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Reduction of Uranyl(VI) by Iron(II) in Solutions: An Ab Initio Study

Timofei Privalov,*,† Bernd Schimmelpfennig,‡ Ulf Wahlgren,† and Ingmar Grenthe§

AlbaNova University Center, Institute of Physics, Stockholm University, Stockholm, Sweden, Laboratory of Theoretical Chemistry, The Royal Institute of Technology, Stockholm, Sweden, and Inorganic Chemistry, Department of Chemistry, The Royal Institute of Technology, Stockholm, Sweden

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The reduction of uranyl U(VI) by Fe(II) in solution has been studied by quantum chemical methods, where the pH dependence of the reaction was simulated by using different numbers of coordinated hydroxide ions. The geometries for the binuclear U(VI)−Fe(II) precursor and the U(V)−Fe(III) successor complexes were optimized at the SCF level, and the reaction energies were calculated at the correlated level using the MP2 method. Effective core potentials were used throughout. Solvent effects were obtained by the polarizable continuum model. The accuracy of the solvent model was investigated for the binuclear complexes with two hydroxide bridges, and the accuracy of the MP2 method was assessed by comparing with CASPT2 and CCSD(T) calculations on the smallest complexes. The general trends in geometry and reaction energy are consistent with experiment.

1. Introduction

The rapid development of both theory and software makes it possible to make detailed studies of the structure, thermodynamics, and reaction mechanisms of actinide complexes in gas phase and solution. Previous studies from our group and others indicate both the problems encountered and the level of detail in the chemical understanding that may be attained.[1−8] Chemical structures and the relative energy of different isomers may be predicted with high accuracy,[1,2] and it seems possible to obtain ab initio reaction energies for gas phase reactions that are in good agreement with experimental observations[3], even though the latter are often hampered by large errors. We have previously also studied ligand exchange mechanisms[4,5] using both experimental and theory-based activation enthalpies as a tool to identify the pathway of lowest activation energy. The present study is focused on redox reactions, an issue also addressed by us in previous studies.[6,7] These reactions are not only of fundamental interest; to understand them is essential when describing how chemical reactions of actinides in surface and groundwater systems affect their mobility in the biosphere and the function of engineered systems for the containment of radioactive waste in underground repositories. In this context, it is important to notice that spent nuclear fuel is predominantly a matrix of UO_2 in which fission products and higher actinides are dispersed. In contact with water, the fuel matrix will dissolve with a resulting release of the different radionuclides; the dissolution is a result of oxidation by radiolysis products or by intruding oxygen. In most technical systems, the nuclear waste is contained in canisters of iron/steel, which provide a large reduction capacity to the system and thus may prevent the transformation of sparingly soluble UO_2 to more soluble U(VI) species. Corrosion and other redox reactions involving iron species are therefore of key importance for the safe performance of many nuclear waste installations; as these have to function over very long time periods, it is highly desirable to base predictions of their future environmental effects on molecular understanding of the chemical reactions taking place. Stumm and Sulzberger[8] have discussed the coupling between various geochemical processes and the Fe(II)−Fe(III) redox cycle, reactions often accelerated by surface sorption of reactants and products. Surface-catalyzed reduction of U(VI) by Fe(II) has been studied by Van Cappellen et al.[9] The catalytic action of Fe(III) in the U(IV)−U(VI) electron exchange in solution was studied by Tomiyasu and Fukutomi.[10] These reactions involve two one electron steps, where U(V) is present as an intermediate at very low concentration. The surface-mediated reactions involve the formation of surface complexes between iron and uranium; the electron exchange reactions in solution also involve specific inner sphere interactions between uranium and iron. It is well-known from experiments that Fe(II) does not reduce U(VI) to U(IV) at low pH, while the reaction is thermodynamically favored at high pH as a result of the formation of strong hydroxide complexes of U(IV) and Fe(III). These are in general polynuclear, containing hydroxide or oxide bridges known to be very efficient pathways for electron transfer between metal ions.[11−13]

