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Effect of Ionic Strength on the Activation Parameters of Fast Electron-Transfer Reactions

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The activation parameters of the V(II)–Fe(III) and U(III)–Fe(III) reactions were determined as a function of ionic strength in perchlorate media. Contrary to expectations, the values of ΔS^\ddagger for these reactions were found to be independent of ionic strength, the changes in rate constant being reflected exclusively in the values of ΔH^\ddagger . Plausible explanations for these observations are discussed.

Introduction

In a recent study, Hyde et al.¹ showed that a plot of ΔF^\ddagger vs. ΔF° for the acid-independent reaction paths for a series of electron-transfer reactions involving the Co(III) ion reached a limiting value of approximately 10 kcal mol⁻¹ for ΔF^\ddagger as ΔF° for the reactions became very negative. This observation has been further confirmed,² but inclusion in the above plot of the appropriate data of reactions involving ions other than Co(III) suggested that the limiting value of ΔF^\ddagger might be a common feature of electron-transfer reactions involving a variety of uncomplexed, hydrated metal ions.

In its most basic form, the Marcus equation³ may be written as

$$\Delta F^\ddagger = \Delta F^* + RT \ln [kT/zh] \quad (1)$$

where

$$\Delta F^* = \Delta F_c^\ddagger + m^2[\lambda_0 + \lambda_1] \quad (2)$$

and in which the symbolism of Reynolds and Lumry⁴ is used. It is generally noted⁴⁻⁶ that whereas $m \approx 1/2$ for electron-exchange reactions with $\Delta F^\circ = 0$, $m \rightarrow 0$ as ΔF° becomes highly negative. Consequently, the measured activation parameters of all electron-transfer reactions involving ions of high charge should contain contributions from Coulombic factors and these contributions should be particularly significant for reactions in which $\Delta F^\circ \ll 0$.

The validity of this proposal can in principle be tested experimentally by examining the ionic strength dependence of the activation parameters of ionic reactions. In particular, the value of ΔS_c^\ddagger , given by eq 3a and 3b,⁴ should be very

$$\Delta S_c^\ddagger = \frac{Z_1 Z_2 e^2 \exp(-\gamma)}{\epsilon^2 r_\ddagger} \left(\frac{\partial \epsilon}{\partial T} \right) + \frac{Z_1 Z_2 e^2 \gamma \exp(-\gamma)}{2\epsilon r_\ddagger} \left[\frac{1}{T} + \frac{\partial \ln \epsilon}{\partial T} \right] \quad (3a)$$

$$\gamma = r_\ddagger \left[\frac{8\pi N_0 I}{1000\epsilon kT} \right]^{1/2} \quad (3b)$$

sensitive to the prevailing ionic strength since calculations show ΔS_c^\ddagger to increase from -35 cal deg⁻¹ mol⁻¹ at $I = 0$ to -15 cal deg⁻¹ mol⁻¹ at $I = 1.0$ for a reaction involving two tripositive ions separated by a distance of 5 Å in the activated complex. This variation is very large and should be readily measurable even for reactions not exclusively controlled by Coulombic factors. The characteristics of reactions suitable for such a test are readily specified as (i) preferably having a large, negative ΔF° value and (ii) not involving a reaction path having either a positive or negative acid dependence, since the

presence of such a path would require a detailed knowledge of the ionic strength dependence of the corresponding protonation or hydrolysis equilibrium.

The reaction of Fe(III) with U(III) ($\Delta F^\circ = -31.8$ kcal mol⁻¹) and with V(II) ($\Delta F^\circ = -23.1$ kcal mol⁻¹) would appear to meet these requirements. Previous studies have shown both the U(III)⁷ and the V(II)⁸ reactions to be rapid and independent of acid concentration. The V(II) reaction is particularly appropriate since the observed rate constant of 1.8×10^4 M⁻¹ s⁻¹ considerably exceeds the rate of coordinated water exchange of both V(II)⁹ and Fe(III)¹⁰ and consequently the mechanism of this reaction appears to be unambiguously outer sphere. A comparison of the activation parameters of the V(II) reaction with those of the U(III) reaction, whose mechanism is uncertain,⁷ might thus be instructive.

