

# Electron Transfer between Neptunium(VI) and Substituted 1,10-Phenanthroline and 2,2'-Bipyridine Complexes of Iron(II)<sup>1</sup>

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The kinetics of electron transfer between Np(VI) and some complexes of iron(II) with phenanthroline-like ligands have been investigated by means of a stopped-flow spectrophotometric technique. The rate constants and the related activation parameters have been discussed in the light of the Marcus theory for outer-sphere electron transfers.

## Introduction

In a recent investigation,<sup>4</sup> the outer-sphere electron transfer between Np(VI) and a series of *N*-alkylphenothiazines was found to follow qualitatively the Marcus theory<sup>5</sup> (i.e., there was a linear dependence of activation energy on the overall free energy of reaction). However, there was also a discrepancy in the calculated and observed rate constants (and the related activation parameters). In order to extend these investigations, we report in this present paper the data concerning the outer-sphere electron transfer between Np(VI) and complexes of 1,10-phenanthroline and 2,2'-bipyridine with iron(II) (later referred to as FeL<sub>3</sub><sup>2+</sup>).

## Experimental Section

**Reagents.** The following iron(II) complexes were prepared and recrystallized as perchlorates according to the described procedure:<sup>6</sup> tris(1,10-phenanthroline)iron(II), Fe(phen)<sub>3</sub><sup>2+</sup>; tris(5-methyl-1,10-phenanthroline)iron(II), Fe(mphen)<sub>3</sub><sup>2+</sup>; tris(2,2'-bipyridine)iron(II), Fe(bpy)<sub>3</sub><sup>2+</sup>; tris(4,4'-dimethyl-2,2'-bipyridine)iron(II), Fe(dmbpy)<sub>3</sub><sup>2+</sup>. The preparation and standardization of the perchloric acid, lithium perchlorate, and neptunium(VI) perchlorate solutions have been previously described.<sup>7</sup>

**Equipment and Procedures.** The computer-interfaced stopped-flow instrumentation as well as the basic procedures and techniques have been detailed previously.<sup>8</sup> The observed OD-*t* data from individual kinetic experiments were treated by standard nonlinear least-squares techniques in terms of the first order rate expression

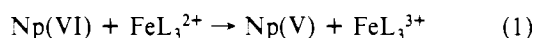
$$OD_t = (OD_0 - OD_\infty) \exp(-k_{\text{obsd}}t) + OD_\infty$$

where *k*<sub>obsd</sub>, OD<sub>0</sub>, and OD<sub>∞</sub> are adjustable parameters. Each kinetic experiment was monitored to at least 90% completion, 800-950 data points being collected during this period. A minimum of seven experimental determinations of *k*<sub>obsd</sub> was made for each set of reaction conditions.

The range of initial concentrations was chosen in order to ensure first-order conditions: [FeL<sub>3</sub><sup>2+</sup>]<sub>0</sub> = 5 × 10<sup>-6</sup>-10<sup>-5</sup> M; [Np(VI)]<sub>0</sub> = 5 × 10<sup>-5</sup>-1.5 × 10<sup>-4</sup> M. The kinetic runs were followed at the wavelength of maximum absorption of FeL<sub>3</sub><sup>2+</sup>.<sup>6</sup>

## Results

**Stoichiometry.** For the reaction 1, the values of the re-



duction potentials<sup>6,9-11</sup> (and the large excess of Np(VI)) ensure

that the reactions go to completion (in the kinetic experiments the final absorbance was virtually 0).

The stoichiometry of eq 1 was verified by measuring the remaining FeL<sub>3</sub><sup>2+</sup>, when operating with an excess of these complexes (within experimental error, Δ[FeL<sub>3</sub><sup>2+</sup>]/Δ[Np(VI)] = 1).

**Kinetics.** The reactions were found to be first order with respect to each of the reactants by independent variations of the concentration of each species. These observations are consistent with the empirical rate law of eq 2. The data

$$-d[\text{FeL}_3^{2+}]/dt = k[\text{FeL}_3^{2+}][\text{Np(VI)}] \quad (2)$$

collected in the tables are average values of the determined second-order parameters. The uncertainties are standard deviations from the mean.

