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Electron-Transfer Reactions of Uranium(V): Kinetics of the Uranium(V)–Uranium(VI) Self-Exchange Reaction

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Uranium(V) has been prepared photochemically; its UV spectrum shows a peak at 255 nm with an extinction coefficient of 660 L mol^{-1} cm^{-1}. Conventional UV/visible, stopped-flow, and laser flash photolysis techniques have been used to study the electron-transfer reactions of uranium(V) and uranium(VI) with a range of chromium, ruthenium, and cobalt complexes. Application of Marcus theory to these results suggests a uranium(VI)/uranium(V) self-exchange rate constant in the range 1–15 L mol^{-1} s^{-1}. Some of the cross-reactions appear to be nonadiabatic, and these are slower than predicted.
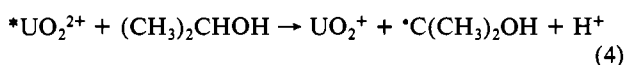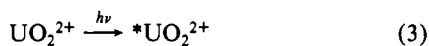
Introduction

Despite considerable efforts directed toward the chemistry of uranium(V) in various circumstances,[1] relatively little quantitative data exist on this oxidation state in aqueous solution. The principal cause for the lack of data is the fact that UO_2^+(aq) is stable only in a very narrow pH range (pH 2–3). The present work utilizes a photochemical method to prepare stable uranium(V) in an aqueous perchlorate medium.

Uranium(V) disproportionates in acidic, aqueous solution according to eq 1. This reaction shows a second-order dependence on [UO_2^+] and is first-order with respect to acid concentration, as shown in eq 2.[2,3]

$$2UO_2^+ + 4H^+ = U(aq)^{4+} + UO_2^{2+} + 2H_2O \qquad (1)$$

$$-d[UO_2^+]/dt = k_d[UO_2^+]^2[H^+] \qquad (2)$$
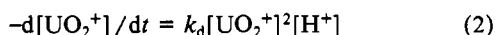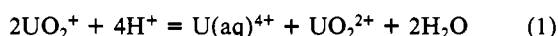
Uranium(V) can be produced photochemically by UV irradiation of a solution of uranium(VI) and an alcohol.[4,5] It is now well accepted that the mechanism involves the abstraction of an H atom of an alcohol by the excited state uranium(VI), forming an α-hydroxyalkyl radical.[6–8] This radical is a good reducing agent; e.g., $\cdot C(CH_3)_2OH$ from 2-propanol has $E° \sim -1.2$ V.[9] We repeat the key reaction steps in eq 3–5, for the case of ROH = 2-propanol, since they constitute the basis of the experimental method used here for the preparation of metastable solutions of UO_2^+. Such solutions are sufficiently kinetically stable as to be useful in this work.

$$UO_2^{2+} \xrightarrow{h\nu} {}^*UO_2^{2+} \qquad (3)$$

$${}^*UO_2^{2+} + (CH_3)_2CHOH \rightarrow UO_2^+ + \cdot C(CH_3)_2OH + H^+ \qquad (4)$$

$$UO_2^{2+} + \cdot C(CH_3)_2OH \rightarrow UO_2^+ + (CH_3)_2CO + H^+ \qquad (5)$$

Uranium(V) solutions are greatly stabilized in the presence of high concentrations of uranium(VI) owing to the formation of $U_2O_4^{3+}$, a uranium(V)–uranium(VI) complex.[2,3] Under the conditions employed here, however, the predominant uranium(V) species is the dioxo cation, UO_2^+, since the stability constant[2,3] for formation of $U_2O_4^{3+}$ is only ~ 20 M^{-1}.

We have thus studied a number of electron-transfer reactions of this neglected species. Since a prior literature was largely absent, we selected a variety of substrates for examination. These include mostly outer-sphere reagents with reported self-exchange rates and standard reduction potentials. We also sought to evaluate the self-exchange rate constant between uranium(VI) and uranium(V) by application of the Marcus equation for outer-sphere electron transfer, for which only an estimate was hitherto available.[10] The reactions ranged from those proceeding relatively slowly, to which conventional spectrophotometry was applicable, to those near the diffusion-controlled limit, for which laser flash photolysis was required. In between, the reactions were followed by the stopped-flow technique. We were also able to determine the UV spectrum of UO_2^+, since the photochemical procedure developed permits nearly quantitative conversion of U(VI) into U(V).