Experimental Section

V(II) solutions were prepared by electrochemical reduction at a mercury cathode of standardized V(IV) solutions prepared as described previously.⁷ The preparation of all other reagents and the methods of acquisition and analysis of the data were similarly identical with those already reported.^{2,7}

Results

A previous examination⁸ has shown the V(II) reaction to be first order with respect to the concentrations of both V(II) and Fe(III), to be independent of acid concentration in the range 0.1–1.0 M, and to have a rate constant of $(1.8 \pm 0.1) \times 10^4$ M⁻¹ s⁻¹ at 25 °C and an ionic strength of 1.0 M. These observations were fully confirmed in this study, the rate constant being determined as $(2.07 \pm 0.07) \times 10^4$ M⁻¹ s⁻¹ at the above conditions. A study of the acid dependence at 20 °C showed the rate constant to decrease from $(1.76 \pm 0.02) \times 10^4$ M⁻¹ s⁻¹ at 0.1 M H⁺ to $(1.56 \pm 0.02) \times 10^4$ M⁻¹ s⁻¹ at 1.0 M H⁺, the ionic strength being maintained constant at 1.0 M using NaClO₄. The above variations are likely to have resulted from media effects and the experimental data were adequately described by the usual Harned equation¹¹ (eq 4)

$$k_{\text{obsd}} = k_4^\circ \exp \{ \alpha [H^+] \} \quad (4)$$

with $k_4^\circ = (1.64 \pm 0.12) \times 10^4$ M⁻¹ s⁻¹ and $\alpha = -0.09 \pm 0.14$, with a root-mean-square deviation¹² (45 runs) of 6.0%.¹³

As noted previously,^{14,15} the addition of anions such as Cl⁻ generally has a marked effect on the rates of an outer-sphere reaction, but a much smaller effect on an inner-sphere one. The chloride ion dependence of the rate constant of the V(II) and U(III) reactions was therefore determined and, as shown in Table I, found to be significant. The data were analyzed in terms of eq 5, yielding values of 14.1 and 4.1 for the ratios

$$k_{\text{obsd}} = k_5^\circ + k_5^{\text{Cl}^-} [\text{Cl}^-] \quad (5)$$

of $k_5^{\text{Cl}^-}/k_5^\circ$ for the V(II) and U(III) reactions, respectively.

The results obtained for the effect of ionic strength and temperature on the rate constants of the V(II)–Fe(III) and

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Table I. Effect of Cl⁻ on the Fe(III)-U(III) and Fe(III)-V(II) Reactions

[Cl ⁻], M	U(III)-Fe(III) ^a 10 ⁻⁵ k, M ⁻¹ s ⁻¹	V(II)-Fe(III) ^b 10 ⁻⁴ k, M ⁻¹ s ⁻¹
0	4.0 ± 0.2	1.73 ± 0.03
0.04	4.2 ± 0.4	2.95 ± 0.04
0.10	5.7 ± 0.5	4.63 ± 0.06
0.20	6.8 ± 0.5	7.1 ± 0.1
0.40	12 ± 1	11.3 ± 0.2

^a [U(III)] = 3.53 × 10⁻⁴ M, [Fe(III)] = 2.44 × 10⁻⁴ M, [H⁺] = 0.10 M, μ = 1.0 M, 20 °C. ^b [V(II)] = 2.88 × 10⁻⁴ M, [Fe(III)] = 1.96 × 10⁻⁴ M, [H⁺] = 0.10 M, μ = 1.0 M, 20 °C. ^c Rate constants are the average of at least eight determinations, the error being the standard deviation.

U(III)-Fe(III) reactions are summarized in Table II, each entry being the average and standard deviation of at least ten determinations. The rate constants obtained for the Fe(III)-U(III) reaction at 10 °C do not fit the otherwise consistent trend but are nevertheless included in the subsequent analysis since it is felt that this discontinuity is a reflection of the unavoidable errors associated with the determination of rate constants of very rapid reactions. The values of the rate constants at zero ionic strength were obtained by fitting the experimental data to the Debye-Hückel relationship (eq 6), the values of the constants *A* and *B* at the appropriate

$$\log k_{\text{obsd}} = \log k_0 + (A\Delta Z^2 I^{1/2}) / (1 + BdI^{1/2}) + CI \quad (6)$$

temperatures being obtained from tables prepared by Robinson and Stokes.¹⁶

The values of the activation parameters of the two reactions at the various ionic strengths (Table III) were obtained by a nonlinear least-squares fit of the experimental data to the Eyring expression¹⁷ (eq 7) in which the transmission coefficient

$$k_{\text{obsd}} = \kappa \left(\frac{k_B T}{h} \right) \exp(\Delta S^\ddagger / R) \exp(-\Delta H^\ddagger / RT) \quad (7)$$

κ was, as usual, assumed to be unity. The results obtained for the Fe(III)-U(III) reaction at ionic strength of 2.0 M are in good agreement with the values determined previously,⁵ although the individual rate constants were found to be higher in the present work. The analogous parameters for the V(II)-Fe(III) reaction have not been previously reported, and it may be noted that the slower reaction rate of the V(II) compared to that of the U(III) reaction is reflected largely in the higher value of ΔH^\ddagger for the former, the values of ΔS^\ddagger being nearly identical for the two reactions.

