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Some Quantum Chemical Aspects on Outer-Sphere Electron-Transfer Reactions: The U(V)/Fe(III)−U(VI)/Fe(II) System

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The activation energy and rate constant of U(V)-Fe(III) to U(VI)−Fe(II) outer-sphere electron-transfer reaction was studied using Marcus model. Experimental values were used for Gibbs energy change of the reaction, and energy surfaces were calculated by quantum chemical methods. The calculated rate constant was in reasonable accord with experimental value.

In a previous publication we have studied the rate and mechanism of the outer-sphere "self" electron exchange between actinyl(V) and actinyl(VI) aqua ions and the inner-sphere mechanism between the corresponding hydroxide, fluoride and carbonate complexes.[1,2] The outer-sphere pathway was studied using both the Marcus model and a simplified quantum chemical model, whereas the inner-sphere pathway was studied using quantum chemical models involving bridging ligands between the actinyl(V) and (VI) ions. The model calculations for the outer-sphere pathways were compared with experimental data using the Marcus cross-relations.[3] In the present study we will expand the previous work by a direct calculation of the rate constant and activation parameters for the following outer-sphere oxidation of UO_2^+ by Fe^{3+}, cf. eq 1, for which the experimental rate constant is 2.5×10^5 M^{-1} s^{-1} at 25 °C in a medium with $[H^+] = 1$ M, and an ionic strength of 2.00 M.[4]

$$UO_2^{\ +}(aq) + Fe^{3+}(aq) \rightarrow UO_2^{\ 2+}(aq) + Fe^{2+}(aq) \qquad (1)$$

Following standard Marcus theory, the electron transfer occurs where the total energy of the reactants coincides with the total energy of the products along the reaction coordinate, as shown in Figure 1. The chemical model used to obtain the potential energy functions in Figure 1 were the complexes $Fe(OH_2)_6^{3+/2+}$ and $UO_2(OH_2)_5^{+/2+}$, with a saturated first hydration shell; the remaining solvent effects, including the second hydration sphere, were described using the CPCM model.[5] All the energy calculations were performed using the MOLCAS 6 packages of programs.[6]

The electron exchange can formally be described using three consecutive reaction steps: formation of a precursor complex between the reactants, followed by electron transfer between U(V) and Fe(III) and finally formation of products.

The rate constant for the total reaction is[7,8]

$$k_{obs} = K_A \kappa_{el} \nu_n e^{-\Delta G^{\ddagger}/RT} \qquad (2)$$

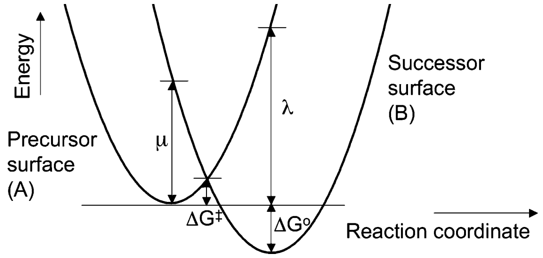

Figure 1. Transition state structure at the intersection of two parabolas U(V)−Fe(III) (A, precursor) and U(VI)−Fe(II) (B, successor).

where K_A is the equilibrium constant for the formation of an outer-sphere ion pair between the reactants, κ_{el} is the electronic transmission coefficient, ν_n is the nuclear frequency factor and $\Delta G^{\ddagger}$ is the activation free energy.

The electron transmission coefficient κ_{el} is given by

$$\kappa_{el} = \frac{2(1 - e^{-\nu_{el}/2\nu_n})}{2 - e^{-\nu_{el}/2\nu_n}} \qquad (3)$$

where the electronic and nuclear frequency factor, ν_{el} and ν_n, are

$$\nu_{el} = \frac{2\pi {H_{12}}^2}{h}\left(\frac{1}{4\pi\lambda RT}\right)^{1/2} \qquad (4)$$

$$\nu_n = \left[\frac{\sum_i {\nu_i}^2 E_i}{\sum_i E_i}\right]^{1/2} \qquad (5)$$

H_{12} is the electron-transfer coupling element; λ is the reorganization energy. E_i and ν_i are the energy change and frequency of the vibrational modes, i, which bring the reactants to the transition state.