In this paper, we will investigate the thermodynamics of the reduction of U(VI) to U(V) by Fe(II) using ab initio methods. The experimental data referred to above indicate that an analysis based on the thermodynamics of the precursor and successor complexes formed before and after the electron transfer between uranium and iron is a suitable first step in the analysis of the electron transfer mechanism. It is known from experiment that this rate is highly variable;[9,10,14] however, the detailed mechanisms of reactions involving actinides are very incompletely known. The overall stoichiometry of the reduction of U(VI) to U(V) by Fe(II) in water solution at different pH and low metal concentrations may be written as

$$UO_2(OH)_p^{\,2-p} + Fe(OH)_q^{\,2-q} \rightarrow UO_2(OH)_r^{\,1-r} + Fe(OH)_s^{\,3-s} \tag{1}$$

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* To whom correspondence should be addressed. Institute of Automation and Electrometry, Siberian Branch, Russian Academy of Science, 6300090, Novosibirsk, Russia. From January 1, 2003: Organic Chemistry, Department of Chemistry, The Royal Institute of Technology, Stockholm, Sweden.

† Stockholm University.

‡ Laboratory of Theoretical Chemistry, The Royal Institute of Technology.

§ Department of Chemistry, The Royal Institute of Technology.

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where $p + q = r + s = n = 4, 5, 6$; the larger values of n are found at higher pH. At low pH, the first coordination shell consists mainly of water molecules that are replaced by hydroxide ions at higher pH. Equation 1 describes the stoichiometry of the redox reaction; the mechanism is more complex (and largely unknown) and involves several steps; we will explore an inner sphere pathway involving two hydroxide bridges between iron(II) and uranium(VI) in the precursor complex and between iron(III) and uranium(V) in the successor complex. The latter is subsequently reduced to U(IV) and/or disproportionates according to

$$2\mathrm{U(V)} \rightarrow \mathrm{U(IV)} + \mathrm{U(VI)} \qquad (2)$$

The overall reduction of U(VI) to U(IV) by Fe(II) in solution is slow, presumably due to a slow reduction of U(V) to U(IV).

The reduction of U(VI) to U(V) as shown in eq 3 involves the transfer of only one electron and minor rearrangements in the coordination spheres between U(VI) and U(V); we expect the reaction to be faster than the following reduction to U(IV). We will use different quantum chemical methods to determine the geometry and relative energy of different U(VI)−Fe(II) precursor and U(V)−Fe(III) successor complexes and the change in total energy for reactions of the type

$$[\mathrm{U(VI)O_2(OH)}_p\mathrm{Fe(II)}]^{4-p} \rightarrow [\mathrm{U(V)O_2(OH)}_p\mathrm{Fe(III)}]^{4-p} \qquad (3)$$

where U(VI) on the left-hand side of reaction 3 is a closed shell system while Fe(II) has four open d shells; on the right-hand side of the reaction, there is one open f shell on U(V) and five open d shells on Fe(III). In the model to be described, we assume that the reduction of U(VI) and the simultaneous oxidation of Fe(II) take place through electron transfer from the iron d shell into the empty 5f shell of uranium, via bridging hydroxide ligands.

The computation problem is very large and will require a number of approximations; the rationale for these will be discussed below. A general problem with actinides is the need to take the strong relativistic effects, the semicore character of the 6s and 6p shells and the active role played by the 5f orbitals, into account. The large number of electrons, which must be treated explicitly in the calculations, restricts the number of atoms that can be included in the model. Another problem, specific for the present study, are the open d shells on Fe(II) and Fe(III). The large number of both doubly occupied orbitals and unpaired electrons makes the calculations technically demanding, and in particular, the correlation treatment becomes cumbersome. The net effect is that it is exceedingly difficult to use a model with a complete first coordination shell.

Density functional theory (DFT)-based methods should in principle be technically well-suited for these systems. However, DFT calculations are very difficult in practice due to the electronic configurations of the precursor (four open d shells on iron(II)) and the successor (five open d shells on iron(II) and one open f shell on uranium(V)). Furthermore, as shown in ref 7, even the gradient-corrected DFT hybrid methods fail to describe the reduction of the uranyl(VI) ions properly.

2.Theory

2.1. Computational Model. Two factors have a strong influence on the choice of strategy for obtaining reliable energies and geometries; one is the problem of obtaining high quality correlation estimates and the other is the description of the solvent.

