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“yl”-Oxygen Exchange in Uranyl(VI) Ion: A Mechanism Involving $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ via U−O_{yl}−U Bridge Formation

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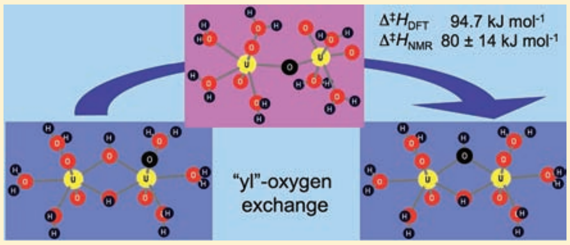
Supporting Information

ABSTRACT: Szabó and Grenthe (*Inorg. Chem.* **2007**, *46*, 9372−9378) suggested from NMR spectroscopy that the “yl”-oxygen exchange in dioxo uranium(VI) ion in acidic solution occurs via an OH-bridged binuclear complex $(UO_2)_2(\mu\text{-}OH)_2^{2+}$. Here, an “yl”-oxygen exchange pathway involving the $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ is studied by B3LYP density functional theory calculations. The oxygen exchange takes place via an intramolecular proton shuttle between the oxygen atoms in $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$. The direct proton transfer from the hydroxo bridge or from the coordinating water to the “yl”-oxygen in $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$ appears to be negligible because of an exceedingly high activation barrier (~170 kJ mol^{-1}). The exchange mechanism in $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$ can be described by a multistep pathway that leads to the formation of an oxo bridge between two uranyl(VI) centers (U−O_{yl}−U bridge). The activation enthalpy $\Delta^{\ddagger}H$ of the reaction obtained at the B3LYP level is 94.7 kJ mol^{-1} and is somewhat larger than the experimental value of 80 ± 14 kJ mol^{-1}. However, the discrepancy between theory and experiment is at the acceptable level. The formation of an oxo bridge between the two uranyl(VI) centers was found to be the key step in proton shuttling, indicating that uranyl(VI) complexes with a stable oxo bridge (such as trinuclear $(UO_2)_3(\mu_3\text{-}O)(OH)_3^{+}$) may have even faster “yl”-oxygen exchange rates than $(UO_2)_2(\mu\text{-}OH)_2^{2+}$.



■ INTRODUCTION

Fortier and Hayton[1] have recently published an excellent review where they discuss the oxo ligand (so-called “yl”-oxygen) functionalization in the uranyl(VI) ion. The authors summarize previous studies on the “yl”-oxygen exchange in dioxo uranium(VI) which have indicated that the exchange of the “yl”-oxygen in uranyl(VI) ion is expected to vary with pH. The detailed mechanism that confers the proton sensitivity, however, has been a subject of controversy over decades (see Table 1 for summary of previous works).

The exchange mechanism for oxygen in UO_2^{2+} in alkaline aqueous solution was first studied by Clark et al.[2] using ^{17}O nuclear magnetic resonance (NMR) spectroscopy as well as $^{16}O/^{18}O$ Raman spectroscopy in 3.5 M tetramethylammonium hydroxide (TMA−OH). Clark et al. correlated the exchange reaction with the prevalence of uranyl(VI) hydroxo species, $UO_2(OH)_4^{2-}$ and $UO_2(OH)_5^{3-}$. Quantum chemical calculations were used by other researchers in attempts to identify the “yl”-oxygen exchange pathway in the uranyl(VI) hydroxo species.[3] However, a direct proton transfer from the coordinating hydroxo ligand to the “yl”-oxygen was found to be unlikely, because the activation barrier of such a mechanism was found to be too high. Szabó and Grenthe[4] performed ^{17}O NMR measurements of UO_2^{2+} in alkaline solution (3.5 M TMA−OH) and found no evidence to support the mechanism claimed by Clark et al. This led Schreckenbach et al.[5] to propose a novel pathway involving $UO_2(OH)_4^{2-}/UO_2(OH)_5^{3-}$ and $UO_3(OH)_3^{3-}$ from density functional theory (DFT) calculations. The latter complex was suggested to result from an intramolecular water elimination within $UO_2(OH)_5^{3-}$. Subsequently, Szabó and Grenthe[6] revisited this system (in 2.91 M TMA−OH) studying by ^{17}O NMR magnetization transfer. The authors revised their previous reaction model and suggested that the exchange reaction takes place via a binuclear complex or transition state with the stoichiometry $(UO_2(OH)_4^{2-})(UO_2(OH)_5^{3-})$. However, they did not exclude the additional mechanism proposed by Schreckenbach et al. Casey et al.[7] studied the pressure dependence of the “yl”-oxygen exchange in 1.5 to 3.0 M TMA−OH and supported the binuclear scenario proposed by Szabó and Grenthe. Since Casey et al. did not cite the work by Schreckenbach et al. and did not discuss the proposed role of the mononuclear $UO_3(OH)_3^{3-}$ complex, there is yet no decisive conclusion on the possible reaction pathways that lead to the “yl”-oxygen exchange in alkaline solution.

