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Kinetics and Mechanisms of the Reactions of Uranium(III) with Vanadium(III), Vanadium(IV), and Iron(III) in Perchlorate Media

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The kinetics and mechanisms of the reactions of U(III) with Fe(III), V(III), and V(IV) have been studied. The reactions of Fe(III) and V(IV) were found to be independent of acid concentration, while the rate of reaction of U(III) and V(III) increased with decreasing acid concentration. The ionic strength dependency of the three reactions was examined and the reaction parameters were measured. The results obtained are compared with those reported for other related systems and reaction mechanisms consistent with the observed results are discussed.

Introduction

U(III) is one of the most powerful reducing agents known ($E° = 0.63$ V) but can be relatively easily prepared and handled in carefully deoxygenaeted solutions.[1] Comparatively few of its reactions have been studied, although a preliminary examination[2] showed that U(III) will reduce a wide range of transition metal ions at measurable rates, and the mechanisms of the oxidations of U(III) by a series of Cr(III)[3] and Co(III)[4] complexes and by U(VI) ions[5] have been investigated. The wide choice of metal ions capable of oxidizing U(III) makes this species particularly suitable for comparative studies, and this paper describes the results obtained from an examination of the kinetics of the reduction of V(III), V(IV), and Fe(III) by U(III).

Experimental Section

Materials. $UO_2(ClO_4)_2$, $NaClO_4$, and $HClO_4$ solutions were prepared and analyzed as described previously.[6] U(III) solutions were prepared by reduction of suitably diluted samples of the stock solution at the mercury cathode of a cell described elsewhere.[6] $VO(ClO_4)_2$ solutions were prepared by repeated precipitations of $VO(OH)_2$ from $VOSO_4$ (Merck) solutions, washing of the precipitate, and redissolving in $HClO_4$. The final solutions were analyzed for V(IV), free acid, V(V), and sulfate, but no measurable concentrations of the latter two species could be detected. V(III) solutions were prepared by mixing V(IV) and V(II) in approximately equimolar ratios, the resulting solution being left to stand for at least 18 hr and then used within 6 hr.[7] Samples of the V(III) solutions were diluted with the appropriate quantities of $NaClO_4$–$HClO_4$ solutions immediately prior to use; $Fe(ClO_4)_3$ solutions were prepared from the solid reagent (Fluka) and analyzed for Fe(III) and free acid. Prior to use, reagent solutions were purged with high-purity argon gas from which residual traces of oxygen were removed by passage of the gas through a column of an appropriate catalyst (BASF catalyst No. R3-11).

Measurements of Reaction Rates and Calculations. The reactions were followed at a variety of wavelengths using the computerized stopped-flow apparatus described previously.[8] For this work, the size of the analog to digital converter in the system was increased from 8 to 10 bits, thus giving a fourfold increase in sensitivity as well as an improvement in the reproducibility of the results. The data were acquired in the form of punched tape and, as discussed in greater detail below, subsequently analyzed according to second-order rate laws, the rate constants being determined by linear least-squares analysis. All nonlinear least-squares analyses described in this paper were carried out using the program of Lietzke,[9] the individual results being weighted according to the reciprocal of the square of the per cent standard error.

Results

Preliminary Data. The U(III)–Fe(III) and U(III)–V(IV) reactions were monitored by following the disappearance of U(III) at 350 nm, the analysis of the results being simplified by the observation that at this wavelength the absorptions of Fe(III), Fe(II), V(IV), and V(III) were negligible. For the U(III)–Fe(III) reaction, excess U(III) was used, the initial U(III) concentration being calculated from the final absorbance (ABSF) using the relationship

$$[U(III)]_0 = [Fe(III)]_0 + (ABSF)(EU3)^{-1} \tag{1}$$

where EU3 is the extinction coefficient of U(III), independently determined as $(1.19 \pm 0.03) \times 10^3\ M^{-1}\ cm^{-1}$ at 350 nm. The calculated values of the initial U(III) concentrations were typically 90–95% of the total uranium concentration. Preliminary experiments showed that the rate of the U(III)–V(IV) reaction was much faster than that of the subsequent U(III)–V(III) reaction, and any interference from the latter was further avoided by using an excess of V(IV).

