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Mechanism of the Reversible Oxidation of Vanadium(IV) by Hexachloroiridate(IV)[1]

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The reversible reaction between V(IV) and Ir(IV),$VO^{2+} + IrCl_6^{2-} + H_2O \rightleftharpoons VO_2^+ + IrCl_6^{3-} + 2H^+$, was studied at 25 °C and 1.00 M ionic strength. The equilibrium constant was determined to be 0.031 ± 0.004 M^2 from spectral changes and 0.029 ± 0.006 M^2 from kinetic measurements. The rate law is $-d[IrCl_6^{2-}]/dt = (A_{-1}[H^+]^{-1} + A_0)[IrCl_6^{2-}][VO^{2+}] - (B_1[H^+] + B_2[H^+]^2)[IrCl_6^{3-}][VO_2^+]$, with $A_{-1} = 0.0966 \pm 0.0021\ s^{-1}$, $A_0 = 0.027 \pm 0.028\ M^{-1}\ s^{-1}$, $B_1 = 3.30 \pm 0.11\ M^{-2}\ s^{-1}$, and $B_2 = 0.59 \pm 0.19\ M^{-3}\ s^{-1}$. Detailed mechanisms are presented and discussed.

Introduction

The reductions of chromium(VI)[2] and vanadium(V)[3,4] by substitution-inert iron(II) complexes exhibit striking similarities in reactivity and mechanism. Direct observation of successor complexes in the vanadium(V) reactions allowed the assignment of an inner-sphere mechanism in which the bridging ligand was supplied by the reducing agent. Similar observations were made for the Fe(II) reduction of Cr(IV),[2] and an inner-sphere mechanism was surmised for the reduction of Cr(VI) on the basis of reactivity patterns.[2,4] Similar results were also obtained in the $Mo(CN)_8^{4-}$ reduction of Cr(VI).[5] Attempts to identify the inner-sphere or outer-sphere nature of the Cr^{VI}–$IrCl_6^{3-}$ reaction failed,[6] due to the inability to distinguish between the absence of a successor complex and its rapid breakdown. Since this system provided some rather unique features in the mechanism of oxidations by Cr(VI) and since parallel studies of V(V) reactions proved fruitful in the past, we decided to undertake a study of the V^V–$IrCl_6^{3-}$ reaction.

This system is also pertinent to the studies of the $IrCl_6^{2-}$ oxidations of V^{2+} and of V^{3+}.[7] The V^{2+} reduction exceeded the capability of the stopped-flow apparatus, implying a second-order rate constant $>4 \times 10^6\ M^{-1}\ s^{-1}$.[7] The reduction by V(III) followed the equation $-d[IrCl_6^{2-}]/dt = k[V(III)][IrCl_6^{2-}][H^+]^{-1}$ with $k = 52.2\ s^{-1}$ at 25 °C and 1.00 M ionic strength.[7] In each case, the redox rate exceeded the rate of substitution on the vanadium species, suggesting an outer-sphere mechanism. No reaction of V(IV) with $IrCl_6^{2-}$ was detected in these studies,[7] but the results to be presented here indicate that this reaction would have proceeded to only a small extent under most of the conditions investigated. The V(IV) reaction could have been observed in some experiments at low $[H^+]$ with [Ir(IV)] in excess over [V(III)], but the lower rate of the V(IV) reaction ($k \approx 1.0\ M^{-1}\ s^{-1}$ for V(IV) vs. 520 $M^{-1}\ s^{-1}$ for V(III) at 0.1 M H^+) probably prevented its detection.

Experimental Section

Solutions of vanadium(V) perchlorate,[3] perchloric acid,[2] and lithium perchlorate[2] were prepared as previously described. Solutions of vanadium(IV) perchlorate were prepared by addition of an equivalent amount of barium perchlorate to a vanadyl sulfate solution[3] or by loading a column of Dowex 50W-X8 50–100 mesh cation-exchange resin with a $VOSO_4$ solution, followed by washing with 0.02 M $HClO_4$ and elution with 1.0 M $HClO_4$. The analysis of VO^{2+} solutions has been described.[3] Sodium hexachloroiridate(III) was prepared and stored as described;[6] it was prepared from Johnson, Matthey, and Co. sodium hexachloroiridate(IV), which was used without further purification. Stock solutions of Na_2IrCl_6 were prepared by weight and analyzed spectrally.[8] Solutions were stored at 0 °C or were frozen between experiments and were used only on the day they were prepared. Na_3IrCl_6 was added as the solid shortly before addition of VO_2^+ to the reaction solution in the thermostated cuvette. Removal of dissolved oxygen by purging with nitrogen had no effect on the kinetic or equilibrium behavior in several experiments, so oxygen was not excluded in most experiments.