Experimental Section

Reagents. Uranium(V) was prepared by irradiating (Hg lamp, λ = 254 nm) a degassed solution of uranium(VI) in 0.5 M 2-propanol at pH 1.7–2.7. At pH 2.7 the uranium(V) formed is kinetically stable, with little decomposition occurring in 1 h. Uranium(VI) concentrations of up to 8×10^{-4} M were used, requiring irradiation times of about 3 min. The UV spectrum of uranium(V), given in Figure 1, shows an absorption maximum at 255 nm, with an extinction coefficient of 660 L mol^{-1} cm^{-1} at this wavelength.
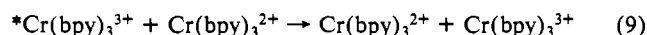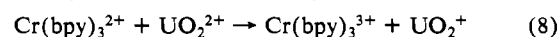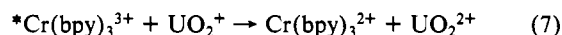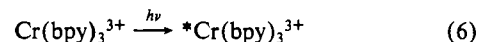
Ru(NH₃)₅py(ClO₄)₃ was prepared from [RuCl(NH₃)₅]Cl₂ by the method of Gaunder and Taube.[11] **Co(sep)²⁺** was prepared by the zinc amalgam reduction of Co(sep)Cl₃. **Co(phen)₃(ClO₄)₃·2H₂O** was prepared by the bromine oxidation[12a] of Co(phen)₃(ClO₄)₂·H₂O.[12b] **Co(bpy)₃-(ClO₄)₃·3H₂O** was prepared from CoCl₂ and 2,2′-bipyridine by the method of Burstall and Nyholm.[13]

Kinetic Procedures. We followed the slower reactions using either Cary 219 or Perkin-Elmer diode array spectrophotometers. The reactions with Ru(NH₃)₅py³⁺ and Co(tim)³⁺ were followed on a Durrum stopped-flow spectrophotometer. The laser flash photolysis system was described earlier.[14] Laser dyes were chosen such that excitation wavelengths of 423 and 460 nm were used.

All the kinetic experiments were run under pseudo-first-order conditions, with the uranium reagent present in a large excess. The ionic strength was maintained at 0.10 M through the addition of lithium perchlorate. All the kinetic experiments were carried out at 25 °C.

Results

Tris(bipyridine)chromium Ions. Laser flash photolysis techniques were used to study the reductive quenching of the excited-state doublet *Cr(bpy)₃³⁺ and the subsequent secondary electron-transfer reaction. The chemical equations for the reactions occurring are shown in eq 6–9.

$$Cr(bpy)_3^{3+} \xrightarrow{h\nu} {}^*Cr(bpy)_3^{3+} \qquad (6)$$

$${}^*Cr(bpy)_3^{3+} + UO_2^+ \rightarrow Cr(bpy)_3^{2+} + UO_2^{2+} \qquad (7)$$

$$Cr(bpy)_3^{2+} + UO_2^{2+} \rightarrow Cr(bpy)_3^{3+} + UO_2^+ \qquad (8)$$

$${}^*Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \rightarrow Cr(bpy)_3^{2+} + Cr(bpy)_3^{3+} \qquad (9)$$

(1) See, for example, the following review: Selbin, J.; Ortego, J. D. *Chem. Rev.* **1969,** *69,* 657.
(2) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965,** *4,* 1166.
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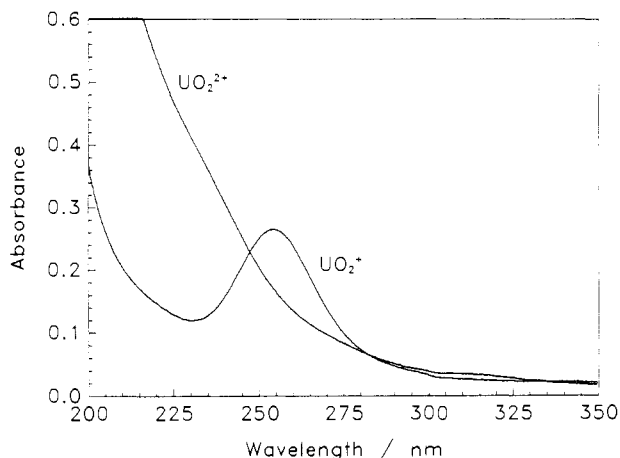(10) Gordon, G.; Taube, H. *J. Inorg. Nucl. Chem.* **1961,** *16,* 272.
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(14) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986,** *25,* 4104.