Correlation would ideally be obtained by some high level method such as CASPT2 or CCSD(T). The latter is precluded because of the size of the system. CASPT2 is in principle feasible, but ideally, the multireference CASPT2 calculations should be carried out with a large valence reference space, including excitations from the oxygen 2s, the uranium 6s and 6p, and, if applicable, 5f and iron 3d orbitals. However, the practical limit is around 16 electrons in 16 orbitals, a limit that is quickly reached, and a careful selection procedure must therefore be used to determine an optimal active space. The alternative is the simple, but for systems with a variable number of open shells, sometimes unreliable MP2 method. Our approach has been to assess its reliability by comparison with CASPT2 results on the smallest systems. This approach will be discussed further in the Results section.

The solvent effects were described using the polarizable continuum model (PCM)[15] as implemented in the Molcas[16] program package. We have considered complexes with 4−6 hydroxide ions in the precursor and successor complexes. Because of computational restrictions, we have not been able to saturate the first hydration shell with water molecules, as desirable when using the PCM model. Its accuracy when used without explicit coordinated water molecules was investigated by adding one or two additional water molecules in the calculations involving four hydroxides where the coordinative unsaturation is largest. For computational reasons, we also had to make symmetry restrictions on the geometry of the complexes.

The structures of the different complexes were optimized in the gas phase at the single reference SCF level using gradient technique with symmetry constraints. Energies in the gas phase and in the water solvent were obtained using the SCF optimized gas phase geometries. Although SCF optimized geometries in our experience are good for ionic actinide complexes, the internal uranyl bond is too short by approximately 0.06 Å at the SCF level.[7] However, this correlation effect on the bond length is similar when the oxidation state changes.[7] Furthermore, the SCF geometries give correct results for the reactions energies at the correlated level for gas phase reactions.[3]

2.2. Basis Sets. The program package Molcas5[16] was used throughout. Effective core potentials (ECP) of the Stuttgart type[17] were used for all atoms except hydrogen; previous studies[6,7] have proved their accuracy. The small core ECP with 32 electrons in the valence shell suggested in ref 18 was used for uranium. The oxygen atom was described by the same type of energy consistent ECPs,[19] but without polarizing d functions; for hydrogen, we used basis set parameters suggested by Huzinaga[20] with 5s functions contracted to 3s. The geometry optimizations were made using a hydrogen basis set without a diffuse p function, and the same basis set was used for the estimation of the correlation contribution to the total electronic energy. The reason for adopting the small basis sets was the severe convergence problems encountered when using extended basis sets with a d function on oxygen and a p function on hydrogen, rather than as a way to decrease the computation times. However, to estimate the accuracy of the calculations, we also made tests with extended basis sets (vide infra).

3. Results and Discussion

The redox reaction between U(VI)/U(V) and Fe(II)/Fe(III) occurs through electron transfer mediated by bridging oxide/hydroxide. The geometry and relative energy of the ground state structure of these binuclear intermediates will be discussed in this and the following sections. Unless explicitly stated, energies

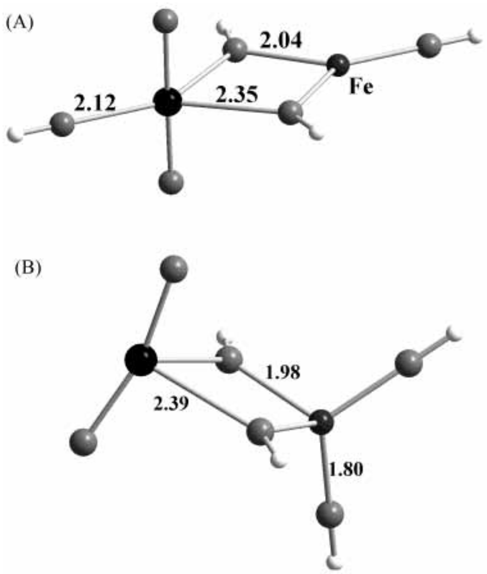

Figure 1. (A,B) SCF optimized ground state structure containing four hydroxide ions of U(VI)Fe(II) and U(V)Fe(III) precursor−successor complexes (see text). Bond lengths are shown in Ångstroms; see Tables S1,2 for details. The U(VI)/U(V) is on the left-hand side, and Fe(II)/Fe(III) is on the right-hand side in the precursor/successor complexes.

quoted in the text have been obtained in the solvent employing the PCM model. They refer to the difference between the total energies of the successor and precursor complexes, and a negative reaction energy refers to an exothermic redox reaction.