Kinetics experiments were carried out with a Gilford Model 240 spectrophotometer, equipped with a Varian A-25 recorder and a thermostated cuvette holder. Most experiments were performed at 490 nm, a wavelength of maximum absorbance for Ir(IV) (ϵ 4000 $M^{-1}\ cm^{-1}$).[8] Solutions were thermostated to 25.0 °C and the ionic strength was adjusted to 1.00 M with $LiClO_4$. The concentrations of VO^{2+} and of VO_2^+ were maintained at least 10× in excess of the initial Ir(IV) or Ir(III) concentration to ensure pseudo-first-order conditions. Plots of log $(A_t - A_\infty)$ vs. time (where A is absorbance) were always linear through at least 95% reaction. Results were independent of the order of addition of the reagents.

Equilibrium constants were measured from the absorbance change observed in each experiment which had Ir(IV) as a reactant. The theoretical absorbance change for complete reaction was calculated as $\Delta A_c = l(\Delta\epsilon)[Ir(IV)]_0$ where $\Delta\epsilon$ was obtained from separately determined spectra of all species. Then $[Ir(III)]_{eq} = [Ir(IV)]_0\Delta A_{obsd}/\Delta A_c$ when $[Ir(III)]_0 = 0$. The equilibrium concentrations of all other species were determined from the value of $[Ir(III)]_{eq}$ and the reaction stoichimetry. Experiments under conditions leading to less than 5% reaction or more than 95% reaction were not used in equilibrium constant calculations because of the excessive errors involved in subtracting two similar numbers.

Results

Stoichiometry. The stoichiometry of the reaction between VO^{2+} and $IrCl_6^{2-}$ is described by

$$VO^{2+} + IrCl_6^{2-} + H_2O \rightleftharpoons VO_2^+ + IrCl_6^{3-} + 2H^+ \qquad (1)$$

This stoichiometry is confirmed by the reasonably constant values of $K = [VO_2^+][IrCl_6^{3-}][H^+]^2/[VO^{2+}][IrCl_6^{2-}]$ calculated from the absorbance changes as described above and by the kinetic behavior to be described below. Values of the equilibrium constant at various $[H^+]$ are presented in Table I. The equilibrium constant can also be calculated from standard oxidation potentials. Depending on the values of $E°$ used,[9-13] the calculated value of the equilibrium constant lies

Table I. Values of the Equilibrium Constant for the V^{IV}-Ir^{IV} Reaction Determined Spectrally at 25 °C and 1.00 M Ionic Strength

$[H^+]$, M	K^a, M^2	No. of values
0.0251	0.023 ± 0.002	12
0.0500	0.029 ± 0.001	5
0.0751	0.030 ± 0.001	10
0.0893	0.033 ± 0.003	21
0.0999	0.028 ± 0.003	9
0.200	0.031 ± 0.006	10
0.300	0.031 ± 0.003	7
0.400	0.032 ± 0.002	7
0.500	0.034 ± 0.001	5
0.601	0.033 ± 0.003	6
0.700	0.035 ± 0.001	4
0.800	0.036 ± 0.002	4
0.900	0.034 ± 0.002	4
0.981	0.032 ± 0.004	4
	Av 0.031 ± 0.004	108

[a] Uncertainties are one average deviation from the average value.

in the range $K = 0.0056$–0.015 M^2, which is in reasonable agreement with that determined spectrally, considering the differences in ionic medium.