Figure 1. UV spectra of uranium(V) and uranium(VI). Conditions: $[UO_2^{2+}] = 4 \times 10^{-4}$ M, [2-PrOH] = 0.5 M, $[H^+]$ = 0.002 M, $[LiClO_4]$ = 0.20 M. UO_2^+ was produced quantitatively by irradiation of the UO_2^{2+} solution in the UV reactor for 1 min. An absorbance maximum for UO_2^+ occurs at λ = 255 nm (ϵ = 660 L mol^{-1} cm^{-1}).
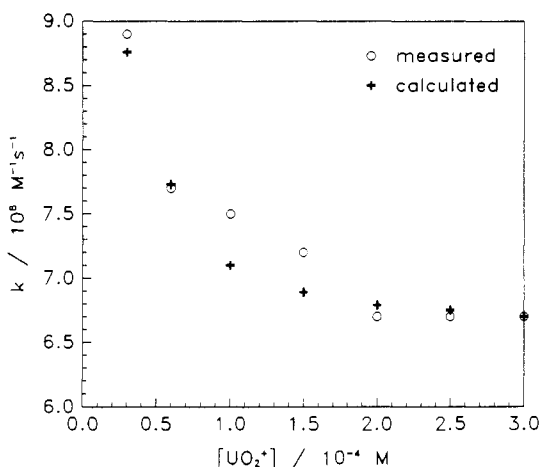
Figure 2. Variation of measured k_1 values with uranium(V) concentration in the reaction of UO_2^+ with $^*Cr(bpy)_3^{3+}$. Conditions: $[H^+]$ = 0.02 M, μ = 0.10 M, $[Cr(bpy)_3^{3+}]_0$ = 2.5 × 10^{-5} M, excitation wavelength 460 nm, monitoring wavelength 727 nm. The rate constants k_7 = 6.4 × 10^8 L mol^{-1} s^{-1}, k_8 = 1.66 × 10^6 L mol^{-1} s^{-1}, and k_9 = 5 × 10^9 L mol^{-1} s^{-1} were used in the kinetic simulation.

The quenching reaction of eq 7 was monitored in emission experiments at 727 nm and in absorption experiments at 560 nm, an absorption maximum of $Cr(bpy)_3^{2+}$. The measured transmittances were converted to absorbances (D), from which first-order rate constants were obtained by least-squares fitting to the pseudo-first-order rate equation $D_t = D_\infty + (D_0 - D_\infty) \exp(-kt)$. The values of k thus determined then gave the second-order rate constant k_7. Values of k_7 fell with increasing values of uranium(V) concentration. The problem was the competing quenching reaction[15] of eq 9. The effect of this competing reaction was minimized by using a large (>10^2-fold) excess of uranium(V) over the concentration of the excited state, which was typically ∼2.5 μM. In addition, a kinetic simulation by methods of numerical integration was carried out with the assistance of the program KINSIM.[16] In these calculations k_9 was set at its known value, 5 × 10^9 M^{-1} s^{-1}. A first-order treatment of the data from several such simulations resulted in apparent values of k_7 that matched those from the actual experiments. The close agreement of experimental data and simulated rate constants is shown in Figure

(15) Bakac, A.; Zahir, K.; Espenson, J. H. *Inorg. Chem.*, in press.
(16) The numerical solutions of the differential equations were carried out with the program KINSIM: Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134.

Table I. Measured Rate Constants for the Reactions of UO_2^{2+} with $Cr(bpy)_3^{2+}$, $Cr(Me_2bpy)_3^{2+}$, $Cr(phen)_3^{2+}$, and $Cr(Cl\text{-}phen)_3^{2+}$