Examination of the ionic strength dependence of the activation parameters determined for the two reactions suggests that the decrease in the rate constant with decreasing ionic

strength is reflected in an increase in the enthalpy of activation (ΔH^\ddagger), the values of ΔS^\ddagger being independent of ionic strength. This effect is most obvious for the V(II)-Fe(III) reaction for which the most accurate data were obtained.

Discussion

As already noted,⁸ the V(II)-Fe(III) reaction appears to be unambiguously outer sphere, a proposal supported by the effect of Cl⁻ ion on the rate constant, the observed ratio of $k_5^{\text{Cl}^-} / k_5^\circ$ of 14.4 being similar to the ratios determined for other outer-sphere electron-transfer reactions.^{14,15} Since the values of the rate constants for the acid-independent reaction paths of the V(II)-V(III)¹⁸ and Fe(II)-Fe(III)¹⁹ exchange reactions at the relevant conditions have been determined, it is possible to apply the Marcus theory (eq 8) to the

$$k_{12} = [k_1 k_2 K_{12} f]^{1/2} \quad (8)$$

V(II)-Fe(III) reaction. This calculation yields a value of 1.0 × 10⁶ M⁻¹ s⁻¹ for the rate constant, which considerably exceeds the observed value of 2.7 × 10⁴ M⁻¹ s⁻¹.

The question regarding the inner- or outer-sphere nature of the U(III)-Fe(III) reaction cannot be answered with certainty at this time since the rate of exchange of water molecules coordinated to U(III) is not known. The effect of Cl⁻ ion on the reaction is larger than is usually observed for inner-sphere reactions²⁰ and the value of ΔS^\ddagger for the U(III) reaction is rather similar to that found for the V(II) reaction, suggesting that the U(III) reaction may also be outer sphere. The Marcus equation similarly cannot be applied rigorously to this reaction, since the value for the rate constant of the U(III)-U(IV) exchange has not been reported. However, by use of a value of 2-20 M⁻¹ s⁻¹ determined for the Pu(III)-Pu(IV) exchange,²¹ a rate constant in the range 7.0 × 10⁸-1.6 × 10⁹ M⁻¹ s⁻¹ can be calculated and compared to an experimental value of 7.2 × 10⁵ M⁻¹ s⁻¹.

From the foregoing, it appears that the Marcus theory only approximates the rate constants of the two reactions under consideration. This result is not unexpected since it has been frequently emphasized by Marcus,^{3,5} and equally frequently overlooked, that the cross-reaction equation is applicable only to reactions in which ΔF° is not too negative since only then will the assumption that $m \approx 1/2$, which is necessary for the deviation of the cross-reaction equation,⁴ be valid. Although the inclusion of the *f* term in eq 8 is expected to partially compensate for any deviation of *m* from a value of 0.5, it is of interest to note that the Marcus theory frequently overestimates rather than underestimates the values of the rate constants of reactions of very negative ΔF° ^{1,2} and that these reactions are, with the exception of the Co(III)-Cr(II) reaction, usually characterized (Table IV) by highly negative ΔS^\ddagger values and small ΔH^\ddagger values, thus indicating that the rates

Table II. Effect of Temperature and Ionic Strength on the Rate Constants of the U(III)-Fe(III) and V(II)-Fe(III) Reactions