Kinetics. The kinetics of the reaction were measured over the initial concentration ranges $[Ir(IV)]_0 = (0–2) \times 10^{-4}$ M, $[Ir(III)]_0 = (0–4) \times 10^{-4}$ M, $[VO^{2+}]_0 = (0.5–10) \times 10^{-3}$ M, $[VO_2^+]_0 = (1.0–20) \times 10^{-3}$ M, and $[H^+]_0 = 0.025–0.98$ M. The vanadium concentrations were always in sufficiently large excess (≥10×) over the iridium concentrations to ensure pseudo-first-order kinetics. The method of data treatment used leads to an observed rate constant which is the sum of the rate constants for the forward and the reverse reactions

$$-\mathrm{d}\ln(A_t - A_\infty)/\mathrm{d}t = k_{\mathrm{obsd}} = k_f + k_r \tag{2}$$

A reasonable initial assumption is that the forward reaction is first order in V(IV) ($k_f = A[VO^{2+}]$) and the reverse reaction is first order in V(V) ($k_r = B[VO_2^+]$), i.e.

$$k_{\mathrm{obsd}} = A[VO^{2+}] + B[VO_2^+] \tag{3}$$

Linearity of plots of k_{obsd} vs. $[VO^{2+}]$ at constant $[VO_2^+]$ and $[H^+]$ and plots of k_{obsd} vs. $[VO_2^+]$ at constant $[VO^{2+}]$ and $[H^+]$ indicate that this equation is correct. Equation 3 can be rearranged to a form containing only one independent variable

$$k_{\mathrm{obsd}}/[VO^{2+}] = A + B[VO_2^+]/[VO^{2+}] \tag{4}$$

A typical plot of this equation is shown in Figure 1. In experiments at each $[H^+]$, identical results were obtained whether Ir(IV) or Ir(III) was added initially. About 15–30 experiments were carried out at each $[H^+]$ in the forward direction and/or the reverse direction over the range of $[VO_2^+]/[VO^{2+}] = 0.025$–$10$. Values of the parameters A and B were obtained from these plots by a linear least-squares procedure and are listed in Table II Values of the equilibrium constant, presented in Table II, were calculated from $K = A/B$ and are in good agreement with the values obtained spectrally (Table I).

The dependence of the parameter A on $[H^+]$ was determined from a plot of A vs. $[H^+]^{-1}$. The principal term involves $[H^+]^{-1}$ but a small positive intercept is also observed

$$A = A_0 + A_{-1}[H^+]^{-1} \tag{5}$$

Linear least-squares treatment of these data leads to $A_0 = 0.027 \pm 0.028$ M^{-1} s^{-1} and $A_{-1} = 0.0966 \pm 0.0021$ s^{-1}, where the uncertainties are one standard deviation. The $[H^+]$ dependence of the parameter B was determined from a plot of B vs $[H^+]$. The principal term involves a first-order dependence on $[H^+]$, but slight curvature demands a second-order term as well

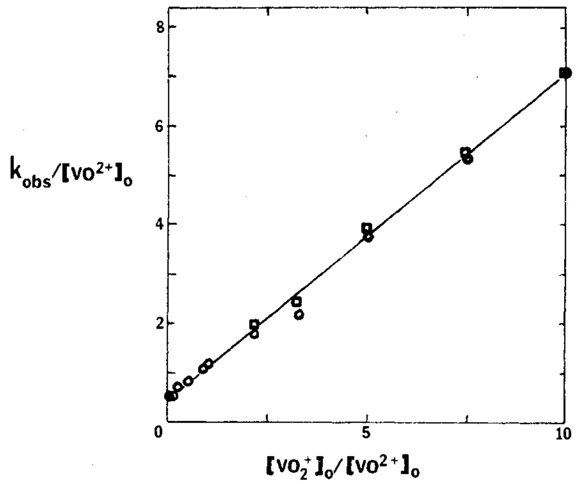

Figure 1. Plot of $k_{\mathrm{obsd}}/[VO^{2+}]_0$ vs. $[VO_2^+]_0/[VO^{2+}]_0$ at 0.200 M H^+, illustrating conformance to eq 4: ○, forward reaction; □, reverse reaction.