3.1. Binuclear U−Fe Complexes Containing Four Hydroxide Ligands. *Ground States of the Precursor and Successor Complexes.* In the precursor complex, the two metal atoms are bound by two hydroxide bridges, with one additional hydroxide attached to uranium and iron, respectively (cf. Figure 1A). The most stable structure of the successor complexes also has a double hydroxide bridge, but in this case, the remaining two hydroxide ions are coordinated to Fe(III) (Figure 1B).

The ground state geometry of both the precursor and the successor complexes agrees with chemical expectations; U(VI) is a stronger acid than Fe(II) but not sufficiently strong to have four coordinated hydroxide ions. Fe(III) is a much stronger acid than U(V), and accordingly, the most stable structure has two terminal hydroxide ions on iron.

Alternative Structures. In addition to the ground state, we considered three precursor isomers of higher energy, one with a double bridge involving one hydroxide ion and one uranyl oxygen, 36 kJ/mol above the ground state (see Supporting Information), one with a double hydroxide bridge and both of the additional hydroxides attached to uranium, 65 kJ/mol above the ground state (see Supporting Information), and one with a double hydroxide bridge but with the two additional hydroxides attached to iron. This latter structure (see Supporting Information) is not stable in the solvent and has the highest energy in the gas phase of all isomers (208 kJ/mol above the ground state). For the successor complex, we also investigated three isomers with higher energy (see Supporting Information). The first one, 77 kJ/mol above the ground state, has two “yl” oxygen bridges and two hydroxide ions on each of U(V) and Fe(III). The second isomer with a mixed hydroxide/oxide bridge is 89 kJ/mol above the ground state, and the third isomer with a double hydroxide bridge and one additional hydroxide on each metal, as in the ground state for the precursor complex, is 119 kJ/mol above the ground state. We were surprised that isomers with bridges involving the yl ions were stable. However, there is experimental evidence that they can be involved in coordination to other metal ions both in the solid state[21] and in aqueous solution.[22] The bond distances in the different structures are reasonably close to the values found experimentally in binary hydroxide complexes, indicating that the model approximations are satisfactory. The geometries and relative energies of four different precursor and successor complexes are given in Tables S1,2 in the Supporting Information.

TABLE 1: Reaction Energies, in kJ/mol, for the Redox Reaction U(VI)−Fe(II) → U(V)−Fe(III) for the Complex with Four Hydroxide Ions (Ground State Geometries Are Considered)[a]

	SCF	CASSCF	MP2	CASPT2
gas phase	−10	155	27	42
PCM	−88	50	−16	−11

[a] A negative energy means that the reaction is exothermic.

Accuracy of the Correlation Treatment. The correlation contribution to the reaction energy is normally large in reactions where the number of open shells varies, and it is thus important that the correlation method used is satisfactory for the system under study. The easiest and most straightforward way to calculate the correlation contribution to the reaction energy is to use the MP2 method. In our case, the precursor has four open d shells on iron and the successor has five open d shells on iron and one open f shell on uranium. It is therefore necessary to assess the reliability of the MP2 method for this system. This was done in two different ways. First, CASPT2 calculations with an active space as large as we could afford and second, CCSD(T) and MP2 calculations on the naked ions UO_2^{2+}/UO_2^{+} and Fe^{2+}/Fe^{3+} in the gas phase.

The size of the complex with four hydroxides precludes a CASPT2 calculation in the full valence space including the oxygen 2s and 2p shells, and the calculations were therefore carried out in a restricted reference space. To determine the stability of the result, a sequence of calculations was carried out where the reference space was gradually increased. The result was assumed stable when the changes became 10 kJ/mol or less. Using this procedure, the CASPT2 results became stable, both in gas phase and in the solvent, with a CAS space generated by distributing 12 electrons in 11 orbitals for the precursor U(VI)−Fe(II) complex and 12 electrons in 12 orbitals in the successor U(V)−Fe(III) complex.