NN	$[UO_2^+]/$ 10^{-4} M	$[UO_2^{2+}]/$ 10^{-3} M	k_8/L mol^{-1} s^{-1}
bpy[a]	0.6	0.25	1.68 (±0.04) × 10^6
bpy[a]	1.5	0.5	1.64 (±0.04) × 10^6
bpy[a]	1.5	1.0	1.51 (±0.04) × 10^6
Me$_2$bpy[b]	1.5	0.5	1.20 (±0.01) × 10^{7c}
Me$_2$bpy[b]	1.5	1.0	9.6 (±0.4) × 10^{6c}
Me$_2$bpy[b]	1.5	1.5	8.3 (±0.4) × 10^{6c}
Me$_2$bpy[b]	1.5	2.0	7.6 (±0.3) × 10^{6c}
Me$_2$bpy[b]	3.0	0.5	1.38 (±0.02) × 10^{7c}
Me$_2$bpy[b]	3.0	1.0	1.17 (±0.02) × 10^{7c}
phen[b]	1.5	1.0	2.44 (±0.07) × 10^6
phen[b]	1.5	2.0	2.41 (±0.06) × 10^6
Cl-phen[b]	1.5	1.0	5.49 (±0.15) × 10^5
Cl-phen[b]	1.5	2.0	5.25 (±0.10) × 10^5

[a] μ = 0.100 M, $[H^+]$ = 0.02 M, $[Cr(bpy)_3^{3+}]$ = 5 × 10^{-5} M, $[Cr(bpy)_3^{2+}] \sim 5 \times 10^{-6}$ M. [b] μ = 0.100 M, $[H^+]$ = 0.02 M, $[Cr(NN)_3^{3+}]$ = 8 × 10^{-5} M, $[Cr(NN)_3^{2+}] \sim 8 \times 10^{-6}$ M. [c] The systematic variability of the apparent values of k_8 for NN = Me$_2$bpy is due to the overlap of quenching reaction 7 and redox reaction 8. The value k_8 = 1.6 × 10^7 L mol^{-1} s^{-1} was obtained by extrapolation to a higher value of $[UO_2^+]/[UO_2^{2+}]$ (see text).

2. On the basis of such trials, k_7 = 6.4 (±0.3) × 10^8 M^{-1} s^{-1}.

The kinetics of the return reaction, eq 8, were studied in experiments in which UO_2^{2+} was added to the solution so that the kinetics could be evaluated under pseudo-first-order conditions. The decay of $Cr(bpy)_3^{2+}$ was monitored at 560 nm where $\epsilon \sim$ 4900 M^{-1} cm^{-1}. The individual rate constants are invariant over a range of $[UO_2^{2+}]$ (see Table I), and the average rate constant is k_8 = 1.61 (±0.09) × 10^6 M^{-1} s^{-1}.

Other $Cr(NN)_3^{3+}$ Complexes. The same laser flash photolysis technique was used to study the secondary electron transfers between $Cr(NN)_3^{2+}$ and UO_2^{2+} occurring after the quenching reactions for complexes where NN is 4,4'-dimethylbipyridine (Me$_2$bpy), 1,10-phenanthroline (phen), and 5-chlorophenanthroline (Cl-phen). These experiments also employed excess (added) uranium(VI) to give pseudo-first-order kinetics. Analyzing wavelengths appropriate to a particular $Cr(NN)_3^{2+}$ species were used to monitor its decay: for Me$_2$bpy, 560 nm ($\epsilon \sim$ 4500 L mol^{-1} cm^{-1}); for phen, 430 nm ($\epsilon \sim$ 3600); for Cl-phen, 440 nm ($\epsilon \sim$ 3000).

The kinetic results are summarized in Table I, the average rate constants (k_8) for $Cr(phen)_3^{2+}$ and $Cr(Cl\text{-}phen)_3^{2+}$ being 2.42 (±0.07) × 10^6 and 5.37 (±0.15) × 10^5 M^{-1} s^{-1}, respectively. The measured rate constant for $Cr(Me_2bpy)_3^{2+}$ falls systematically with increasing concentration of uranium(VI) and with decreasing uranium(V). This is a result of considerable overlap between the rates of quenching and secondary electron transfer, which are the respective formation and decomposition rates of $Cr(Me_2bpy)_3^{2+}$. Estimation of the apparent k_8 value at higher values of the $[UO_2^+]/[UO_2^{2+}]$ ratio gives an approximate value, $k_8 \sim 1.6 \times 10^7$ M^{-1} s^{-1}.

