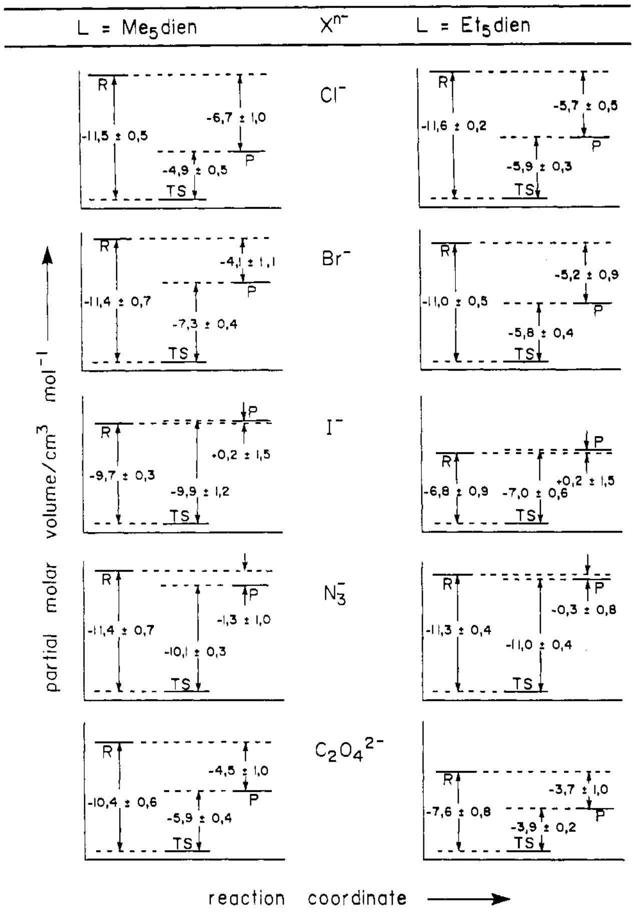

R = reactants; TS = transition state; P = products
Data taken from Table I and II

Figure 1. Volume profiles for the reaction $Pd(L)X^{(2-n)+} + H_2O \rightleftarrows Pd(L)H_2O^{2+} + X^{n-}$.

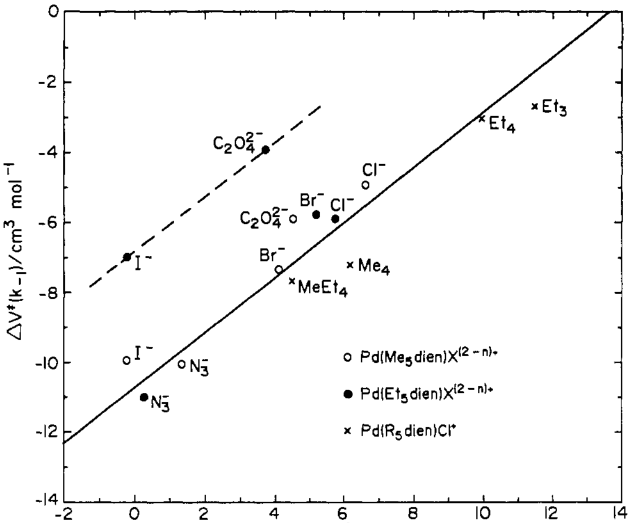

Figure 2. Plot of $\Delta V^{\ddagger}(k_{-1})$ versus $\Delta\bar{V}$ for a series of anation reactions of the type $Pd(R_5dien)H_2O^{2+} + X^{n-} \rightarrow Pd(R_5dien)X^{(2-n)+} + H_2O$ (data taken from Figure 1 and ref 6).