Temp, °C	Ionic strength					
	0 ^c	0.1	0.5	1.0	1.5	2.0
	Fe(III)-U(III) ^a					
5.1	0.044 ± 0.001	0.78 ± 0.03	2.2 ± 0.1	3.4 ± 0.1	4.6 ± 0.1	5.7 ± 0.4
10.0	0.067 ± 0.007	0.80 ± 0.03	1.9 ± 0.1	3.0 ± 0.3	5.0 ± 0.2	5.6 ± 0.5
15.1	0.056 ± 0.005	0.99 ± 0.04	2.6 ± 0.2	4.2 ± 0.2	4.8 ± 0.3	6.8 ± 0.3
20.0	0.054 ± 0.001	1.05 ± 0.04	2.9 ± 0.1	4.6 ± 0.2	6.1 ± 0.2	7.1 ± 0.3
25.0	0.079 ± 0.004	1.25 ± 0.05	3.1 ± 0.1	5.0 ± 0.2	6.3 ± 0.2	8.0 ± 0.2
	Fe(III)-V(II) ^b					
9.5	0.064 ± 0.002	0.45 ± 0.01		1.34 ± 0.01		2.06 ± 0.04
15.1	0.086 ± 0.003	0.57 ± 0.01		1.54 ± 0.03		2.37 ± 0.05
20.0	0.115 ± 0.004	0.68 ± 0.01		1.79 ± 0.03		2.72 ± 0.05
25.1	0.124 ± 0.004	0.79 ± 0.01		2.07 ± 0.07		3.09 ± 0.08

^a [U(III)] = 3.53 × 10⁻⁴ M, [Fe(III)] = 3.91 × 10⁻⁴ M, [H⁺] = 0.1 M; units of *k* are 10⁻⁵ M⁻¹ s⁻¹. ^b [V(II)] = 2.88 × 10⁻⁴ M, [Fe(III)] = 1.96 × 10⁻⁴ M, [H⁺] = 0.1 M; units of *k* are 10⁻⁴ M⁻¹ s⁻¹. ^c Extrapolated values, obtained using the Debye-Hückel equation (eq 6).

Table III. Summary of Activation Parameters

Ionic strength	ΔH^\ddagger ,	ΔS^\ddagger ,	dev
	kcal mol ⁻¹	cal deg ⁻¹ mol ⁻¹	
Fe(III)-U(III)			
0	2.5 ± 0.9	-24 ± 3	15
0.10	3.1 ± 0.4	-25 ± 1	2.6
0.50	2.3 ± 0.3	-26 ± 1	1.5
1.00	2.4 ± 0.1	-24.3 ± 0.4	0.7
1.50	2.1 ± 0.6	-25 ± 2	6.0
2.00	2.3 ± 0.3	-24 ± 1	1.7
Fe(III)-V(II)			
0	6.5 ± 1.0	-22 ± 3	5.1
0.10	5.5 ± 0.2	-22.4 ± 0.6	0.7
1.00	4.0 ± 0.2	-25.5 ± 0.5	1.1
2.00	3.8 ± 0.1	-25.3 ± 0.3	0.4

Table IV. Summary of the Activation Parameters for Some Fast Electron-Transfer Reactions^a

Reaction	$-\Delta F^\circ$, ^b	ΔH^\ddagger ,	ΔS^\ddagger ,	Ref
	kcal mol ⁻¹	kcal mol ⁻¹	cal deg ⁻¹ mol ⁻¹	
U(VI)-U(III)	15.8	4.15 ± 0.07	-26.1 ± 0.4	22
Np(III)-Np(VI)	22.6	0.96 ± 0.11	-35.5 ± 0.4	22
V(II)-Fe(III)	23.1	3.80 ± 0.10	-25.3 ± 0.3	This work
Np(VII)-V(IV)	23.1	6.7 ± 0.9	-22 ± 3	23
Fe(II)-Co(III)	25.1	9.1	-23	24
Fe(III)-Cr(II)	26.7	5.2 ± 4.4	-28 ± 16	25
Fe(III)-Eu(II)	27.2	3.5	-29	26
Fe(III)-U(III)	31.8	2.3 ± 0.3	-24 ± 1	This work
Co(III)-Cr(II)	51.8	9.5 ± 0.4	-7.8 ± 1.5	1
Co(III)-U(III)	55.7	2.0 ± 0.3	-26 ± 1	2

^a Values quoted refer only to the acid-independent reaction path. ^b Calculated from the standard electrode potentials obtained from M. M. Latimer, "Oxidation Potentials", 2d ed, Prentiss-Hall, New York, N.Y., 1952, p 304.

of these reactions are largely entropy controlled.