Table I. Observed Second-Order Rate Constants[a]

Reactant A	Reactant B	Range of concn × 10^4, M: Reactant A	Range of concn × 10^4, M: Reactant B	No. of determins	k_{obsd},[b] M^{-1} sec^{-1}
U(III)	Fe(III)	3.9	1.8–2.9	22	$(3.92 \pm 0.20) \times 10^5$
U(III)	Fe(III)	1.4–5.0	1.0–4.7	31	$(1.31 \pm 0.09) \times 10^5$ [c]
U(III)	V(III)	24–60	1.5–4.2	60	$(3.38 \pm 0.08) \times 10^2$
U(III)	V(IV)	1.4–4.8	2.3–9.0	67	$(3.66 \pm 0.20) \times 10^5$

[a] Conditions: $[H^+] = 1.00\ M$, $\mu = 2.00$, 20.0°. [b] Uncertainties are standard deviations. [c] Conditions $\mu = 0.200$, $[H^+] = 0.100\ M$, 20°.

The U(III)–V(III) reaction was measured at 520 nm, where small corrections due to the absorbance of V(III), V(IV), and U(IV) had to be applied. The initial concentrations of U(III) and V(III) were calculated from the initial and final absorbances, respectively, using the measured U(III) extinction coefficient of $134 \pm 2\ M^{-1}\ cm^{-1}$ at 520 nm. The calculated values of the initial U(III) and V(III) concentrations were typically within 3% of the expected values. Plots of the integrated second-order rate equations were straight lines up to 90% reactions for all three systems studied, and the values of the second-order rate constants obtained showed no systematic variation with changes in the initial reagent concentrations (Table I).

Acid Dependency. Examination of the acid dependency at constant ionic strength of the rate constants for the three reactions showed that the U(III)–Fe(III) and U(III)–V(IV) reactions exhibited only a slight increase with increasing acid concentration. For the U(III)–Fe(III) reaction, the value of $k_{obsd}^{Fe(III)}$ increased from $(3.78 \pm 0.15) \times 10^5\ M^{-1}$ sec^{-1} in 0.204 M $[H^+]$ to $(4.66 \pm 0.32) \times 10^5\ M^{-1}$ sec^{-1} in 2.00 M $[H^+]$. Similarly, the value of $k_{obsd}^{V(IV)}$ increased from $(3.59 \pm 0.17) \times 10^5\ M^{-1}$ sec^{-1} at 0.502 M $[H^+]$ to $(4.71 \pm 0.51) \times 10^5\ M^{-1}$ sec^{-1} at 2.00 M $[H^+]$. These variations can probably be ascribed to media effects and the experimental results could be reproduced very well by the Harned function[10] of the type

$$k_{obsd} = k_2 \exp\{\alpha[H^+]\} \tag{2}$$

the values for k_2 and α determined for the two reactions being summarized in Table II.

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Table II. Summary of the Harned Function Parameters Obtained for the Reactions of U(III) with Fe(III) and V(IV)[a]

Reacn	Acid concn range, M	No. of determins	$10^{-5}k_2, M^{-1}$ sec^{-1}	$10^2\alpha$	% rms[b]
U(III)–Fe(III)[c]	0.204–2.00	31	3.66 ± 0.15	7.5 ± 3.7	5.0
U(III)–V(IV)[d]	0.502–2.00	57	3.40 ± 0.11	1.6 ± 0.1	4.8

[a] Values of k_2 and α calculated by least-squares analysis of the data according to eq 2. Uncertainties are standard deviations, ionic strength 2.00, 20°, reaction measured at 350 nm. [b] Percent root-mean-square deviation: $100\{(1/n)\Sigma[(\text{obsd} - \text{calcd})^2/(\text{obsd})^2]\}^{1/2}$. [c] $[\text{U(III)}]_0 = 3.87 \times 10^{-4}\ M$, $[\text{Fe(III)}]_0 = 2.93 \times 10^{-4}\ M$. [d] $[\text{U(III)}]_0 = 2.41 \times 10^{-4}\ M$, $[\text{V(IV)}]_0 = 2.88 \times 10^{-4}\ M$.

