMR showed a trace (<2%) of the dihydrogen adduct. IR (KBr pellet, cm^{-1}; corresponding peaks in spectrum of $NaBPh_4$ are listed in italics): 3286 (s), 3227 (s), 3167 (s), 3047 (s, *3054*), 3020 (s, *3012*), 2994 (s, *2858*), 2055 (w), 1956 (w, *1968*), 1883 (w, *1898*), 1829 (w, *1837*), 1608 (m), 1570 (m, *1574*), 1470 (m, *1473*), 1420 (m, *1421*), 1313 (s), 1148 (w, *1140*), 1030 (w, *1030*), 845 (w, *850*), 734 (s, *741*), 703 (s, *705*), 608 (m, *593*). NMR (acetone-d_6, 300 MHz): δ 7.42–6.75 (BPh_4), 5.95 (m, ≈1H), 5.07 (m, ≈0.5H), 4.44 (s, ≈2H), 4.0 (br, exchangeable with D_2O, possibly cis NH_3). An identical Os(II) solution was allowed to stand in H_2O under N_2 for 13 min, followed by precipitation with $NaBPh_4$ and isolation as above. The NMR spectrum was identical to that of the above sample, with the exception of a new peak at 4.7 ppm (≈1H). A sample isolated in the same manner after 35 min in H_2O displayed an unchanged IR spectrum, with the exception of a new band at 1687 cm^{-1} (m), and increased intensity of the band at 2053 cm^{-1}. Preparation of $(NH_3)_5Os^{II}$ in D_2O followed by $NaBPh_4$ precipitation after 35 min gave a sample with the following IR spectrum (KBr, cm^{-1}): 3053 (s), 3025 (s), 2990 (s), 2453 (s), 2357 (s), 2319 (s), 2055 (w), 1957 (w), 1893 (w), 1829 (w), 1574 (m), 1478 (s), 1424 (s), 1261 (w), 1178 (w), 1146 (w), 1010 (m), 842 (w), 733 (s), 702 (s), 606 (m). A $(NH_3)_5Os^{II}$ solution freshly prepared in D_2O showed no ^1H NMR resonances other than the residual solvent signal. A sample was prepared in H_2O and evaporated to dryness in vacuo over 2 h. NMR (acetone-d_6, 300 MHz): δ 5.40 (br, trans NH_3), 4.54 (br, cis NH_3), 3.93 (br, residual H_2O).

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Supplementary Material Available: Table I, giving the details of kinetics measurements (2 pages). Ordering information is given on any current masthead page.

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(17) (a) Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188–190. (b) See footnote 11 in: Scheller, K. H.; Scheller-Krattiger, V.; Martin, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 6833–6839.