In Table I are collected the data for the four iron(II) complexes at 0.010 M HClO<sub>4</sub> (no added salt) with the related activation parameters.

The variation of the rate constants with acidity has been investigated at μ = 1.0 M (LiClO<sub>4</sub>) for the reaction with Fe(phen)<sub>3</sub><sup>2+</sup> (Table II). The ionic strength effect on this same reaction has been measured at 0.010 M HClO<sub>4</sub> by addition of LiClO<sub>4</sub> (Table III).

## Discussion

The experimentally determined rate law defines the composition of the activated complex as containing one ion of each reactant, and the absence of any marked effect of acidity suggests that no protolytic preequilibria are involved in the investigated acidity range (a "medium" effect could account for the slight variations).

The dependence of the rate constants on the ionic strength can be analyzed in terms of the interactions of two doubly charged positive species. A plot of log *k* as a function of μ<sup>1/2</sup>/(1 + μ<sup>1/2</sup>) is satisfactorily linear with the expected slope of 4 (*k* at 0 ionic strength can be extrapolated to be (1.7 ± 0.2) × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> for Fe(phen)<sub>3</sub><sup>2+</sup>).

It is evident from Table I that the rate constants increase with a decrease in the reduction potential of the FeL<sub>3</sub><sup>3+/2+</sup> couple. Data for the reduction potentials in the present conditions of acidity and ionic strength are not known for all the FeL<sub>3</sub><sup>3+/2+</sup> couples. However, the data of Irvine et al.<sup>13</sup> for Fe(phen)<sub>3</sub><sup>3+/2+</sup> allow one to estimate *E*<sup>0'</sup> = 1.12<sub>5</sub> V for [HClO<sub>4</sub>] = 0.01 M, and values of *E*<sup>0'</sup> for the other couples may be extrapolated from known values with the assumption that acidity, ionic strength, and medium effects are the same on the different couples.<sup>6,9,12,13</sup> The value of *E*<sup>0'</sup> = 1.17<sub>5</sub> V for the Np(VI)/Np(V) couple can be extrapolated.<sup>11</sup>

A plot of Δ*G*<sup>‡</sup> as a function of Δ*G*<sup>0'</sup><sub>12</sub> is linear as predicted by Marcus theory,<sup>5</sup> and the slope of 0.37<sub>5</sub> is to be compared with the predicted value of 0.50. The importance of including the work term has been noted,<sup>14</sup> and it is of interest that a

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Table I. Rate Constants at Different Temperatures and Activation Parameters for Reactions of Np(VI) with FeL<sub>3</sub><sup>2+</sup> <sup>a</sup>

FeL <sub>3</sub> <sup>2+</sup>	E <sup>o</sup> , V <sup>b</sup>	10 <sup>-3</sup> k, M <sup>-1</sup> s <sup>-1</sup>				ΔH <sup>‡</sup> , kcal/mol	ΔS <sup>‡</sup> , cal/(deg mol)
		1.0 °C	12.0 °C	25.0 °C	35.0 °C		
Fe(phen) <sub>3</sub> <sup>2+</sup>	1.125 <sup>c,e,f</sup>	1.48 ± 0.01	2.58 ± 0.04	4.34 ± 0.03	5.51 ± 0.18	6.60 ± 0.28	-19.8 ± 0.95
Fe(bpy) <sub>3</sub> <sup>2+</sup>	1.10 <sup>d,f</sup>	1.62 ± 0.025	2.85 ± 0.02	4.82 ± 0.04	6.37 ± 0.30	6.52 ± 0.34	-19.8 ± 1.2
Fe(5mphen) <sub>3</sub> <sup>2+</sup>	1.085 <sup>c,e</sup>	3.07 ± 0.045	5.52 ± 0.26	7.99 ± 0.07	11.5 ± 0.2	5.90 ± 0.19	-20.9 ± 0.64
Fe(dmppy) <sub>3</sub> <sup>2+</sup>	0.93 <sup>d</sup>	29.9 ± 0.6	43.7 ± 1.9	68.8 ± 2.1	109.6 ± 19	5.09 ± 0.15	-19.3 ± 0.54

<sup>a</sup> [HClO<sub>4</sub>] = 0.01 M; μ = 0.01 M. <sup>b</sup> Extrapolated from the data in reference indicated by assuming the same effect of acidity and ionic strength on the different FeL<sub>3</sub><sup>3+/2+</sup> couples. <sup>c</sup> Reference 6. <sup>d</sup> Reference 9. <sup>e</sup> Reference 12. <sup>f</sup> Reference 13.