These observations suggest the presence of rate-controlling factors which are not normally taken into consideration. For reactions of Co(III) ions, it is frequently suggested²⁷ that the $t_{2g}^6-t_{2g}^5e_g^1$ spin equilibrium is involved, but the observation² that the reactions of ions other than Co(III) show a limiting rate similar to those of Co(III) would seemingly eliminate this possibility. Factors which remain to be considered would thus include work terms required to overcome electrostatic repulsion between ions of like charge, diffusion control, the possibility of nuclear tunneling and a nonadiabatic mechanism involving electron tunneling.

As already stated (eq 3), the contribution of electrostatic factors toward the entropy of activation is, as shown in Figure 1, predicted to exhibit a significant ionic strength dependence, the numerical magnitude of which should be a function of the charges of the ions involved in the reaction and of the internuclear separation in the activated complex. It should be noted that although it can obviously not be expected that the calculated values of Figure 1 (and Figure 2) should fit the observed ones, a similar trend in the ionic strength dependence, particularly of the ΔS^\ddagger values, would have been expected. The apparent complete absence of any ionic strength dependence of ΔS^\ddagger for both reactions is thus quite surprising even when the approximate nature of eq 3 is taken into consideration.²⁸ The observed results seemingly imply that Coulombic factors do not make a significant contribution to ΔS_c^\ddagger , a conclusion which, if eq 3 is accepted as valid, would require the internuclear distances in the activated complex to be very large. Alternatively, the results may of course imply that although Coulombic factors are relevant, eq 3 fails completely to predict the influence of ionic strength, and it is perhaps significant that the calculated values of ΔS_c^\ddagger at $I = 0$ agree reasonably well with the experimentally determined values of ΔS^\ddagger . It may

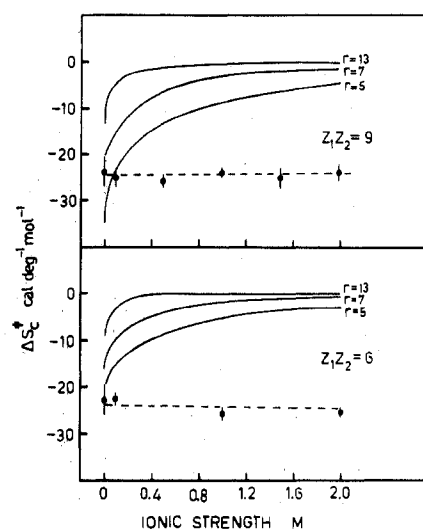


Figure 1. Comparison of the calculated (solid lines) and observed (broken lines) dependency of ΔS^\ddagger on the ionic strength, the upper figure showing the results of the Fe(III)-U(III) reaction ($Z_1Z_2 = 9$) and the lower figure the results of the V(II)-Fe(III) reaction ($Z_1Z_2 = 6$). For both figures the solid lines were calculated from eq 3a and 3b using the indicated values in angstroms of the internuclear distance in the activated complex.

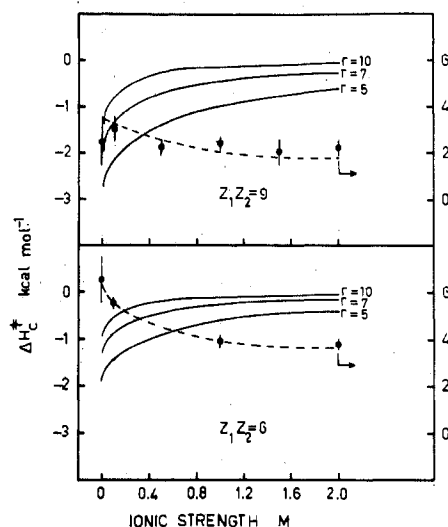


Figure 2. Comparison of the calculated (solid lines) and observed (broken lines) dependency of ΔH^\ddagger on the ionic strength. The upper figure shows the results obtained for the Fe(III)-U(III) reaction ($Z_1Z_2 = 9$) and the lower figure the results of the V(II)-Fe(III) reaction ($Z_1Z_2 = 6$). For both figures, the solid curves were calculated as explained in the text using the indicated values in angstroms of the internuclear distances in the activated complex.

also be noted that the use of a dielectric constant less than 78.5 in eq 3, corresponding to a partially or wholly saturated dielectric medium, would make the calculated values of ΔS_c^\ddagger more negative and the corresponding ionic strength dependence more pronounced than those shown in Figure 1 and those observed.