Table III. Summary of the Values of k_3' and k_3'' for the U(III)–V(III) Reaction[a]

Temp, °C	$10^{-1}k_3'$,[b] M^{-1} sec^{-1}	$10^{-1}k_3'$,[c,d] M^{-1} sec^{-1}	$10^{-2}k_3''$,[b] sec^{-1}	$10^{-2}k_3''$,[c,e] sec^{-1}
15.1	4.47 ± 0.18	4.29	2.06 ± 0.01	2.06
20.0	5.42 ± 0.37	5.80	2.78 ± 0.02	2.77
25.0	8.47 ± 1.70	7.82	3.87 ± 0.09	3.70
28.0	8.92 ± 1.04	9.31	4.54 ± 0.01	4.39
33.0	12.6 ± 0.7	12.3	5.57 ± 0.05	5.78

[a] $[\text{U(III)}]_0 = 3.61 \times 10^{-3}\ M$, $[\text{V(III)}]_0 = 2.59 \times 10^{-3}\ M$, 20°, $\mu = 2.00$. [b] Calculated from eq 3 using nonlinear least-squares analysis, with percent rms values in the range 1.4–2.2; uncertainties are standard deviations. For each temperature, at least eight measurements of k_{obsd} were obtained for each of six acid concentrations in the range 0.2–2.0 M. [c] Calculated by nonlinear least-squares analysis using the Eyring equation.[11] [d] $\Delta H^* = 9.77 \pm 0.62$ kcal mol^{-1}, $\Delta S^* = -17.1 \pm 2.1$ cal mol^{-1} deg^{-1}, % rms = 1.3. [e] $\Delta H^* = 9.48 \pm 0.29$ kcal mol^{-1}, $\Delta S^* = -15.0 \pm 0.99$ cal mol^{-1} deg^{-1}, % rms = 0.2.

Table IV. Effect of Temperature on the Rate Constant for the Reactions of Fe(III) and V(IV) with U(III)

Reactant	Temp, °C	No. of determins	$10^{-5}k, M^{-1}$ sec^{-1}	
			Obsd	Calcd[c]
Fe(III)[a]	16.0	4	3.69 ± 0.59	3.75
	18.0	4	3.67 ± 0.29	3.84
	20.0	4	4.12 ± 0.19	3.94
	22.0	4	3.99 ± 0.11	4.03
	24.0	4	3.96 ± 0.61	4.13
	26.0	3	4.63 ± 0.14	4.23
	28.0	5	4.05 ± 0.20	4.33
	29.9	4	4.39 ± 0.47	4.43
V(IV)[b]	14.4	12	3.17 ± 0.15	3.12
	17.2	11	3.44 ± 0.20	3.53
	20.0	11	4.00 ± 0.11	3.93
	25.0	9	4.64 ± 0.18	4.75
	30.0	9	5.91 ± 0.33	5.72

[a] $[\text{U(III)}]_0 = 4.89 \times 10^{-4}\ M$, $[\text{Fe(III)}]_0 = 2.93 \times 10^{-4}\ M$, $[\text{H}^+] = 1.02\ M$, $\mu = 2.00$. [b] $[\text{U(III)}]_0 = 2.41 \times 10^{-4}\ M$, $[\text{V(IV)}]_0 = 2.88 \times 10^{-4}\ M$, $[\text{H}^+] = 1.00\ M$, $\mu = 2.00$. [c] Calculated according to the Eyring equation.[11] For the U(III)–Fe(III) reaction, $\Delta H^* = 1.53 \pm 0.89$ kcal mol^{-1}, $\Delta S^* = -27.7 \pm 3.0$ cal mol^{-1} deg^{-1}, and % rms = 5.7; for the U(III)–V(IV) reaction, $\Delta H^* = 6.04 \pm 0.43$ kcal mol^{-1}, $\Delta S^* = -12.3 \pm 1.5$ cal mol^{-1} deg^{-1}, and % rms = 2.4.