The “yl”-oxygen exchange studies in acidic solution are even more scarce. The earliest report dates back to the work of Crandall[8] in 1949 in 0.8 M HCl solution. But the first quantitative study on the “yl”-oxygen exchange in acidic media (0.09 to 0.9 $HClO_4$) was reported by Gordon and Taube[9] who correlated the rate of exchange with the concentration of UO_2OH^{+}. However, recent studies by Suglobov et al.[10] at pH 1 to 4 and Szabó and Grenthe[4] at pH 1 to 3 did not find evidence for the UO_2OH^{+} being involved in the “yl”-oxygen exchange and argue that the reaction rather takes place via a binuclear $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ and possibly via other poly nuclear hydroxo

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Table 1. Summary of Previous Studies on "yl"-Oxygen Exchange in UO_2^{2+}

author(s)	year	medium	method	species involved in "yl"-oxygen exchange	ref.
Clark et al.	1998	base (3.5 M TMA−OH)	NMR, Raman	$UO_2(OH)_4^{2-}$, $UO_2(OH)_5^{3-}$	2
Szabó and Grenthe	2007	base (3.5 M TMA−OH)	NMR	no measurable exchange	4
Schreckenbach et al.	2008		DFT	$UO_2(OH)_4^{2-}$, $UO_2(OH)_5^{3-}$, and $UO_3(OH)_3^{3-}$	5
Szabó and Grenthe	2010	base (2.9 M TMA−OH)	NMR magnetization transfer	$(UO_2(OH)_4^{2-})(UO_2(OH)_5^{3-})$	6
Casey et al.	2011	base (1.5−3.0 TMA−OH)	NMR pressure dependence	uranyl(VI) dimeric complex	7
Crandall	1949	acid (0.8 M HCl)	Raman	UO_2^{2+}	8
Gordon and Taube	1961	acid (0.1−1.0 $HClO_4$)	mass spectroscopy	$UO_2(OH)^+$	9
Suglobov et al.	2004	acid (pH 1−4 HNO_3)	IR	$(UO_2)_2(\mu\text{-}OH)_2^{2+}$	10
Szabó and Grenthe	2007	acid (pH 1−3 $HClO_4$)	NMR	$(UO_2)_2(\mu\text{-}OH)_2^{2+}$	4

species. In these studies, the "yl"-oxygen of UO_2^{2+} was labeled with an oxygen isotope and the exchange reaction was tracked by NMR or infrared absorption (IR) spectroscopy. These methods do not allow a direct observation of short-lived transition states or intermediate species, therefore the exchange pathway remains equivocal. Quantum chemical calculation, on the other hand, is a powerful tool in exploring the "yl"-oxygen exchange pathway because the method is capable of calculating geometries and energies of the complexes including also hypothetical structures. The most stable structure and the reaction pathway can be identified through comparisons of relative energies. This, however, becomes complicated in case of $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$ because there are a number of different "yl"-oxygen exchange pathways that need to be considered, thereby making it extremely challenging to identify the unique reaction pathway. On the other hand, there is an important clue given by the work of Szabó and Grenthe[4] where they show that the "yl"-oxygen exchange does not occur in the complex $(UO_2)_2(\mu\text{-}OH)_2(F)_2(\text{oxalate})_2^{4-}$. This indicates that the oxygen exchange in $(UO_2)_2(\mu\text{-}OH)_2(F)_2(\text{oxalate})_2^{4-}$ (and most likely $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ as well) cannot take place via a direct exchange between the "yl"-oxygen and a water oxygen. Therefore, an intermolecular exchange mechanism is extremely unlikely, except for the very end of the reaction pathway, where an exchange of a solvent molecule with an OH ligand or with a coordinating water molecule may occur.