The effect of ionic strength on the observed enthalpy of activation (ΔH^\ddagger) is equally difficult to interpret with any confidence. As will be discussed further below, the observed values of ΔH^\ddagger are similar to the enthalpy of activation for the diffusion of simple ions in solution. However, the enthalpy changes resulting from Coulombic factors (ΔH_c^\ddagger) are negative in sign²⁹ and are calculated³⁰ to become less negative as the ionic strength increases (Figure 2). If therefore the observed enthalpy changes (ΔH^\ddagger) are simply the result of the Coulombic

contribution (ΔH_c^\ddagger) and another constant contribution, from, for example, a diffusion process, the observed values of ΔH^\ddagger are predicted to decrease with increasing ionic strength. In summary then, the effects of increasing ionic strength on the activation parameters of a reaction controlled by Coulombic factors are predicted to result in increasingly less negative values of both ΔS^\ddagger and ΔH^\ddagger , whereas experimentally the values of ΔS^\ddagger are found to be constant and those of ΔH^\ddagger to become less positive.

The possibility that the mechanism of the two reactions under study involves a combination of ionic diffusion and electron tunneling can also be considered, particularly since the enthalpies of activation of fast electron-transfer reactions (Table IV) are at least comparable to the activation energies for the diffusion of ions in liquids, normally quoted to be in the range 3–4 kcal mol⁻¹.³¹ On this basis, the values of ΔH^\ddagger could be attributed largely to a diffusion process, while the uniformly highly negative ΔS^\ddagger values could be interpreted as reflecting a transmission coefficient having a value much less than unity. A similar electron tunneling mechanism for a homonuclear electron-exchange reaction has been examined in detail elsewhere,³² but the application of these concepts to the heteronuclear reactions presently under consideration is exceedingly difficult, so that this interpretation cannot easily be verified or discounted.

In conclusion it may be noted again that the apparent absence of any ionic strength effect on the value of ΔS^\ddagger in the present reactions is rather perplexing and the results suggest that the mechanisms of these at first sight simple reactions may, in fact, be very much more complicated. Similar studies on the effects of ionic strength on the activation parameters of other reactions may be of value in the interpretation of the unusual effects observed in this study.

Registry No. U(III), 22578-81-0; Fe(III), 20074-52-6; V(II), 15121-26-3; Cl⁻, 16887-00-6.

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Kinetics of the Neptunium(IV)–Plutonium(VI) and the Neptunium(IV)–Neptunium(VI) Reactions in Aqueous Perchlorate Solutions¹

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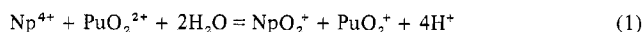
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The oxidation of Np(IV) by Pu(VI) was studied at four temperatures from 30 to 45 °C in 1 M (H,Li)ClO₄ solutions with [H⁺] between 0.04 and 0.6 M. Calculations were made to allow for the complications due to further reaction of Pu(V) and other products. The rate law for the predominant reaction is $-d[\text{Np(IV)}]/dt = k[\text{Np}^{4+}][\text{PuO}_2^{2+}]$, where k depends on [H⁺]: $k = a[\text{H}^+]^{-2} + b[\text{H}^+]^{-3}$ or, alternatively, $k^{-1} = (c[\text{H}^+]^{-2})^{-1} + (d[\text{H}^+]^{-3})^{-1}$. ΔH^\ddagger values associated with a , b , c , and d are 31.1 ± 0.9, 40.1 ± 2.0, 33.5 ± 0.8, and 37.3 ± 2.5 kcal/mol, respectively. The corresponding ΔS^\ddagger values are 30 ± 3, 53 ± 6, 39 ± 3, and 50 ± 8 cal/(mol deg). Sulfate was found to inhibit the reaction. The oxidation of Np(IV) by Np(VI) was studied at 25 and 35 °C in 1 M (H,Li)ClO₄ solutions with [H⁺] between 0.04 and 0.5 M. Except for the details of the hydrogen ion dependence the results were in agreement with the previous work of Hindman et al.^{4,5}

Introduction

The oxidation of Np(IV) by Pu(VI), reaction 1, is typical



of a class of actinide oxidation–reduction reactions. Kinetic

studies have been made on eight reactions of this type, among the ions of uranium, neptunium, plutonium, and americium. Four of the reactions, the disproportionations of UO₂²⁺, PuO₂²⁺, and AmO₂²⁺ and the NpO₂²⁺–AmO₂²⁺ reaction, occur in the direction opposite to that of (1). For the forward direction, the free energy values (ΔG°) range from –12.3 to +12.5