Tris(bipyridine)cobalt(III) Ions. The reaction of $Co(bpy)_3^{3+}$ with excess uranium(V) was followed by monitoring the increasing absorbance at 220 nm due to $Co(bpy)_3^{2+}$ formation with the use of conventional spectrophotometry. A plot of the measured first-order rate constant versus the uranium(V) concentration (shown in Figure 3) is linear, confirming that the reaction is first-order with respect to uranium(V) concentration. A value for the second-order rate constant of 153 (±20) L mol^{-1} s^{-1} is obtained.

Tris(1,10-phenanthroline)cobalt(III) Ions. The reaction between $Co(phen)_3^{3+}$ and excess uranium(V) was studied by observing the absorbance changes at 235 and 270 nm. These wavelengths were chosen, as they correspond to absorbance change maxima. The measured rate constants are given in Table II. An increase in uranium(V) concentration resulted in a decrease in the apparent second-order rate constant, implying that more than one reaction is occurring, one possibly involving an impurity. A plot of first-order rate constant versus uranium(V) concentration is linear
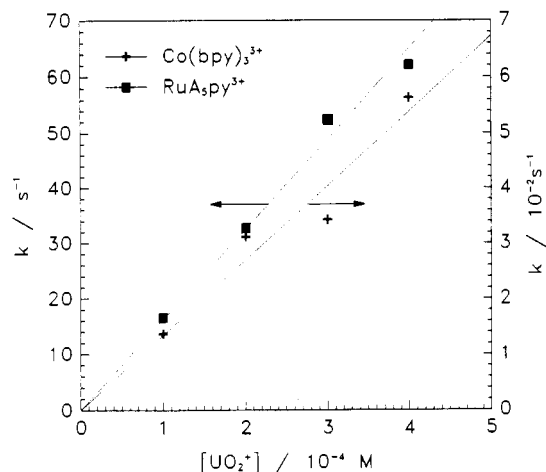
Figure 3. Measured first-order rate constants for the reactions of uranium(V) with $Co(bpy)_3^{3+}$ and $Ru(NH_3)_5py^{3+}$. For the $Co(bpy)_3^{3+}$ reaction, $[Co(bpy)_3^{3+}] = (2.0-4.0) \times 10^{-5}$ M, $[H^+] = 0.002$ M, $\lambda = 220$ nm, and $\mu = 0.10$ M. For the $Ru(NH_3)_5py^{3+}$ reaction, $[Ru(NH_3)_5py^{3+}] = 2.5 \times 10^{-5}$ M, $[H^+] = 0.001$ M, $\lambda = 407$ nm, and $\mu = 0.10$ M.

Table II. Measured Rate Constants for the $Co(phen)_3^{3+}/UO_2^+$ Reaction[a]

| $[UO_2^+]/$ 10^{-4} M	$[Co(phen)_3^{3+}]/$ 10^{-5} M	$k/10^{-2}$ s^{-1}	k/L mol^{-1} s^{-1}
0.91[b]	1.2	3.85	423
1.35[b]	2.0	4.20	311
1.90[b]	1.4	5.26	277
2.89[b]	1.5	6.50	225
3.84[b]	2.0	8.1	211
0.95[c]	1.4	3.00	316
1.89[c]	2.0	5.48	290
2.89[c]	1.5	7.8	270
3.89[c]	1.5	8.8	226

[a] $[H^+] = 0.002$ M. [b] $\lambda = 235$ nm. [c] $\lambda = 270$ nm.

with a slope of 1.7×10^2 L mol^{-1} s^{-1} and an intercept of 2.0×10^{-2} s^{-1}. This implies that the unknown reaction has a rate constant independent of uranium(V) concentration. Thus the desired second-order rate constant is 1.7×10^2 L mol^{-1} s^{-1}.

Pentaammine(pyridine)ruthenium(III) Ions. The reaction between $Ru(NH_3)_5py^{3+}$ and excess uranium(V) was studied by monitoring the formation of $Ru(NH_3)_5^{2+}$ at 407 nm ($\epsilon \sim 7800$ L mol^{-1} cm^{-1}). The results are shown in Figure 3. The results were not highly reproducible owing to difficulties in totally excluding oxygen from the system. Oxygen rapidly oxidizes uranium(V) to uranium(VI), resulting in uranium(V) concentrations lower than those calculated. The results obtained indicate a second-order rate constant of $1.9 (\pm 0.1) \times 10^5$ L mol^{-1} s^{-1}.