the reactant or product states, in agreement with the associative reaction mode. Similar volume profiles can be constructed for the solvolysis of $Pd(R_5dien)Cl^+$, where R_n = 1,1,7,7-Me$_4$, 1,1,4-Et$_3$, 1,1,7,7-Et$_4$, and 4-Me-1,1,7,7-Et$_4$, and the corresponding reaction volumes, calculated as the difference in activation volumes, are −6.2, −11.5, −10.0, and −4.5 cm^3 mol^{-1}, respectively.[6] A plot of $\Delta V^{\ddagger}(k_{-1})$ versus $-\Delta\bar{V}$ (i.e. $\Delta\bar{V}$ for the reverse anation process) in Figure 2 demonstrates that for most of the available data there is a linear correlation between these parameters with a slope of 0.79. This means that an increase in $\Delta V^{\ddagger}(k_{-1})$ is accompanied by an increase in $\Delta\bar{V}$ for the anation process (i.e. a decrease in $\Delta\bar{V}$ for the aquation process). Only the data points for $Pd(Et_5dien)X^{(2-n)+}$ (X^{n-} = I$^-$, C$_2$O$_4^{2-}$) deviate from this correlation, although they do exhibit the same trend. $\Delta V^{\ddagger}(k_{-1})$ should be significantly more negative for these two points to fall on the line. In terms of eq 2, a plot of $\Delta V^{\ddagger}(k_{-1})$ versus $-\Delta\bar{V}$ should for closely related systems exhibit a slope of 1 and a common intercept of $\Delta V^{\ddagger}(k_{-1})$. Although the slope of the plot is slightly smaller than 1, the intercept for 12 systems is ca. −11 cm^3 mol^{-1}, in agreement with the constant volume of activation found for the solvolysis reactions. The substantially higher intercept of ca. −7 cm^3 mol^{-1} for the two deviating systems results from the significantly different solvolysis activation volume found for these complexes (see earlier discussion).

The main correlation in Figure 2 means that there is a linear relationship between the partial molar volumes of $Pd(Et_5dien)X^{(2-n)+}$ and the transition state for the anation process, since H_2O is the common leaving ligand. Thus, intrinsic and solvational volume contributions[7] affect the partial molar volume of the transition and product states in a similar way and will be governed by the nature of R$_5$dien and X^{n-}. Similar correlations have been used to interpret the nature of the mechanism for series of aquation and base hydrolysis reactions of octahedral complexes.[16-19]

The exact nature of the transition state has been discussed in much detail before.[4,6,8] Volume changes during the activation process involve not only those associated with the entrance of a fifth ligand into the square-planar coordination sphere but also subsequent changes associated with a tetragonal-pyramidal to trigonal-bipyramidal transition. The extent of bond lengthening in the latter case will partially balance the volume decrease due to bond formation during the associative process. We thoroughly believe that the type of activation volumes reported in this and some of our other papers[2-6] are typical of limiting associative substitution reactions. The volume profiles not only underline our earlier conclusions but also clearly demonstrate the compact nature of the transition state on a volume basis.

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Registry No. Pd(Me$_5$dien)Cl$^+$, 21007-58-9; Pd(Me$_5$dien)Br$^+$, 118141-56-3; Pd(Me$_5$dien)I$^+$, 118141-57-4; Pd(Me$_5$dien)N$_3^+$, 118141-58-5; Pd(Me$_5$dien)C$_2$O$_4$, 118141-59-6; Pd(Me$_5$dien)OH$_2^{2+}$, 85344-11-2; Pd(Et$_5$dien)Cl$^+$, 70472-44-5; Pd(Et$_5$dien)Br$^+$, 118141-60-9; Pd(Et$_5$dien)I$^+$, 88056-32-0; Pb(Et$_5$dien)N$_3^+$, 118141-61-0; Pd(Et$_5$dien)C$_2$O$_4$, 118141-62-1; Pd(Et$_5$dien)OH$_2^{2+}$, 118169-65-6; Cl$^-$, 16887-00-6; Br$^-$, 24959-67-9; I$^-$, 20461-54-5; N$_3^-$, 14343-69-2; C$_2$H$_4^{2-}$, 338-70-5; H$_2$O, 7732-18-5.

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Pulse Radiolysis Studies on Pertechnetate and Perrhenate in Aqueous Media. Decay of the Technetium(VI) Transient[1]

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The radiolysis of Tc(VII) and Re(VII) in aqueous media, and especially the nature and reactivity of the unstable M(VI) species