At constant ionic strength, the rate constant for the U(III)–V(III) reaction was found to decrease with increasing acid concentration, plots of $k_{\text{obsd}}^{\text{V(III)}}$ *vs.* $[\text{H}^+]^{-1}$ being straight lines (Figure 1) exhibiting a nonzero intercept. This observation suggests the functional relationship

$$k_{\text{obsd}}^{\text{V(III)}} = k_3' + k_3''[\text{H}^+]^{-1} \tag{3}$$

the values of k_3' and k_3'' determined in the temperature range 15–33° being summarized in Table III.

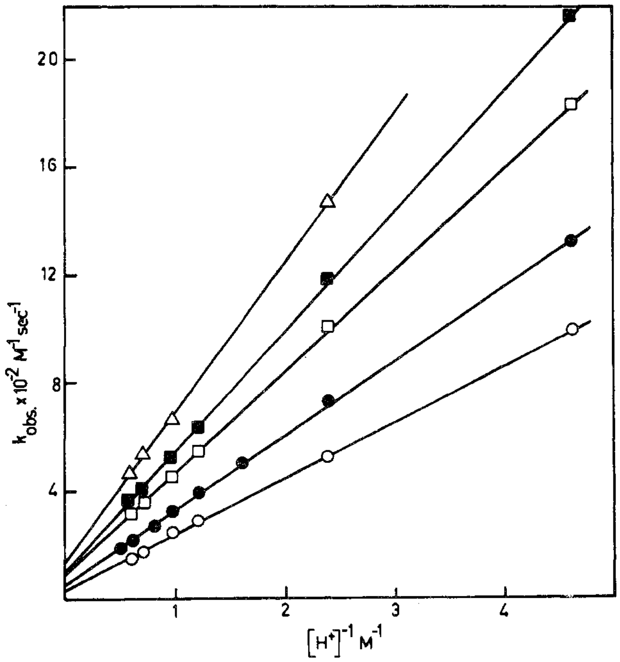

Figure 1. Acid dependency of the U(III)–V(III) reaction at various temperatures, plotted according to the equation $k_{\text{obsd}} = k_3' + k_3''[\text{H}^+]^{-1}$. $[\text{U(III)}]_0 = 3.61 \times 10^{-3}\ M$, $[\text{V(III)}]_0 = 2.59 \times 10^{-3}\ M$, $\mu = 2.00$. Temperature: ○, 15.1°; ●, 20.0°; □, 25.0°; ■, 28.0°; △, 33.0°.

Temperature Dependency. The temperature dependency of the three reactions was measured in the range 14–30°, the results obtained for the U(III)–Fe(III) and U(III)–V(IV) reactions being summarized in Table IV, which includes values of ΔH^* and ΔS^* determined by analysis of the data in terms of the usual Eyring equation.[11]

A similar analysis for the acid-independent path of the U(III)–V(III) reaction (k_3', eq 3) yielded values of 9.77 ± 0.62 kcal mol^{-1} and −17.1 ± 2.1 cal mol^{-1} deg^{-1} for ΔH^* and ΔS^*, respectively, while values of 9.48 ± 0.29 kcal mol^{-1} and −15.0 ± 0.99 cal mol^{-1} deg^{-1} were obtained for ΔH^* and ΔS^* of the acid-dependent path (k_3'', eq 3) of this reaction (Table III).

Ionic Strength Dependency. Examination of the ionic strength dependency of the reaction of U(III) with Fe(III) and V(IV) showed that in accordance with the Debye–Huckel equation

$$\log k_{\text{obsd}} = \log k_0 + [A\Delta Z^2 I^{1/2}/(1 + BdI^{1/2})] + cI \tag{4}$$

the rate of reaction increased with increasing ionic strength, the values of the constants k_0, d, and c found in this study being summarized in Table V.