The oxygen exchange mechanism proposed by Szabó and Grenthe for $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ is a purely intramolecular process. With respect to DFT calculations, this allows modeling the outer sphere water molecules by a dielectric continuum, because they do not participate directly in the oxygen exchange reaction. It is important to be aware of the accuracy and the limitations of DFT calculations. In principle, if the pathway with the lowest activation barrier ($\Delta^{\ddagger}H$) has been identified and if $\Delta^{\ddagger}H$ is in acceptable agreement with experiment, it can be concluded that a realistic pathway has been described. This, however, needs to be done with great caution because the calculated energy is subject to computational error. For example, if two different pathways with $\Delta^{\ddagger}H$ of 60 kJ mol^{-1} and 70 kJ mol^{-1} have been found, the energy difference of only 10 kJ mol^{-1} is surely too small to draw any conclusion. Dixon et al.[11] studied the water exchange reaction in UO_2^{2+} aquo ion and found that the reaction energy heavily depends on the solvation model and solvent parameters they used. On the other hand, Grenthe et al.[12] successfully studied fluoride exchange reactions between UO_2F^+ and UO_2^{2+} at Hartree−Fock, B3LYP, and MP2 level calculations. They concluded that the rate-determining step of the fluoride exchange is the formation and cleavage of the U−F−U bridge. The activation enthalpy ($\Delta^{\ddagger}H$) of 30.9 kJ mol^{-1} calculated at the B3LYP level was virtually identical to the experimental value of 31 kJ mol^{-1}. However, this excellent match between theory and experiment is merely a coincidence as the expected accuracy is not better than ±20 kJ mol^{-1} in this type of energy calculations.[13] The accuracies of quantum chemical calculations regarding reaction energies and activation energies of uranyl(VI) complexes have been extensively discussed in the literatures.[5,12−22] At the B3LYP level with the use of small core ECP on U and with polarizable dielectric continuum the accuracy is at best ±20 kJ mol^{-1}.

Quantum chemical calculations of poly nuclear uranyl(VI) species are still computationally challenging and there are only few examples found in the literatures.[23−25] This paper is the first effort to study the "yl"-oxygen exchange mechanism in a poly nuclear uranyl(VI) system at the B3LYP level. It will be shown that a realistic reaction pathway for "yl"-oxygen exchange can be suggested at the expense of a reduced accuracy of the method which is in the range of at best ±20 kJ mol^{-1}, as reasoned above.

■ QUANTUM CHEMICAL CALCULATIONS

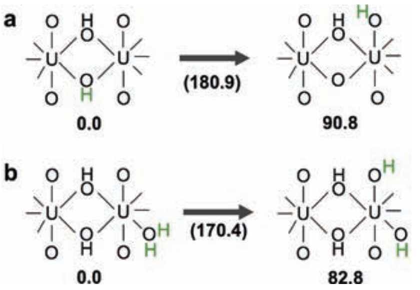
Calculations were performed in aqueous phase using the Gaussian 03 program[26] employing the DFT method with Becke's three-parameter hybrid functional[27] and Lee−Yang−Parr's gradient-corrected correlation functional (B3LYP)[28] through the use of the conductor-like polarizable continuum model (CPCM)[29] using UAHF radii.[30] Two other hybrid functionals PBE[31] and M06[32] were also tested (M06 calculations were performed using Gaussian 09 program[33]) using the same solvation model. The energy-consistent small-core effective core potential (ECP) and the corresponding basis set suggested by Dolg et al. were used for uranium[34] and oxygen.[35] The most diffuse basis functions on uranium with the exponent 0.005 (all s, p, d, and f type functions) were omitted as in previous studies.[12,25] The d-function on oxygen and the g-function on uranium were included. For hydrogen, valence triple-ζ plus polarization basis[36] was used. The Gibbs energy correction to the electronic energy was calculated at the B3LYP level from the vibrational energy levels in aqueous phase and the molecular partition functions. The structures were confirmed to be energy minima through vibrational frequency analysis where no imaginary frequency was found to be present. The transition states were identified through a single imaginary frequency that describes the translation movement across the energy barrier. Spin−orbit effect and the basis set superposition error (BSSE) corrections were neglected. The use of present combination of theory and basis sets has been proven to give reasonable results for the calculations of long-ranged interactions in uranyl(VI) complexes, for example, hydrogen abstraction[37] and photochemical dissociation.[38]

■ RESULTS AND DISCUSSIONS

Direct Proton Transfer from Coordinating OH or H_2O to the "yl"-Oxygen. First, a direct proton transfer from the bridging OH or from the coordinating H_2O to the "yl"-oxygen in $(UO_2)_2(\mu\text{-OH})_2(OH_2)_6^{2+}$ was investigated. The initial structure was taken from the previous study,[25] but it was reoptimized because the basis sets that were used here are not identical to those in the previous study.