The calculated reaction energy for reaction 3 is shown in Table 1. The effect of correlation is large, both in the gas phase and in the solvent. The correlation effect is severely overestimated by the CAS calculation, which is not surprising since no dynamic correlation is accounted for (the contribution from dynamic correlation has usually the opposite sign as compared to that from static correlation). The agreement between the MP2 and the CASPT2 results is satisfactory; MP2 overestimates the correlation effect with 15 kJ/mol in the gas phase and 5 kJ/mol in the solvent. These results indicate that MP2 is a reasonable method to use for these systems.

As an additional test, we also carried out MP2 and CCSD(T) calculations on UO_2^{+} and UO_2^{2+} and on Fe^{3+} and Fe^{2+} in the gas phase. The reaction energy for the reaction

$$UO_2^{2+} + Fe^{2+} \rightarrow UO_2^{+} + Fe^{3+} \qquad (4)$$

is 1541 kJ/mol at the MP2 level and 1511 kJ/mol at the CCSD(T) level. MP2 thus overestimates the reaction energy with 30 kJ/mol relative to CCSD(T). This difference between the MP2 and the CCSD(T) results is acceptable.

Redox Reaction. From the results in Table 1, it is seen that the correlation effect is larger for the U(VI)−Fe(II) than for the U(V)−Fe(III) system, as expected since the number of closed shells is larger in the former system than in the latter; correlation thus tends to make the reaction less favorable. The solvent effect works in the opposite direction, favoring the U(V)−Fe(III) complex. The solvent effect is of the same magnitude as that for correlation, about 50 kJ/mol (at the correlated level). It is a coincidence that the reaction energy obtained at the SCF level in the gas phase agrees with the correlated result in the solvent. The reason for the larger solvent effect for the U(V)−Fe(III) system is presumably its larger polarity as compared to the precursor. At the MP2 level, the reaction is exothermic by 16 kJ/mol (Table 1).

The electron transfer reaction in the 4 OH^- system involves a structure change where one hydroxide moves from the uranium to the iron. In the solvent, this reorganization will probably be mediated by proton transfer reactions with the solvent. The change in the bond distances between the metal centers and the bridging hydroxides is moderate.

All structures were optimized with symmetry constraints, and the reaction energies might therefore change if the hydroxides are allowed to bend out of the equatorial plane. For example, for the $UO_2(OH)_4^{2-}$ complex in solution, the energy difference between a geometry where all of the hydroxide ions are constrained to the equatorial plane and the true minimum, which is a trans configuration with two hydroxide hydrogen atoms pointing upward and two downward, is 55.3 kJ/mol (the hydroxide oxygens are all close to the equatorial plane) or close to 14 kJ/mol for each hydroxide. However, from Figure 1, it is clear that the effect of allowing the hydroxides to bend out of the equatorial plane will be similar on the ground states of both the precursor and the successor complexes; hence, we do not expect that the symmetry constraint will result in a large error in the estimate of the reaction energy.

The U(VI)O$_2$(OH)$_4$Fe(II)·2H$_2$O Complex. The model with four hydroxide ligands and no coordinated water molecules leaves both the uranium and the iron centers coordinatively unsaturated. Therefore, the PCM model cannot be expected to describe the detailed interactions between the solvent molecules and the solute complex with a high accuracy. It is therefore desirable to saturate the first hydration shell before using this model, but this was not possible in our case. To estimate the error caused by an incomplete first coordination sphere when using the PCM model, we have added one or two water molecules to the precursor and successor complexes. These calculations could only be made on the structures with a high symmetry, otherwise they become prohibitively large; for the precursor, we used the isomer with both hydroxides coordinated to uranium, 65 kJ/mol above the ground state (Figure S3, Supporting Information). The information obtained from this investigation is used to estimate the errors in the solvent model when using an incomplete coordination shell, assuming that the solvent effect is approximately the same for all isomers. The bond distances of the hydrated complexes are given in Table S5 of the Supporting Information.

TABLE 2: Reaction Energies, in kJ/mol, for the Redox Reaction U(VI)−Fe(II) → U(V)−Fe(III) for the Complex with Four Hydroxide Ions and No. 1 and 2 Water Molecules[a]

	no H_2O SCF	no H_2O MP2	one H_2O SCF	one H_2O MP2	two H_2O SCF	two H_2O MP2
gas phase	−176	−118	−109	−43	−77	−23
in solvent	−153	−67	−104	−13	−81	−19

[a] A negative energy means that the reaction is exothermic. The precursor has a double hydroxide bridge and two hydroxides attached to uranium. For the complex with no added water molecules, this isomer is 65 kJ/mol above ground state (see text).