Table V. Summary of the Debye–Hückel Equation Parameters Determined for the Reaction of U(III) with Fe(III) and V(IV)

Reacn	No. of determins	Ionic strength range, M	$10^{-3}k_0, M^{-1}$ sec^{-1}	10^8d, cm	c, M^{-1}	rms, %
U(III)–Fe(III)[a]	32	0.300–2.03	5.79 ± 0.11	14.3 ± 1.4	0.10 ± 0.03	4.6
U(III)–V(IV)[b]	64	0.210–2.01	4.47 ± 0.60	9.1 ± 0.8	0.13 ± 0.06	3.6

[a] $[\text{U(III)}]_0 = 3.87 \times 10^{-4}\ M$, $[\text{Fe(III)}]_0 = 2.93 \times 10^{-4}\ M$, $[\text{H}^+] = 0.102\ M$, 20°, $\Delta Z^2 = 18$, $A = 0.5070$, $B = 0.3282$. [b] $[\text{U(III)}]_0 = 2.41 \times 10^{-4}\ M$, $[\text{V(IV)}]_0 = 2.88 \times 10^{-4}\ M$, $[\text{H}^+] = 0.201\ M$, 20°, $\Delta Z^2 = 12$, $A = 0.5070$,[10] $B = 0.3282$.[10]

Table VI. Summary of the Effect of Ionic Strength on the U(III)–V(III) Reaction Rate[a]

Ionic strength	k_3',[b] M^{-1} sec^{-1}	k_3'',[b] sec^{-1}	k_3'',[c] sec^{-1}
0.565	68.2 ± 10.1	162 ± 3	161
0.780	40.4 ± 9.3	195 ± 3	190
1.04	44.5 ± 2.6	214 ± 1	216
1.54	48.9 ± 7.9	257 ± 2	252
2.04	46.3 ± 13.2	276 ± 2	278

[a] Conditions: $[\mathrm{U(III)}]_0 = 3.61 \times 10^{-3}$ *M*, $[\mathrm{V(III)}]_0 = 2.59 \times 10^{-3}$ *M*, 20.0°. [b] Calculated according to eq 3, by nonlinear least-squares analysis, with per cent rms values in the range 0.5–1.4. For each ionic strength, at least eight measurements of k_{obsd} were obtained for each of five acid concentrations in the range 0.1–0.5 *M*. Uncertainties are standard deviations. [c] Calculated according to eq 4, with $\Delta Z^2 = 18$, $A = 0.5070$,[10] $B = 0.3282$,[10] $k_0 = 2.85 \pm 1.71$, $d = 11.8 \pm 2.2$, and $c = (-0.6 \pm 4.0) \times 10^{-2}$.

The effect of ionic strength on the values of k_3' and k_3'' (eq 3) for the U(III)–V(III) reaction was also studied. As shown in Table VI, the values of the rate constants of the acid-independent path (k_3') are of insufficient accuracy to permit the application of the Debye–Hückel equation, while the values of k_3'' were found to be reproduced by eq 4 with $k_0 = 2.85 \pm 1.71$, $d = 11.8 \pm 2.2$, and $c = (-0.6 \pm 4.0) \times 10^{-2}$.

Discussion

All three reactions investigated are completely quantitative as judged from the appropriate oxidation potentials.[12] For the Fe(III) reaction, the subsequent oxidation of U(IV) by excess Fe(III) is too slow[13] to require consideration, while the present study has shown that a similar situation is applicable to the V(III)–U(III) reaction which may follow the reaction of V(IV) with U(III).

The rate constants of the reactions of U(III) with both Fe(III) and V(IV) were found to be essentially independent of acid concentration, the slight increase in the rate constants accompanying the progressive replacement of Na^+ by H^+ ions being adequately described by the Harned equation (eq 2), which required values of the Harned parameter commonly encountered in other similar systems.[14] These observations suggest that for both reactions the predominant activation process involves reaction between the hydrated ions.

The absence of any significant reaction path involving hydrolyzed species in the Fe(III)–U(III) reaction is quite striking, particularly in view of the prominence which these routes usually occupy in other reactions of the Fe(III) ion.[15] It is however noteworthy that the reaction between V(II) and Fe(III) has also been found[16] to be independent of acid concentration, and as the rate constant for this reaction exceeded the rates of the replacement of coordinated water for both V(II) and Fe(III), an outer-sphere electron transfer was postulated. A similar mechanism may be considered for the Fe(III)–U(III) reaction, but while the observed rate constant (3.5×10^5 M^{-1} sec^{-1}) greatly exceeds the rate of exchange of the water molecules coordinated to the Fe(III) ion,[17] the corresponding value for the U(III) ion is not known but might be expected to be of an order similar to that (10^8 sec^{-1}) found for the trivalent lanthanide ions.[18] Under these circumstances, no definite conclusion regarding the inner or outer-sphere nature of this reaction can be drawn, although as discussed below, the comparison of the rate parameters for these reactions does suggest that the Fe(III)–U(III) reaction proceeds by an outer-sphere mechanism.