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generated by e_{aq}^- reduction of these M(VII) ions, are of interest for a number of reasons. For instance, the ^{99}Mo/^{99m}Tc generator is widely used in nuclear medicine to provide solutions of ^{99m}Tc(VII) (i.e., pertechnetate[^{99m}*Tc*]); radiolytic reduction of pertechnetate[^{99m}*Tc*] in the high-radiation environment of the generator is presumed to be an important factor affecting the elution yields of these generators,[4-7] but the absence of quantitative data on the chemistry and reactivity of Tc(VI) precludes a detailed evaluation of this presumption. Similarly, the chemistry and reactivity of Tc(VI) are important in the syntheses of ^{99m}Tc radiopharmaceuticals by chemical reduction of ^{99m}Tc(VII).[8] The proposed uses of the ^{188}W/^{188}Re generator,[9,10] ^{188}Re radiopharmaceuticals,[11] and ^{186}Re radiopharmaceuticals[12] in therapeutic nuclear medicine applications raise the same considerations for rhenium.[12] In addition, it should be noted that the radiolytic reduction of pertechnetate[^{99}*Tc*] in high-level nuclear waste may be an important factor in determining the environmental mobility of technetium-99.[13]

A few studies on the reactions of either perrhenate or pertechnetate with radical species have been reported.[4,14,15] This note describes further pulse radiolysis experiments to (a) monitor the rate of reaction of perrhenate and pertechnetate with various radical species, (b) spectrophotometrically characterize the Tc(VI) and Re(VI) transients produced by reaction with the hydrated electron, and (c) obtain information about the rate and mechanism of decay of these transients.

Experimental Section

Materials. All chemicals were of ultrapure quality or were recrystallized three times from triply distilled water. *tert*-Butyl alcohol was purified by repeated recrystallization of the neat material. Technetium-99 of greater than 99% radiochemical purity was obtained from Oak Ridge National Laboratory, Oak Ridge, TN, as ammonium pertechnetate, which was then converted to potassium pertechnetate by metathesis with KOH. Potassium pertechnetate and potassium perrhenate were recrystallized three times from triply distilled water. All solutions were prepared in triply distilled water and deaerated by a syringe technique.[16] Solution pH was adjusted with lithium hydroxide or sodium hydroxide and with perchloric acid.

Pulse Radiolysis. Aqueous solutions in optical quartz cells of 2.00-cm path length were irradiated by microsecond pulses of 15-MeV electrons generated by the Argonne linear accelerator. Delivered doses were calibrated by conventional methods.[16] Radicals were produced in micromolar concentrations, while metal ion concentrations ranged from 5×10^{-5} to 1×10^{-2} M. Reactions of e_{aq}^- were conducted in the presence of 0.1 M *tert*-butyl alcohol to scavenge hydroxy radicals and, unless otherwise noted, were monitored at 600 nm where none of the other species investigated exhibit any significant absorbance. The 2-propanol radical was generated by two methods: (a) Solutions were saturated with N_2O to convert e_{aq}^- into $OH^•$ at a diffusion-controlled rate; the $OH^•$ radical then reacts with added 2-propanol to generate the desired radical. (b) Solutions containing both acetone and 2-propanol were saturated with helium; the e_{aq}^- radical generated in these solutions reacts with acetone to yield the deprotonated form of the desired radical. Absorption spectra of transient species were obtained by the streak camera method,[17-19] while kinetic measurements were obtained by conventional photomultiplier techniques.[20] Procedures used to analyze the kinetic data have been previously described.[21]

Results and Discussion

Reaction with the Hydrated Electron. 1. Pertechnetate. $Tc^{VII}O_4^-$ reacts with the hydrated electron at a diffusion-controlled rate to generate a short-lived transient that is formulated as technetate, $Tc^{VI}O_4^{2-}$. The visible–UV spectrum of this Tc(VI) transient[1] is characterized by a broad absorbance centered at about 500 nm and a peak centered at about 340 nm. These spectral characteristics are qualitatively in agreement with the diffuse-reflectance spectrum reported for solid $[(CH_3)_4N]_2TcO_4$.[22] When the Tc(VI) transient absorbance is generated by pulse techniques in aqueous media, its intensity is a strong function of solution pH. For solutions having identical concentrations of pertechnetate, and receiving the same dose of electrons, the largest transient absorbances are observed in unbuffered water; smaller transient absorbances are observed in either acidic or alkaline media.

The specific rate of reaction of the hydrated electron with pertechnetate (k_2) at pH 13 is $(2.48 \pm 0.05) \times 10^{10}$ M^{-1} s^{-1} (average of 18 independent determinations; data obtained at 600, 500, 325, and 280 nm show no wavelength dependence). The rate is identical in unbuffered water ($k_2 = (2.48 \pm 0.04) \times 10^{10}$ M^{-1} s^{-1}; average of three independent determinations). These results are in coarse agreement with those of Heller-Grossman et al.[4] ($k_2 = 1.9 \times 10^{10}$ M^{-1} s^{-1}), and of Pikaev et al.[14] ($k_2 = (1.3 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}), which were obtained in neutral solution.