Co(Me₄[14]tetraeneN₄)³⁺. The reaction of $Co(tim)^{3+}$ with excess uranium(V) was studied by monitoring the formation of $Co(tim)^{2+}$ at 545 nm ($\epsilon = 3960$ L mol^{-1} cm^{-1}). Difficulties were again experienced in totally excluding oxygen from the system, resulting in an uncertainty of around 10% for the measured first-order rate constants. These are shown in Figure 4 for a range of uranium(V) concentrations. The plot in Figure 4 is linear and passes through the origin, indicating that the reaction is first order in uranium(V) concentration. Its slope yields a second-order rate constant of $2.1 (\pm 0.1) \times 10^3$ L mol^{-1} s^{-1}.

Cobalt(II) Sepulchrate Ions. The reaction of $Co(sep)^{2+}$ with excess uranium(VI) was followed by monitoring the increase in absorbance at 230 nm due to the formation of $Co(sep)^{3+}$ ($\Delta\epsilon = 16\,000$ L mol^{-1} cm^{-1}). The results obtained are given in Table III. Variation of the uranium(VI) concentration produced constant values for the second-order rate constant, confirming the first-order dependence on $[UO_2^{2+}]$. Measurements were carried out at two ionic strengths, 0.0020 and 0.10 M. A value of $1.82 (\pm 0.13) \times 10^3$ L mol^{-1} s^{-1} was obtained at an ionic strength of 0.10 M, as compared to $4.66 (\pm 0.12) \times 10^2$ L mol^{-1} s^{-1} at 0.0020 M.
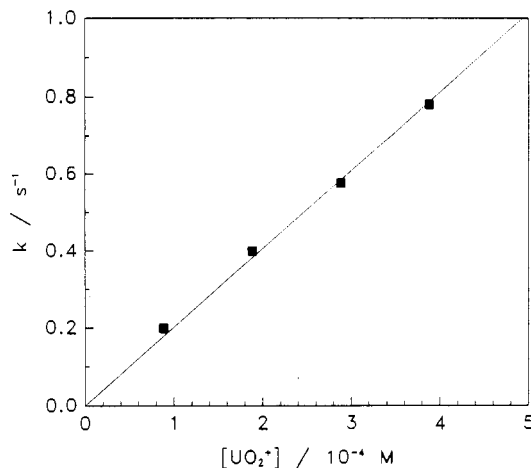
Figure 4. Variation of measured first-order rate constants with uranium(V) concentration in the reaction of UO_2^+ with $Co(tim)^{3+}$. Conditions: $[Co(tim)^{3+}] = 2.5 \times 10^{-5}$ M, $[H^+] = 0.002$ M, $\lambda = 545$ nm, $\mu = 0.10$ M.

Table III. Measured Rate Constants for the Reaction between UO_2^{2+} and $Co(sep)^{2+}$[a]

$[UO_2^{2+}]/$ 10^{-4} M	$k/$ 10^{-2} s^{-1}	k/L mol^{-1} s^{-1}	$[UO_2^{2+}]/$ 10^{-4} M	$k/$ 10^{-2} s^{-1}	k/L mol^{-1} s^{-1}
0.85	4.15	488	2.81	12.8	456
1.34	6.02	449	0.81[b]	14.0	1.73×10^3
1.81	8.48	469	0.81[b]	15.5	1.91×10^3

[a] $[Co(sep)^{2+}] = 2.5 \times 10^{-5}$ M, $[H^+] = 0.002$ M, $\mu = 0.002$ M. [b] $\mu = 0.10$ M.

Discussion

Literature values are available for the reduction potentials and self-exchange rate constants of all the redox couples whose reactions with the UO_2^+ or UO_2^{2+} have been studied in the present work. The measured cross-reaction rate constants can therefore be used in electrostatics-corrected Marcus calculations to determine values for the self-exchange rate constant of the uranium(V)–uranium(VI) couple. The calculations were performed by using eq 10–12.[17]

$$\Delta G_{12}^* = \tfrac{1}{2}(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{12}^\circ - w_{11} - w_{22} + w_{12} +$$
$$w_{21}) + \frac{(\Delta G_{12}^\circ + w_{21} - w_{12})^2}{8(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22})} \quad (10)$$