For the V(III)–U(III) reaction, the results show that the rate law for the reaction is given by the expression

$$-\mathrm{d}[\mathrm{U(III)}]/\mathrm{d}t = [\mathrm{U(III)}][\mathrm{V(III)}]\{k_3' + k_3''[\mathrm{H}^+]^{-1}\} \qquad (5)$$

which clearly implies two activation processes, one of which involves only the hydrated ions while the other requires the loss of a proton prior to the formation of the activated complex (eq 6). A possible interpretation of the latter reaction path

$$\mathrm{U^{3+} + V^{3+} + H_2O \rightarrow [UOHV^{5+}]^* + H^+} \qquad (6)$$

is the sequence (7)–(9) in which the compositions but not

$$\mathrm{V^{3+} + H_2O \underset{}{\overset{K_H}{\rightleftarrows}} VOH^{2+} + H^+} \quad \text{(fast)} \qquad (7)$$

$$\mathrm{V^{3+} + U^{3+} \xrightarrow{k_8} [V{\cdot}U^{6+}]^*} \qquad (8)$$

$$\mathrm{VOH^{2+} + U^{3+} \xrightarrow{k_9} [V{\cdot}OH{\cdot}U^{5+}]^*} \qquad (9)$$

necessarily the structures of the activated complexes are indicated. For the above reactions it can be readily shown that $k_3' = k_8$ and $k_3'' = k_9K_H$ as $[H^+] >> K_H$. The alternative reaction sequence, in which the UOH^{2+} ion replaces the VOH^{2+} in eq 7–9, is also a possibility but is considered less likely since by virtue of its greater ionic radius,[19] the hydrolysis of the U^{3+} ion is expected to be less significant than that of the V^{3+} ion, although this effect can be compensated by a correspondingly greater rate constant for the reaction equivalent to eq 9 but involving the UOH^{2+} ion.

The value of K_H for V(III) has been estimated[20] as 2×10^{-3} M^{-1} at 20°, thus giving a value of 1.4×10^5 M^{-1} sec^{-1} for k_9 at this temperature. Comparison of this value with that obtained for k_8 (54.2 M^{-1} sec^{-1}) illustrates the efficiency of the OH group as a bridging ligand in this reaction. It has been suggested previously[3] that, in reactions involving the oxidation of U(III), the OH group stabilizes the transition state because the incipient U^{4+} ion is highly acidic and a rate-determining step involving the inner-sphere transfer of the OH group to the uranium ion would appear possible for reaction 9. Similarly, because the value of k_8 is very low compared to the rates of water exchange of the U(III) and V(III)[21] ions, an inner-sphere mechanism for this reaction path seems again likely.

The details of the mechanism of the V(IV)–U(III) reaction are more uncertain. The reductions of V(IV) by V(II)[21] and Cr(II)[22] both lead to the formation of binuclear intermediates, suggesting an inner-sphere mechanism. A similar mechanism, possibly involving an oxo bridge, has been proposed[23] for the reduction of V(IV) by Eu(II), although no obvious evidence for the presence of a binuclear intermediate was obtained. The present results on the U(III)–V(IV) reaction are analogous to those reported for the equivalent Eu(II) reaction, particularly with respect to the absence of any acid dependency and of any evidence for a binuclear intermediate. If the U(III)–V(IV) reaction were of the inner-sphere type, it would presumably occur by the replacement of the water molecule in the trans position to the vanadyl oxygen atom, which has a very high rate of exchange ($k = 10^9$ sec^{-1}), while the rate of exchange of the four water molecules in the equatorial plane of the V(IV) ion is too slow ($k \approx 10^3$ sec^{-1}) for these to be involved in the reaction.[24] Alternatively, the V(IV) oxygen atom may function as an oxo bridge in the transition complex. This role may be indicated by the high rate constant for this reaction compared to the Fe(III)–U(III) reaction, particularly when the differences in $\Delta G°$ for the two reactions and the relative slowness of reactions involving the destruction of metal–oxygen bonds are taken into consideration.