Table II. Values of Rate and Equilibrium Constants for the V^{IV}-Ir^{IV} Reaction at 25 °C and 1.00 M Ionic Strength

$[H^+]$, M	$A^{a,b}$	$B^{a,b}$	Equilibrium const^b ($K = A/B$)
0.0251	3.86 ± 0.07	0.115 ± 0.047	0.021 ± 0.009
0.0500	2.00 ± 0.03	0.180 ± 0.018	0.028 ± 0.003
0.0751	1.27 ± 0.09	0.319 ± 0.017	0.022 ± 0.003
0.0893	1.11 ± 0.02	0.289 ± 0.008	0.031 ± 0.001
0.0999	1.03 ± 0.07	0.373 ± 0.014	0.028 ± 0.003
0.200	0.468 ± 0.056	0.656 ± 0.012	0.029 ± 0.004
0.300	0.367 ± 0.043	1.02 ± 0.01	0.032 ± 0.004
0.400	0.325 ± 0.093	1.35 ± 0.02	0.038 ± 0.011
0.500	0.233 ± 0.036	1.82 ± 0.01	0.032 ± 0.005
0.601	0.253 ± 0.017	2.111 ± 0.004	0.043 ± 0.003
0.700	0.148 ± 0.060	2.67 ± 0.02	0.027 ± 0.011
0.800	0.095 ± 0.076	3.18 ± 0.02	0.019 ± 0.016
0.900	0.054 ± 0.203	3.55 ± 0.05	0.012 ± 0.046
0.981	0.145 ± 0.035	3.64 ± 0.12	0.038 ± 0.010
		Av	0.029 ± 0.006^c

[a] Defined in eq 3 and 4. [b] Uncertainties are one standard deviation. [c] The uncertainty is the average deviation of the individual values from the average value.

$$B = B_1[H^+] + B_2[H^+]^2 \tag{6}$$

Linear least-squares treatment of data reorganized as $B[H^+]^{-1}$ vs. $[H^+]$ leads to the values $B_1 = 3.30 \pm 0.11$ M^{-2} s^{-1} and $B_2 = 0.59 \pm 0.19$ M^{-3} s^{-1}. To be consistent with the requirements of microscopic reversibility, the relations $K = A_0/B_2$ and $K = A_{-1}/B_1$ must hold. The values obtained are 0.046 ± 0.063 M^2 and 0.0293 ± 0.0016 M^2, respectively, in good agreement with the values of K obtained spectrally and from the ratios of A/B.

The final form of the rate law is thus given by

$$\begin{aligned}-\mathrm{d}[IrCl_6^{2-}]/\mathrm{d}t &= (A_{-1}[H^+]^{-1} + A_0)[IrCl_6^{2-}][VO^{2+}] \\ &\quad - (B_1[H^+] + B_2[H^+]^2)[IrCl_6^{3-}][VO_2^+]\end{aligned} \tag{7}$$

Discussion

The form of the rate law suggests the mechanism

$$VO^{2+} + H_2O \underset{\text{fast}}{\overset{K_a}{\rightleftharpoons}} VOOH^+ + H^+ \tag{8}$$

$$VOOH^+ + IrCl_6^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} VO_2^+ + IrCl_6^{3-} + H^+ \tag{9}$$

$$VO^{2+} + IrCl_6^{2-} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} VO_2^+ + IrCl_6^{3-} + 2H^+ \tag{10}$$

where $K_a = (1.0\text{–}4.4) \times 10^{-6}$ M,[14] $k_1K_a = A_{-1}$, $k_2, = B_1$, $k_3 = A_0$, and $k_4 = B_2$. It is quite likely that protonated forms of V(V) are implicated as immediate products of reactions 9 and 10 and as precursors in the reverse of these reactions. However, no definitive evidence has been obtained for the protonation of V(V), so the mechanism is written in the simpler manner.

The loss of one proton prior to electron transfer in the principal path for the forward reaction is typical for the $VO^{2+} \rightarrow VO_2^+$ transformation.[15,16] In general, when reactant and product differ in the number of protons, some of the protons are lost or gained prior to the rate-determining step, presumably resulting in a lowering of the energy barrier since the transition state will then more closely resemble the products. The $[H^+]$ dependence observed here is identical with that for the VO^{2+}–$Fe(bpy)_3^{2+}$ reaction[4] (bpy = 2,2′-bipyridyl) and resembles that for the Fe^{2+}–VO_2^+ reaction,[17,18] where the principal path involves a first-order dependence on $[H^+]$, but terms having orders of −1, 0, and +2 were also observed.