The Gibbs energy surfaces of the precursor and successor complexes in the Marcus theory are assumed to be quadratic functions of the reaction coordinate, symmetric around the point where the electron transfer takes place in self-exchange reac-

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tions, but not in the general case. The two parabolas in Figure 1 describe the systems U(V)−Fe(III) (A) and U(VI)−Fe(II) (B), respectively. The origin is the minimum of parabola A, and the reaction coordinate, q, is 1.0 at the minimum of parabola B. Using these definitions, one can determine the parabolas from the reorganization energies λ and μ and the Gibbs energy change, $\Delta G°$, for the electron-transfer reaction. The reorganization energies were obtained from the total energy curves, adding the nonequilibrium solvation correction obtained from the Marcus equation[3]

$$\lambda^{\mathrm{sol}} = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R_{12}}\right)\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \tag{6}$$

where a_1 and a_2 are the radii of the cavities around the metal centers including their first hydration shells, R_{12} is the distance between them, and ϵ_0 and ϵ_∞ are the static and dynamic dielectric constants of the solvent. Because λ^{sol} refers to the Gibbs energy, the two parabolas correspond to the Gibbs energies of the $UO_2(OH_2)_5{}^{+}$−$Fe(OH_2)_6{}^{3+}$ (A) and $UO_2(OH_2)_5{}^{2+}$−$Fe(OH_2)_6{}^{2+}$ (B) systems, respectively. The electronic energy of the (A) and (B) systems was calculated using the geometry of the optimized $UO_2(OH_2)_5{}^{2+/+}$ and $Fe(OH_2)_6{}^{3+/2+}$ structures taken from ref 9; they are gas-phase unrestricted MP2 (UMP2) optimized geometries without symmetry constraints. The reaction coordinate and the activation energy were calculated using the reaction coordinate zero for the precursor and one for the successor at their equilibrium geometry. From the Marcus theory, where it is assumed that the parabolas (A) and (B) systems (Figure 1) have the same curvature, we have $\lambda = \mu + \Delta G°$ and $\Delta G^\ddagger = (\lambda - \Delta G°)^2/4\lambda$. It is only marginally more complicated to calculate the activation energy without the assumption of equal curvatures of the two potential functions.

The electronic transition coefficient κ_{el} is related to the adiabatic character of the electron-transfer process; a process is considered adiabatic if the nuclear motion is slow on the time scale of changes in the electronic wave function. Hence the ratio $\nu_{\mathrm{el}}/\nu_{\mathrm{n}}$ is large and the electronic transmission coefficient, κ_{el}, is close to 1. The rate of the electron transfer is determined by the probability of arriving at the “proper” geometric configuration (transition state) for precursor and successor; the rate is independent of the size of the electronic coupling element as long as the coupling is large enough for the process to be adiabatic.

For a nonadiabatic electron transfer, the electronic coupling is so small that the system needs multiple passes through the “proper” geometry for the electron transfer to take place; hence, the ratio $\nu_{\mathrm{el}}/\nu_{\mathrm{n}}$ is small and the electronic transmission coefficient κ_{el} is approximately equal to $\nu_{\mathrm{el}}/\nu_{\mathrm{n}}$. The total electron-transfer rate then becomes independent of ν_{n} but depends quadratically on the electronic coupling element H_{12}.

The nuclear frequency factor is known to be insensitive to the distance at which the electron transfer occurs between the reactants. In contrast to this the electronic coupling element, and consequently also the electronic frequency factor, decreases exponentially with an increasing distance between the species. Thus the outer-sphere mechanism is expected to be less adiabatic than the inner-sphere mechanism.

The curvatures for the two parabolas are virtually identical (the ratio between the coefficient for the quadratic term in the two parabolas is 0.99998), and consequently, the original Marcus assumption of identical parabolas can be used to obtain the energy barrier $\Delta G^\ddagger$. However, the crossing point, that is, the transition state, depends critically on $\Delta G°$. The experimental determination of $\Delta G°$ is straightforward, but this is not the case for the quantum chemical calculation, where appreciable errors are expected.[9] We have therefore used the experimental value −65 kJ/mol to locate the transition state. In ref 9 the Gibbs energy change of reaction obtained at the minimal CASPT2 level was −67 kJ/mol, in excellent agreement with experiment, but the energy obtained at the more sophisticated spin-restricted CCSD(T) level was −36 kJ/mol, a value that differs appreciably from the observed one. The value of the reaction coordinate at the transition state, obtained from the parabolas in Figure 1, is 0.25, and the barrier for the reaction U(V) + Fe(III) → U(VI) + Fe(II) using this value for the reaction coordinate is 8.0 kJ/mol.