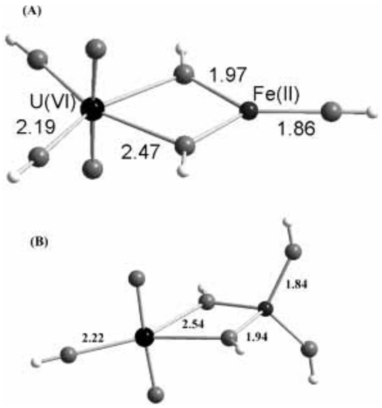

Figure 2. SCF optimized geometry of precursor (A) and successor (B) complexes with five OH groups. Bond distances are in Ångstroms. The U(VI)/U(V) is on the left-hand side, and Fe(II)/Fe(III) is on the right-hand side in the precursor/successor complexes.

The reaction energies are shown in Table 2. At the SCF level, the reaction energy in the solvent decreases from −151 kJ/mol for the four hydroxide complex to −104 kJ/mol with one added water molecule and to −81 kJ/mol with two added water molecules. The solvation effect at the SCF level decreases from 25 kJ/mol for no water, to 5 kJ/mol for one water, to 4 kJ/mol for two water molecules. At the MP2 level, the reaction energies in the solvent are −67, −13, and −19 kJ/mol, and the solvation effect is 51, 30, and 4 kJ/mol. These results show that already one water molecule has an appreciable effect and that two water molecules essentially mimic the saturation of the first coordination shell of both iron and uranyl.

Two conclusions concerning the PCM model may be drawn from these results. First, the reaction energy obtained for the four hydroxide complex is overestimated. Second, precursor/successor complexes with five ligands (including the bridging hydroxides) provide a reasonable description of the solvent effects, and six ligands mimic the saturation of the first coordination shells of both metal ions.

3.2. Binuclear U−Fe Complexes Containing Five and Six Hydroxide Ligands. For the complexes with five and in particular six coordinated hydroxide groups, a new difficulty is that the electronic ground states in gas phase and in the solvent were different for the successor complex; the open 5f shell on uranium changed character from (5f−6d) to a pure 5f in solution. The effect on the geometry of a change in the character of the open 5f shell should be minor due to the localized character of this orbital. We have therefore used the gas phase geometries (see Figures 2 and 3) to obtain reaction energies in the solvent. However, the reaction energies in the gas phase and in solution can no longer be compared, and we therefore restrict the discussion to the reaction energies in solution.

Electronically, precursor/successor complexes with four, five, and six hydroxides are very similar. We are therefore confident that MP2 is reliable also for the five and six hydroxide complexes. In the previous section, we showed that the computed solvent effects are described in a satisfactory way with five and six coordinated ligands.

A summary of the reaction energies for the complexes with four, five, and six hydroxide ligands is given in Table 3 (the bond distances of the five and six hydroxide complexes are

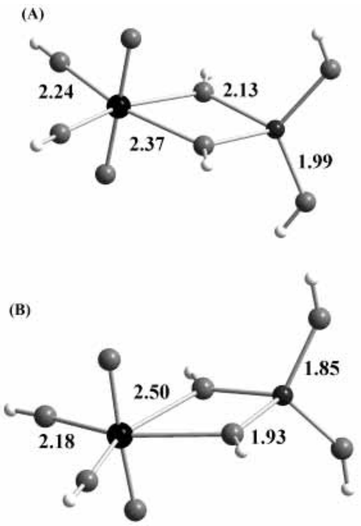

Figure 3. SCF optimized geometry of precursor (A) and successor (B) complexes with six OH groups. Bond distances are in Ångstroms. The U(VI)/U(V) is on the left-hand side, and Fe(II)/Fe(III) is on the right-hand side in the precursor/successor complexes.