The form of the rate law (eq 7) provides no information regarding the inner-sphere or outer-sphere nature of the reaction between VO^{2+} and $IrCl_6^{2-}$ (or VO_2^+ and $IrCl_6^{3-}$). The absorbance changes observed for the reaction were consistent with a simple one-step mechanism and no evidence could be obtained for the presence of appreciable amounts of precursor or successor binuclear complexes. Some information can be derived by examination of the magnitude of the rate constants. If the redox rate constant is greater than the rate constant for substitution on the most labile metal complex in a reacting pair, then the reaction must necessarily be of the outer-sphere type. No data are available on the rate of substitution on VO_2^+, but the rate of ^{18}O exchange with solvent water is known for VO^{2+}. The first-order rate constants for exchange are <20 s^{-1} for V=O, 500 s^{-1} for V—OH_2(equatorial), and ca. 5×10^8 s^{-1} for V—OH_2(axial),[19,20] which convert to second-order rate constants of <0.4, 9.1, and ca. 10^7 M^{-1} s^{-1}, respectively, upon dividing by the concentration of solvent water. Using a value of $K_a = 10^{-6}$ M, the rate constant for the principal path, reaction between $VOOH^+$ and $IrCl_6^{2-}$, is 9.7×10^4 M^{-1} s^{-1}. This value exceeds that for substitution at an equatorial site but not at an axial site. A detailed molecular orbital treatment[21] of $(H_2O)_5VO^{2+}$ suggests that the unpaired electron is in the d_{xy} orbital and is thus most accessible to oxidant substitution into the equatorial plane. The equatorial plane has also been shown to be the thermodynamically most stable site for substitution by NCS^-.[22] These results strongly suggest that the $VOOH^+ + IrCl_6^{2-}$ reaction (eq 9) must follow an outer-sphere mechanism. Microscopic reversibility demands that the transition state for the $VO_2^+ + IrCl_6^{3-} + H^+$ reaction also must be outer-sphere. No conclusion can be reached concerning the minor path (eq 10) for the V^{IV}–Ir^{IV} reaction since the redox rate does not exceed the equatorial substitution rate. Furthermore, it is not possible to rule out an inner-sphere mechanism for the principal path if substitution occurs at the axial site and is accompanied by appropriate rapid electronic or molecular rearrangements.

Further information is provided by examination of the rate constants for the V^V–Ir^{III} reaction. We have previously shown that a comparison of the rate constants for Ce(IV) oxidation of some substitution-inert iron(II) complexes with the rate constants for oxidation by V(V) or Cr(VI) provides a criterion for distinguishing between inner-sphere and outer-sphere mechanisms.[2–4] Values of k_{Ce}/k_V fall in the range of 1–10 for the known inner-sphere reactions of V(V) with $Fe(CN)_6^{4-}$, $Fe(bpy)(CN)_4^{2-}$, and $Fe(bpy)_2(CN)_2$ (where the Ce(IV) oxidations are outer-sphere[23]), while the outer-sphere V(V) oxidation of $Fe(bpy)_3^{2+}$ gives a ratio of $k_{Ce}/k_V \le 6.8 \times 10^6$.[4] A similar comparison of k_{Ce}/k_V for oxidation of $IrCl_6^{3-}$ should be informative. An experimental value of k_{Ce} is not available, but Sutin et al.[23] were highly successful in calculating values of rate constants for Ce^{IV}–Ce^{III} and Ir^{IV}–Ir^{III} reactions with a variety of other species, using the Marcus equations.[24] Using the same parameters as Sutin,[23] but a more reliable value for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ electron-exchange rate constant,[25] we calculate a rate constant of 9.5×10^6 M^{-1} s^{-1} for the reaction between Ce(IV) and $IrCl_6^{3-}$ in 0.5 M H_2SO_4. The value for the V(V) oxidation of $IrCl_6^{3-}$ in 0.5 M $HClO_4$ is 1.8 M^{-1} s^{-1}, giving a ratio of $k_{Ce}/k_V = 5.3 \times 10^6$. This value is in remarkably good agreement with that observed for the outer-sphere $Fe(bpy)_3^{2+}$ reaction,[4] providing further evidence that the principal path for the $V(IV) + Ir(IV) \rightleftharpoons V(V) + Ir(III)$ reaction is outer sphere.[26] These results are in complete accord with the trend established in the V(II) and V(III) reductions of $IrCl_6^{2-}$.[7]

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