2. Perrhenate. The hydrated electron reacts with perrhenate to generate a transient species that is formulated as rhenate, $Re^{VI}O_4^{2-}$. This transient exhibits a broad absorbance centered at about 260 nm (pH 13) in qualitative agreement with the reflectance spectrum reported for solid $[(CH_3)_4N]_2ReO_4$ generated electrochemically in nonaqueous solvents.[22] Lawrance and Sangster[15] report that in neutral solution ReO_4^{2-} exhibits an absorption maximum at 290 nm. The specific rate governing the reduction of perrhenate by the hydrated electron (k_2) at pH 13 is $(1.52 \pm 0.04) \times 10^{10}$ M^{-1} s^{-1} (average of eight independent determinations at 600 nm). This result is in good agreement with that obtained by Lawrance and Sangster in neutral solution[15] ($k_2 = 1.3 \times 10^{10}$ M^{-1} s^{-1}) and is significantly slower than the rate of reduction of pertechnetate. The relative rates of reduction of TcO_4^- and ReO_4^- can be qualitatively understood on the basis that TcO_4^- is a stronger oxidant by 0.23 V[12] or on the basis that Re is slightly larger than Tc (metallic radius 1.373 vs 1.358 Å).[28]

Reactions with Other Radicals. The 2-propanol radical, $(CH_3)_2CHO$, reacts with pertechnetate at a specific rate of 7×10^8 M^{-1} s^{-1}, independent of the method used to generate the radical (vide supra). This rate is not diffusion controlled and is significantly slower than the rate of e_{aq}^- reduction of pertechnetate. The hydrogen radical, $H^•$, produced at pH values less than 4, reacts with pertechnetate to yield a species that eventually decomposes to yield the insoluble, polymeric $Tc^{IV}O_2$. No evidence could be obtained for the reaction of pertechnetate with the hydroxyl radical, $OH^•$, but perrhenate reacts with this species to yield a transient spectrum with maxima at 240, 420, and 600 nm.[1]

Reactions of the Technetate(VI) Transient. The rate of decay of the Tc(VI) transient is strongly dependent on solution pH. In alkaline media (pH > 10) the Tc(VI) transient is very stable (no

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detectable decay within the several-millisecond duration of the photomultiplier experiment) and in neutral media it decays at a measurable rate, while in acidic media (pH < 4) the reduction of pertechnetate by H• rapidly yields polymeric TcO_2. These observations are qualitatively consistent with the known behavior of the manganate congener ($Mn^{VI}O_4^{2-}$), which is stable in alkaline media but rapidly disproportionates to permangante and polymeric MnO_2 in neutral or acidic media.[23]

In unbuffered water the Tc(VI) transient decays by second-order kinetics with $2k/\epsilon l = (1.05 \pm 0.09) \times 10^5$ s^{-1} (average of 14 independent determinations at 360 nm).

$$-d[Tc(VI)]/dt = 2k[Tc(VI)]^2 \qquad (1)$$

Independent experiments[24] yield an estimated Tc(VI) extinction coefficient at 360 nm of 1220 M^{-1} cm^{-1}, resulting in a calculated value of $k = 1.3 \times 10^8$ M^{-1} s^{-1}. Lawrance and Sangster[15] have estimated the equivalent rate for Re(VI) to be an order of magnitude larger, i.e. $(1.7 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.

The decay of Tc(VI) by a second-order process is entirely consistent with the expected decomposition of this species via disproportionation to Tc(VII) and, ultimately, Tc(IV). Second-order decay of Tc(VI) means, of course, that the net rate of disappearance of this species is a function of its concentration. Thus, competition between Tc(VI) disproportionation (to yield TcO_2) and various first-order processes (e.g., ligand trapping of Tc(VI) to ultimately yield a Tc complex) will depend directly on the total concentration of Tc in solution.[8] This fact has obvious consequences in ^{99m}Tc radiopharmaceutical syntheses, where TcO_2 is an undesirable product, and in nuclear waste disposal processes, where TcO_2 is the desirable product.