TABLE 3: Reaction Energies, in kJ/mol, for the Redox Reaction U(VI)−Fe(II) → U(V)−Fe(III) for the Complex with Four, Five, and Six Hydroxide Ions in the Solvent[a]

complex	SCF	MP2
four hydroxides	−88	−16
five hydroxides	−67	−13
six hydroxides	−57	−23

[a] A negative energy means that the reaction is exothermic.

given in Tables S6 and S7 in the Supporting Information). The reaction is exothermic for all complexes. However, our investigation of the solvent effect showed that the reaction energy is overestimated in the unsaturated four hydroxide complex and that the reaction would probably turn out to be endothermic with a better solvation model. The reaction energy for the precursor−successor reaction for the six coordinated hydroxides (the equilibrium constant for $UO_2(OH)_2^-$ has been assumed to be the same as for $NpO_2(OH)_2^-$), −23 kJ/mol, is close to the experimental value for the Gibbs energy of reaction for reaction 1, about −20 kJ/mol,[23] but this agreement is fortuitous.

4. Estimation of Basis Set Errors and Spin−Orbit Effects

The calculations have been done using a rather small basis set without polarizing functions on O and H. To investigate how sensitive the results are to the size of the basis set, we recalculated the geometry and total energy for the complex with four hydroxides with one d function on oxygen and one p function on hydrogen added to the basis set.

A larger basis set introduced new computational difficulties. At the MP2 level, the calculations for the U(V)−Fe(III) complexes became unstable due to large contribution of configurations with small denominators in the perturbation expansion. The problem is similar to that with intruders in excited state calculations. A well-tested method to eliminate the problem of small denominators is to use the level shift technique proposed in ref 24. A level shift of 0.1 Hartrees makes the MP2 results stable for the successor complex. To compare the energies of the precursor and the successor complexes, we have to use the same level shift for both systems. When we use this procedure, the reaction energy changes from 16 kJ/mol (exothermic) to 26 kJ/mol (endothermic). The energy change remains almost the same with further increase of the level shift up to 0.5 Hartrees. From these results, we conclude that the large basis set stabilizes the precursor complex by about 40 kJ/mol relative to the successor complex.

Spin−orbit effects will stabilize Fe(II) relative to Fe(III), since the atomic ground state for the latter, ^6S, is not split by spin−orbit effects, while the U(V) will be stabilized relative to the closed shell U(VI) system. The spin−orbit effect in Fe(II), estimated from the experimental atomic fine structure, is about 8 kJ/mol, while a calculation on UO_2^+ gave a spin−orbit effect of 25 kJ/mol. The latter result is consistent with the spin−orbit effect on the reduction of UO_2^{2+} to $UO(OH)^+$ reported in ref 6. The spin−orbit effect will thus stabilize the U(V)−Fe(III) complex by 15−20 kJ/mol.

An increased basis set and the spin−orbit effects give opposite contributions to the total energy. The net result indicates a slight stabilization of the precursor complex by about 20 kJ/mol. Our best estimate is thus that the reaction for the four hydroxide complex is slightly endothermic while the reactions for the five and six hydroxide complexes are close to thermoneutral (endothermic by 7 kJ/mol and exothermic by −3 kJ/mol, respectively). This is in fair agreement with the experimental observations.[23]

5. Conclusions

The U(VI)−Fe(II) and U(V)−Fe(III) complexes contain double hydroxide bridges both in solution and in the gas phase. Experimentally, the reaction is endothermic at low pH and exothermic at high pH. According to our calculations, the reaction is thermoneutral or slightly exothermic for five and six hydroxide ligands. We have good reasons to believe that the solvent effects, obtained with the PCM model, overestimate the reaction energy in the four hydroxide complex and that a better calculation would render the reaction endothermic. Such a calculation would be very difficult unless the computational model is simplified. At the present level of accuracy, our results are consistent with experimental observations. The theoretical U(V)−Fe(III) and U(VI)−Fe(II) distances are comparable with the experimental U(VI)−Fe(III) distances of uranyl(VI) ions sorbed on the Fe(III)-containing minerals (see ref 24 for details).

Our model is consistent with experimental data, but it is not possible to improve the solvent model by adding more water molecules or to apply it to cases with larger ligands such as carbonate. We are investigating the possibility to simplify the model by a more approximate treatment of the Fe(II) and Fe(III) ions, and the results are promising. This will be the subject of a forthcoming paper.

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Supporting Information Available: Figures S1−S3 and Tables S1−S7 showing the structures of precursor and successor complexes with, respectively, 4−6 coordinated hydroxide ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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