$$w_{ij} = \frac{\alpha Z_i Z_j}{a(1 + \beta a \mu^{1/2})} \quad (11)$$

$$k = Z \exp(-\Delta G^*/RT) \quad (12)$$

In these equations w_{ij} is an electrostatic work term, α is equal to 1.75×10^{-6} J mol^{-1} m, β is equal to 3.285×10^9 m^{-1} L$^{1/2}$ mol$^{-1/2}$, Z_i and Z_j are the charges on the ions, and μ is the ionic strength. The distance of closest approach, a, is given by the sum of the appropriate ionic radii. Z, a collision frequency, is taken[18] as 10^{11} L mol^{-1} s^{-1}. Equation 10 yields a quadratic in ΔG_{11}^*, the positive square root solution giving the correct self-exchange rate constant.

The results of all the Marcus calculations are summarized in Table IV. Values of the uranium(VI/V) self-exchange rate, k_{11}, were obtained by both simple and electrostatics-corrected Marcus calculations. Three cross-reactions by other workers were also used to calculate values of k_{11}, and these are also included in Table IV.

(17) Stanbury, D. M.; Gaswick, D.; Brown, G. M.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1975.

(18) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679, 2654.

Table IV. Marcus Calculations of the Uranium(V)–Uranium(VI) Self-Exchange Rate Constant

reacn	$\Delta E°/V$	$r^a/Å$	$k_{22}/L \ mol^{-1} \ s^{-1}$	$k_{12}/L \ mol^{-1} \ s^{-1}$	$k_{11}{}^b/L \ mol^{-1} \ s^{-1}$	$k_{11}{}^c/L \ mol^{-1} \ s^{-1}$
$UO_2{}^{2+}/Cr(Cl\text{-}phen)_3{}^{2+}$	0.23	7.0	$2 \times 10^{9\,d}$	5.37×10^5	0.034	0.032
$UO_2{}^{2+}/Cr(bpy)_3{}^{2+}$	0.32	6.8	$2 \times 10^{9\,d}$	1.66×10^6	0.017	0.017
$UO_2{}^{2+}/Cr(phen)_3{}^{2+}$	0.34	7.0	$2 \times 10^{9\,d}$	2.42×10^6	0.020	0.019
$UO_2{}^{2+}/Cr(Me_2bpy)_3{}^{2+}$	0.51	6.8	$2 \times 10^{9\,d}$	1.6×10^7	0.0053	0.0063
$UO_2{}^+/Ru(NH_3)_5py^{3+}$	0.25	3.8	$4.3 \times 10^{5\,e}$	1.90×10^5	9.7	6.6
$UO_2{}^+/Co(bpy)_3{}^{3+}$	0.255	6.7/6.9	17.5^f	1.53×10^2	0.11	0.086
$UO_2{}^{2+}/Co(sep)^{2+}$	0.32	4.4/4.6	2.0^g	1.82×10^3	14.5	15
$UO_2{}^+/Co(phen)_3{}^{3+}$	0.31	7.0	41.7^f	1.7×10^2	0.0080	0.0066
$UO_2{}^+/Co(tim)^{3+}$	0.504	4.5	0.05^h	2.1×10^3	1.6	1.4
$UO_2{}^+/(SCN)_2{}^-$	1.23		$3 \times 10^{3\,i}$	$1.46 \times 10^{9\,j}$	0.69	
$UO_2{}^+/Cl_2{}^-$	2.03		$1 \times 10^{-6\,k}$	$6.5 \times 10^{8\,k}$	0.51	
$UO_2{}^{2+}/MV^+$	0.51		$5.4 \times 10^{8\,l}$	$4.76 \times 10^{7\,m}$	0.21	