Competition between second-order Tc(VI) disproportionation and first-order scavenging of Tc(VI) is illustrated by experiments in which 0.01 M hydrogen peroxide is added to solutions of pertechnetate before irradiation. In unbuffered water where Tc(VI) is relatively reactive, the added H_2O_2 has no effect on the rate or form of Tc(VI) decay. However, at pH 12 where Tc(VI) is relatively stable, the added H_2O_2 induces a pseudo-first-order decay of Tc(VI) (k_{obs} = ca. 10^3 s^{-1}). From this observation the second-order rate constant governing reaction of Tc(VI) with H_2O_2 at pH 12 is estimated to be 10^5 M^{-1} s^{-1}. The stoichiometry of this reaction is presumed to be

$$Tc^{VI}O_4^{2-} + H_2O_2 \rightarrow Tc^{VII}O_4^- + OH^- + OH^\bullet \qquad (2)$$

General Chemistry. The reactivity patterns observed for the Tc(VI) and Re(VI) transients can be qualitatively understood on the basis of what is known about the stable Mo(VI) and W(VI) analogues MoO_4^{2-} and WO_4^{2-}. These tetrahedral anions are stable in alkaline media, but in acid they convert into octahedral species, which then rapidly undergo polymerization.[25] In complex formation reactions W(VI) usually reacts somewhat more rapidly than Mo(VI),[26,27] nicely accounting for the fact that the Re(VI) transient is more reactive than the Tc(VI) transient. The greater reactivity of third-row elements, relative to their second-row congeners, is usually ascribed to their slightly greater size, which allows a more facile expansion of the first coordination sphere. This phenomenon presumably also accounts for the fact that perrhenate reacts with OH•, while no such reaction is observed for pertechnetate.

Acknowledgment. Financial support was provided in part by the National Institutes of Health, Grant No. HL-21276 (E.D.), and in part by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38.

Registry No. TcO_4^-, 14333-20-1; TcO_4^{2-}, 16050-83-2; ReO_4^{2-}, 15626-53-6; ReO_4, 14333-24-5; $(CH_3)_2CHO$, 3958-66-5; H, 12385-13-6; OH, 3352-57-6; H_2O_2, 7722-84-1; water, 7732-18-5.

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^{1}H NMR Kinetic Study of Dimethyl Sulfoxide Exchange on Tetrakis(dimethyl sulfoxide)platinum(II) at Variable Temperature and Pressure[1,2]

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Determination of activation volumes from the pressure dependence of exchange rates for solvated metal ions is a useful method for the diagnosis of mechanisms.[4] For octahedrally coordinated solvated cations, there are now sufficient data to correlate both the sign and the magnitude of ΔV^* with the intimate mechanism.[5]

For square-planar solvates, the interpretation of activation volumes in molecular terms is expected to be more complex, since these solvates are subject to large changes in coordination geometry when passing from the ground state to the transition state. Few square-planar solvent-exchange reactions have been studied,[6-9] and only three values of ΔV^* have been reported so far.[7-9] The activation volumes for the water exchanges on the tetraaqua cations of palladium(II) and platinum(II) have small negative values.[8,9] Attribution of the stoichiometric mechanism (interchange, I_a, or limiting associative, A) is however still an open question, and more data are needed before ΔV^* can be used for detailed mechanistic assignments in square-planar solvates.

The present report is a ^{1}H NMR investigation of the dimethyl sulfoxide exchange on $Pt(Me_2SO)_4^{2+}$ as a function of temperature and pressure in CD_3NO_2. Dimethyl sulfoxide is an ambidentate ligand, and the complex contains two O-bonded and two S-bonded ligands that are exchanging with the free ligand at different rates. It is favorable to follow these exchanges in a noncoordinating diluent like nitromethane, since it allows variation of the ligand concentration, thus giving an opportunity to establish the rate law. The use of a diluent of high dielectric constant and of uncharged ligands minimizes the electrostriction changes along the reaction path, so that the measured volumes of activation will reflect primarily the intrinsic changes of molecular volumes on going to the transition state.[7]

Experimental Section

Chemicals and Solutions. Dimethyl sulfoxide, Me_2SO (Merck, spectral grade), was distilled and dried overnight over 4-Å molecular sieves

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