Table II. Effect of Acidity on the Reaction Rate of Fe(phen)<sub>3</sub><sup>2+</sup> with Np(VI)<sup>a</sup>

[HClO <sub>4</sub> ], M	10 <sup>-4</sup> k, M <sup>-1</sup> s <sup>-1</sup>	[HClO <sub>4</sub> ], M	10 <sup>-4</sup> k, M <sup>-1</sup> s <sup>-1</sup>
0.010	8.24 ± 0.16	1.00	6.07 ± 0.18
0.10	7.65 ± 0.34		

<sup>a</sup> 25.0 °C; μ = 1.0 M (LiClO<sub>4</sub>).

Table III. Ionic Strength Effect on the Reaction Rate of Fe(phen)<sub>3</sub><sup>2+</sup> with Np(VI)<sup>a</sup>

μ, M	10 <sup>-3</sup> k, M <sup>-1</sup> s <sup>-1</sup>	μ, M	10 <sup>-3</sup> k, M <sup>-1</sup> s <sup>-1</sup>
0.010	4.36 ± 0.04	0.050	11.4 ± 0.2
0.020	6.15 ± 0.05	0.100	15.4 ± 0.2
0.030	7.97 ± 0.18		

<sup>a</sup> [HClO<sub>4</sub>] = 0.010 M. Ionic strength was adjusted with LiClO<sub>4</sub> at 25.0 °C.

similar plot of ΔG<sup>‡</sup><sub>12</sub> + 0.5RT ln f vs. ΔG<sup>o</sup> gives a line of slope 0.43. These results suggest a more detailed analysis of the kinetic parameters with the aid of the eq 3–6 where ΔG<sup>\*\*</sup><sub>ij</sub> = ΔG<sup>\*</sup><sub>ij</sub> - w<sub>ij</sub>, Z is the collision frequency in solution, 10<sup>11</sup> M<sup>-1</sup> s<sup>-1</sup>, ΔG<sup>\*</sup><sub>11</sub> and ΔG<sup>\*</sup><sub>22</sub> are the activation energies for self electron exchange, and w<sub>ij</sub> is the Coulombic work term.

$$\Delta G^{**}_{12} = \lambda_{12}(1 + \Delta G^{\circ}_{12}/\lambda_{12})^2/4 \quad (3)$$

$$\lambda_{12} = 2(\Delta G^{**}_{11} + \Delta G^{**}_{22}) \quad (4)$$

$$\Delta G^{\circ}_{12} = \Delta G^{\circ}_{12} + w_{21} - w_{12} \quad (5)$$

$$k = Z \exp(-\Delta G^{\circ}_{12}/RT) \quad (6)$$

Since, in the present case, the ionic strength is in the Debye-Hückel region, it is possible to take into account the work terms w<sub>12</sub> and w<sub>21</sub> through expression<sup>15</sup> 7 where z<sub>1</sub> and z<sub>2</sub> are

$$w_{ij} = (4.22z_1z_2/r^*)10^{-0.143r^*\mu^{1/2}} \quad (7)$$

the charge of the reactants and r\* is the radius of the activated complex, taken as the sum of the radii of the reactants, 7 Å for FeL<sub>3</sub><sup>2+</sup><sup>16</sup> and 3.7 Å for Np(VI)<sup>17</sup>. For the calculation of λ<sub>12</sub>, the values of self-exchange rates at high ionic strength were adopted, thus assuming ΔG<sup>\*\*</sup> ≈ ΔG<sup>\*</sup>; for Fe(phen)<sub>3</sub><sup>3+/2+</sup>, the value ΔG<sup>\*</sup> = 6 kcal mol<sup>-1</sup>,<sup>18</sup> and for Np(VI)/Np(V), ΔG<sup>\*</sup> = 14.63 kcal/mol.<sup>19</sup> With these parameters, ΔG<sup>\*</sup><sub>12</sub> is calculated to be 8.4 kcal/mol (μ = 0.01 M), which is to be compared with the experimental value of 10.0 kcal/mol. The

discrepancy is slightly more than 1 order of magnitude (in terms of the rate constant); it is, however, to be noted that the difference could increase if the work terms in the self-exchange rates are taken into account or if smaller values of activation energy for the Fe(phen)<sub>3</sub><sup>3+/2+</sup> couple are used.<sup>20</sup> In the case of the Np(VI) reaction with N-alkylphenothiazines, the difference between calculated and experimental rate constants was of 2 orders of magnitude.<sup>4</sup>