^{a}The radius of $UO_2{}^{2+/+}$ is 3.3 Å; radii of the other couples are as given. Where two numbers are given, they refer to the oxidized and reduced forms of the couple. ^{b}Calculated by using the equation $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$, $\log f = (\log K_{12})^2/(4 \log (k_{11}k_{22}/Z^2))$. ^{c}Calculated by using electrostatics-corrected Marcus theory. ^{d}Ferraudi, G. J.; Endicott, J. F. *Inorg. Chim. Acta* **1979**, *37*, 219. ^{e}Taube, H. *Adv. Chem. Ser.* **1977**, No. *162*, 127. ^{f}Cummings, D.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5158. ^{g}From a value of 5.1 L mol^{-1} s^{-1} at $\mu = 0.2$ M by: Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016. ^{h}Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431. ^{i}Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715. ^{j}Burrows, M. D.; Pedrosa de Jesus, J. D. *J. Photochem.* **1976**, *5*, 2. ^{k}Lierse, C.; Sullivan, J. C.; Schmidt, K. H. *Inorg. Chem.* **1987**, *26*, 1408. ^{l}Rieger, A. L.; Rieger, P. H. *J. Phys. Chem.* **1984**, *88*, 5845. ^{m}Howes, K. R.; Pippin, G.; Sullivan, J. C.; Meisel, D.; Espenson, J. H.; Bakac, A., submitted for publication.

The calculated uranium(VI/V) self-exchange rate constants range from 0.0063 to 15 L mol^{-1} s^{-1}. Caution must be exercised in interpreting these values, as they are sensitive functions of the reduction potentials used. Also, the reported k_{22} values are often not well established, resulting in a further source of error. Nevertheless, the range in k_{11} values is so large that the nonconstancy must be considered real.

The usual adiabatic Marcus equation can be rewritten[19] to include a factor to allow for any nonadiabaticity in the self-exchange or cross-reactions, as shown in eq 13.

$$k_{12} = \frac{p_{12}(k_{11}k_{22}K_{12}f)^{1/2}}{(p_{11}p_{22})^{1/2}}$$

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/p_{11}p_{22}Z^2)} \qquad (13)$$

The term p is the probability of electron transfer in the activated complex; for an adiabatic reaction $p = 1$, for a nonadiabatic reaction $p < 1$. If only the cross-reaction is nonadiabatic, i.e. $p_{11} = p_{22} = 1$, and $p_{12} < 1$, the calculated cross-reaction rate constant is higher than the actual rate constant, or in the present case, the calculated self-exchange rate constant is lower than the true rate constant and is given by eq 14.

$$k_{11}(\text{calcd}) = p_{12}{}^2 k_{11} \qquad (14)$$

Cross-reactions involving the $Co(bpy)_3{}^{3+/2+}$ and $Co(phen)_3{}^{3+/2+}$ couples have previously been shown[20] to be nonadiabatic, although the self-exchange reactions of these couples were assumed to be adiabatic. It thus seems plausible that the $UO_2{}^+/Co(bpy)_3{}^{3+}$ and $UO_2{}^+/Co(phen)_3{}^{3+}$ reactions are also nonadiabatic. Given the similarity of the calculated $UO_2{}^+/UO_2{}^{2+}$ self-exchange rate constants derived from all of the cobalt and chromium polypyridyl complexes, it would appear that the reactions of the chromium polypyridyls are also nonadiabatic. The most trustworthy values of the $UO_2{}^+/UO_2{}^{2+}$ self-exchange rate constant are, therefore, those in the range 1–15 M^{-1} s^{-1}.

A minimum value of the uranium(VI/V) self-exchange rate constant has been deduced from a study[10] of oxygen exchange between $UO_2{}^{2+}$ and water. A value of 52 L mol^{-1} s^{-1} was reported in 1 M perchloric acid at $\mu = 3.8$ M. The agreement between this value and our results is very good, especially when the effect of ionic strength is taken into consideration.

Registry No. Cr(bpy)$_3{}^{3+}$, 15276-15-0; Cr(Me$_3$bpy)$_3{}^{3+}$, 58220-56-7; Cr(phen)$_3{}^{3+}$, 15276-16-1; Cr(Cl-phen)$_3{}^{3+}$, 51194-62-8; Co(bpy)$_3{}^{3+}$, 19052-39-2; Co(phen)$_3{}^{3+}$, 18581-79-8; Ru(NH$_3$)$_5$py^{3+}, 33291-25-7; Co-(tim)$^{3+}$, 112506-20-4; Co(sep)$^{2+}$, 63218-22-4; Cr(bpy)$_3{}^{2+}$, 17632-84-7; Cr(Me$_2$bpy)$_3{}^{2+}$, 47837-99-0; Cr(phen)$_3{}^{2+}$, 47836-39-5; Cr(Cl-phen)$_3{}^{2+}$, 51194-68-4; [UO$_2{}^+$], 21294-41-7; [UO$_2{}^{2+}$], 16637-16-4.

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