Table VII summarizes the values of the rate parameters and of the formal ionic entropy (S^*)[25] of the activated complexes determined for the reactions studied. Comparison of the parameters for the reactions of U^{3+} with Fe^{3+} and V^{3+}, both of which lead to an activated complex with a charge of 6+ shows that ΔS^* for the V^{3+} reaction is some 10 cal deg^{-1} mol^{-1} more positive than the value determined for the Fe^{3+} reaction. Further, when the differences in charge carried by the activated complex are taken into consideration, the value of S^*/Z (the

Table VII. Rate Constants and Rate Parameters of Some Reactions of U(III)

Activation process	$\Delta G°$, kcal mol^{-1}	k, M^{-1} sec^{-1}	ΔG^*, kcal mol^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	S^*,[c] cal deg^{-1} mol^{-1}	S^*/Z, cal deg^{-1} mol^{-1}
$V^{3+} + U^{3+} \rightarrow [\ ^{6+}]^*$[a]	−8.6	54.2 ± 3.7	14.8	9.77 ± 0.62	−17.1 ± 2.1	−118.3	−19.7
$V^{3+} + U^{3+} + H_2O \rightarrow [\ ^{5+}]^* + H^+$[a]	+11.0	278 ± 2	13.9	9.48 ± 0.29	−15.0 ± 1.0	−97.3	−19.5
$UO^{2+} + U^{3+} \rightarrow [\ ^{5+}]^*$[b]	−15.8	$(1.20 \pm 0.04) \times 10^4$	11.9	4.15 ± 0.07	−26.1 ± 0.3	−85.1	−17.0
$VO^{2+} + U^{3+} \rightarrow [\ ^{5+}]^*$[a]	−22.3	$(3.66 \pm 0.20) \times 10^5$	9.6	6.04 ± 0.43	−12.3 ± 1.5	−80.1	−16.0
$Fe^{3+} + U^{3+} \rightarrow [\ ^{6+}]^*$[a]	−31.8	$(3.92 \pm 0.20) \times 10^5$	9.7	1.53 ± 0.89	−27.7 ± 3.0	−139.9	−23.3

[a] $[H^+] = 1.00$, $\mu = 2.00$, 20°. [b] Data taken from ref 5; $[H^+] = 0.10\,M$, 25.1°. [c] The formal ionic entropy of the activated complexes defined in ref 25. $S°$ values obtained from ref 12, except $S°_{U(III)}$ which has been calculated as −42.1 cal deg^{-1} mol^{-1} by R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, 9, 922 (1970).

ionic entropy of the transition complex divided by the charge) for the Fe(III)–U(III) reaction is again found to be the most negative of any of the reactions of U(III) studied to date. This observation would provide further support for an outer-sphere electron-transfer mechanism for the Fe(III)–U(III) reaction, if the suggestion[26] that for similar reactions those proceeding by an inner-sphere mechanism have a more positive ΔS^* value is applicable to the present system.

The reaction of V(IV) with U(III), the acid-dependent path of the V(III)–U(III) reaction, and the reaction of U(III) with U(VI)[5] all result in a transition complex of charge 5+ and yield values of S^*/Z in the range 16.0–19.5 cal deg^{-1} mol^{-1} which are typical of those encountered for similar reactions of ions of the actinides[15a,25] and transition metals.[15c,d] It is interesting to note however, that the ΔS^* values for the acid-independent (k_3') and acid dependent (k_3'') reaction paths for the V(III)–U(III) reaction are so similar, as it is usually found[27] that for reactions of this type the ΔS^* value for the reaction path involving hydrolyzed species is more positive than the ΔS^* value for the acid-independent route. This observation presumably implies an unusual structure for the transition state formed in eq 9 and may be a reflection on the strongly acidic character of the U(IV) ion.[3]

Registry No. U^{3+}, 22578-81-0; Fe^{3+}, 20074-52-6; V^{3+}, 22541-77-1; VO^{2+}, 20644-97-7.

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