Scheme 1 illustrates two reaction pathways which have been studied. Scheme 1a assumes that the proton transfer occurs from the bridging OH to one of the "yl"-oxygens. This reaction has a ΔG of 90.8 kJ mol^{-1} and a twice as large activation enthalpy $\Delta^{\ddagger}H$ of 180.9 kJ mol^{-1}. The high activation barrier renders this mechanism unlikely when compared to the experimental value of 80 ± 14 kJ mol^{-1}.[4]

Scheme 1. Illustration of Selected Reaction Products and Their Precursors with the Corresponding Relative Gibbs energies (ΔG) for Proton Transfer Reactions in $(UO_2)_2(\mu\text{-OH})_2(H_2O)_6^{2+}$ via Direct Proton Transfer to "yl"-Oxygens from (a) the OH Bridge, or from (b) the Coordinating Water[a]



[a] The activation enthalpies ($\Delta^{\ddagger}H$) are given in parentheses. Hydrogen atoms are labeled with green to allow tracking them in the pathway. The energy unit is kJ mol^{-1}. The activation energies of the direct proton transfer pathways depicted here are too high to allow for the involvement of these mechanisms in the experimentally observed "yl"-oxygen exchange.

Szabó and Grenthe[4] have shown that coordinated water in the first shell of the binuclear complex is required for the "yl"-oxygen exchange which, consequently, was not observed in the binuclear complex $(UO_2)_2(\mu\text{-OH})_2(F)_2(\text{oxalate})_2^{4-}$. Therefore, a more likely pathway would involve the direct proton transfer from the coordinating H_2O to the "yl"-oxygen as shown in Scheme 1b. This pathway is feasible compared to Scheme 1a also from energetic point of view. Both ΔG and $\Delta^{\ddagger}H$ are about 10 kJ mol^{-1} lower than for Scheme 1a indicating that the proton transfer from the coordinating water is more favorable than that from the bridging OH. However, the activation barrier 170.4 kJ mol^{-1} is still too high when compared to the experimental value. Therefore, neither of the addressed reaction pathways is likely to contribute significantly to the experimentally observed "yl"-oxygen exchange.

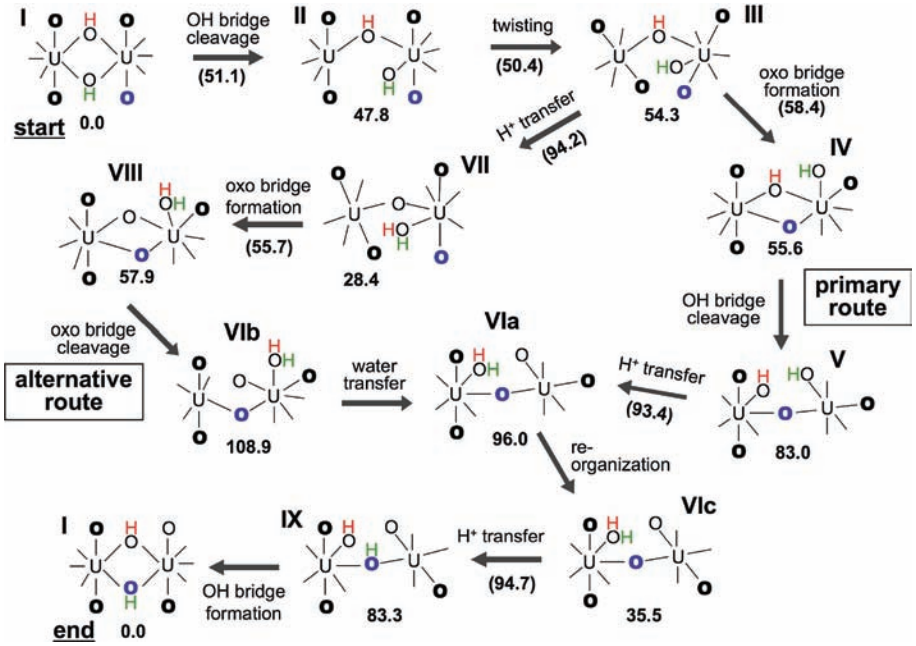
Proton Transfer through an Oxo-Bridge Intermediate. Since a direct proton transfer from either the OH or the H_2O ligand to the "yl"-oxygen was found to be unlikely, another stepwise proton transfer mechanism has been studied here as depicted in Scheme 2. The structural parameters such as U−O and U−U distances are given in Table 2. In this pathway, the primary reaction is the cleavage of one of the two OH bridges in $(UO_2)_2(\mu\text{-OH})_2(H_2O)_6^{2+}$ (**I** → **II**). For this reaction, an activation enthalpy of 51.1 kJ mol^{-1} was obtained. In a second reaction step a twist of the two equatorial planes takes place (**II** → **III**). In the complex with a single OH bridge (**III**), the reaction can proceed to either of the states shown in **IV** and **VII**.