Further details can be obtained from the comparison of the experimental and calculated activation parameters, through eq<sup>21</sup> 8 and 9 where α = ΔG<sup>o</sup><sub>12</sub>/4(ΔG<sup>\*</sup><sub>11</sub> + ΔG<sup>\*</sup><sub>22</sub>).

$$\Delta H^*_{12} = \left( \frac{\Delta H^*_{11}}{2} + \frac{\Delta H^*_{22}}{2} \right) (1 - 4\alpha^2) + \frac{\Delta H^{\circ}_{12}}{2} (1 + 2\alpha) \quad (8)$$

$$\Delta S^*_{12} = \left( \frac{\Delta S^*_{11}}{2} + \frac{\Delta S^*_{22}}{2} \right) (1 - 4\alpha^2) + \frac{\Delta S^{\circ}_{12}}{2} (1 + 2\alpha) \quad (9)$$

The Coulombic contribution to the calculated ΔH<sup>\*</sup><sub>12</sub> and ΔS<sup>\*</sup><sub>12</sub> can be taken into account; in fact the entropy change which accompanies the Coulombic free energy, as defined by eq 7, is (for aqueous solutions at 25.0 °C)<sup>15</sup> given by eq 10.

$$\Delta S^*_{\text{coul}} = -z_1z_210^{-0.143r^*\mu^{1/2}} \left( \frac{19.3}{r^*} + 0.83\mu^{1/2} \right) \quad (10)$$

Then, with the assumption of the thermodynamic parameters for Fe(phen)<sub>3</sub><sup>3+/2+</sup> of ΔH<sup>o</sup> = -32 kcal mol<sup>-1</sup>, ΔS<sup>o</sup> = -21 cal deg<sup>-1</sup> mol<sup>-1</sup>, ΔH<sup>\*</sup><sub>11</sub> = 3 kcal mol<sup>-1</sup>, and ΔS<sup>\*</sup><sub>11</sub> = -10 cal deg<sup>-1</sup> mol<sup>-1</sup>,<sup>13,18</sup> and for Np(VI)/Np(V) of ΔH<sup>o</sup> = -29 kcal mol<sup>-1</sup>, ΔS<sup>o</sup> = -7 cal deg<sup>-1</sup> mol<sup>-1</sup>, ΔH<sup>\*</sup><sub>22</sub> = 7.75 kcal mol<sup>-1</sup>, and ΔS<sup>\*</sup><sub>22</sub> = -23 cal deg<sup>-1</sup> mol<sup>-1</sup>,<sup>10,19</sup> the values derived are ΔH<sup>\*</sup><sub>12</sub>(calcd) = 6.4 kcal mol<sup>-1</sup> (to be compared with the experimental 6.6 kcal mol<sup>-1</sup>) and ΔS<sup>\*</sup><sub>12</sub>(calcd) = -15 cal deg<sup>-1</sup> mol<sup>-1</sup> (experimental, -19.8 cal deg<sup>-1</sup> mol<sup>-1</sup>). In the present case, a good agreement is observed for the enthalpic term while a discrepancy is present in the entropic term: this last observation supports the idea previously advanced of a nonadiabaticity of the electron-transfer reactions involving actinide ions.<sup>4,22</sup>

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**Registry No.** NpO<sub>2</sub><sup>2+</sup>, 18973-22-3; Fe(phen)<sub>3</sub><sup>2+</sup>, 14708-99-7; Fe(bpy)<sub>3</sub><sup>2+</sup>, 15025-74-8; Fe(5mphen)<sub>3</sub><sup>2+</sup>, 15226-32-1; Fe(dmppy)<sub>3</sub><sup>2+</sup>, 15187-18-5.

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