The rate depends on the barrier and on the coupling matrix element H_{12}. To obtain an estimate of the latter, we used a simplified model of the Fe−U complex, with only one water molecule in the first hydration shell, linked by two hydrogen bonded water molecules in the second coordination sphere; the rest of the first and the second coordination spheres, as well as the solvent, were described using the CPCM model.[5] This model turned out to be quite successful in the previous self-exchange studies.[1,2] The interaction energy between the two states describing U(VI)−Fe(II) and U(V)−Fe(III) is twice the coupling element H_{12} and can be found from a (nonorthogonal) 2 × 2 CI at the point where the parabolas cross. This point can be calculated using gradient techniques, with the condition that the energy difference between the precursor and the successor should be zero at the transition state. However, this is a difficult procedure because a reasonable geometry at the transition state requires a good theoretical value for $\Delta G°$. In the present case we have instead used a simpler procedure to find the geometry of the transition state. We have optimized the geometry of the precursor and successor complexes separately, and by assuming that all coordinates vary linearly with the reaction coordinate, it is simple to estimate the geometry of the transition state with linear interpolation using the value of the reaction coordinate at the crossing of the parabolas in Figure 1.

Using the estimated geometry for the transition state, we obtained the coupling matrix element from a 2 × 2 nonorthogonal CI in the gas phase using minimal CASSCF without spin−orbit coupling, in which the two diagonal matrix elements were put equal to zero to ensure a proper estimate of the interaction energy. The calculations were done using the big basis sets, including the very diffuse functions with an exponent of 0.005 in the symmetries s, p, d and f on uranium. The value obtained for H_{12} was 0.224 kJ/mol. Using K_A (eq 2) = 0.033 calculated from the Fuoss−Eigen equation,[10] we obtained rates for the reactions U(V) + Fe(III) → U(VI) + Fe(II) of 1.6×10^6 s^{-1}. The experimental value, determined by Newton et al.,[11] is 2.5×10^5 s^{-1} and is in reasonable agreement with the calculated one.

H_{12} is different for different states.[1] Because the spin−orbit interaction will mix different states, this could affect the effective $(H_{12})^2$. The contribution of the different LS-coupled states to the effective $(H_{12})^2$ will essentially be the $(H_{12})^2$ for that state multiplied by the corresponding weight (see ref 1). The spin−orbit effect is small for the iron complexes and the weight of the leading configuration is 0.9 in the U(V) complex. The effect of the spin−orbit coupling on the effective $(H_{12})^2$ is thus not expected to be important.

Due to the long distance between uranium and iron at the transition state, 8.1 Å, H_{12} is sensitive to the diffuse functions in the basis set. If the outermost basis functions of s, p, d and f-type (with exponents 0.005) are deleted from the basis set of uranium, H_{12} decreases by a factor of 10, and the rate by a factor of 100, whereas the energy is hardly affected at all. There is hitherto little experience on how to choose basis sets for calculating properties such as coupling matrix elements, and this needs further investigations. However, the “best” value for the coupling element is clearly obtained with the largest basis set.

Rotzinger used another procedure to calculate H_{12} for the M(II)/M(III) redox couples, with M = V, Ru and Fe, and the M(III)/M/(IV) redox couples for V and Ru.[12] Using a $[M(OH_2)_6]_2^{5+}$ cluster, he estimated H_{12} from the orbital energies, assuming the splitting of the d-orbitals at different M−M distances to reflect the splitting of the states. Rotzinger used a rather limited basis set, and the M−M distance was estimated by maximizing H_{12} vs R_{12} or, in the case of Fe(II)/Fe(III), by comparing theoretical and experimental rates.

The procedure used by Rotzinger involves several approximations and assumptions that are not justified and appears to us, therefore, as somewhat uncertain.

From the results presented in this study we conclude that reasonable electron-transfer rates can be obtained for outer-sphere electron-transfer reactions, provided that accurate values for $\Delta G°$ can be obtained. However, the results depend heavily on the diffuse parts of the basis sets, and this problem needs further investigations.

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