The pathway through complex **IV** is the primary route and proceeds clockwise in Scheme 2, beginning with the formation of new oxo bridge (**III** → **IV**). This oxo bridge formation has a very small activation barrier of 3.8 kJ mol^{-1} and also the Gibbs energy difference between the complexes with and without the oxo bridge is only 1.3 kJ mol^{-1}. The new oxo bridge is weak despite its modest U−O distance of 2.498 Å. The molecular orbitals (MOs) of complex **IV** were analyzed, and two MOs which are representative of the new oxo bond are depicted in Figure.1. It can be seen that the HOMO-5 (fifth MO below the highest occupied MO) comprises the uranyl σ_u orbital. The O 2p MO of the new oxo bridge has antibonding character with respect to this uranyl σ_u orbital. Therefore, the HOMO-5 does not contribute to the bonding interactions between the two uranyl centers. On the other hand, the HOMO-8 also comprises the uranyl σ_u orbital but has a bonding interaction with the O 2p MO of the new oxo bridge as obvious from Figure.1. The oxo bridge formation is followed by cleavage of the OH bridge (**IV** → **V**). Since the ΔG of the reaction is +27.4 kJ mol^{-1} cleavage of the OH bridge clearly destabilizes the complex. It was not possible to identify the transition state between **IV** and **V**. However, in the analogous reaction **I** → **II** an OH bond cleavage occurs as well and its back reaction (**II** → **I**) exhibits a very small activation barrier. Therefore, the activation barrier of the back reaction **V** → **IV** is supposed to be also low. Hence, the activation barrier for the **IV** → **V** relative to complex **I** can be reasonably assumed to be not greater than ~85 kJ mol^{-1}. Finally, a proton transfer takes place between two OH ligands in complex **V** leading to the formation of new oxo ligand and a water molecule (**VIa**). The $\Delta^{\ddagger}H$ of the proton transfer (**V** → **VIa**) is 10.1 kJ mol^{-1}, and the activation enthalpy relative to **I** is 93.4 (= 83.3 + 10.1) kJ mol^{-1}.

An alternative pathway which proceeds counterclockwise after formation of complex **III** in Scheme 2 may take place via complex **VII**. In this pathway, a proton transfer takes place first (**III** → **VII**) with an activation barrier of 39.6 kJ mol^{-1}, corresponding to 94.2 kJ mol^{-1} (= 54.6 + 39.6) relative to complex **I**. The complex **VII**, with the formula $(UO_2)_2(\mu\text{-O})(H_2O)_7^{2+}$ is very stable with a Gibbs energy of 28.4 kJ mol^{-1} relative to **I**. This suggests that complex **VII** may exist as a stable species under certain condition. Hattori et al.[39] found by EXAFS spectroscopy that the uranyl(VI) hydroxo dimeric species sorbed on Gibbsite have the U−U distance of 4.30 Å, that is, close to the U−U distance found in complex **VII** (4.200 Å). Complex **VII** further reacts by oxo bridge formation (**VII** → **VIII**) followed by oxo bridge cleavage (**VIII** → **VIb**). The former (**VII** → **VIII**) has an activation enthalpy of 16.6 kJ mol^{-1}. The transition state between **VIII** and **VIb** could not be identified. The relatively high Gibbs energy of complex **VIb** (108.9 kJ mol^{-1} relative to the precursor complex **I**) suggests that the first pathway via complex **IV** predominates, even if the second pathway cannot be excluded.

In the final step, a proton is transferred from a water molecule to the oxo bridge in complex **VIa**. The reaction takes place first by reorganization of the UO_3 unit on the right-hand-side of **VIa** resulting in the formation of **VIc**. This is followed by a proton transfer from coordinating H_2O to the oxo bridge (**VIc** → **IX**). The latter reaction has an activation barrier of 55.8 kJ mol^{-1} which is 94.7 kJ mol^{-1} relative to **I**. The step **VIc** → **IX** has the highest activation barrier relative to complex **I** so that the rate determining step in the entire pathway is the **VIc** → **IX**

Scheme 2. Illustration of the Stepwise Proton Transfers in $(UO_2)_2(\mu\text{-}OH)_2(H_2O)_6^{2+}$ Leading to the Oxygen Exchange between the O_{yl} and OH Ligand[a]



[a]Hydrogen atoms in OH bridges in the complex **I** are labeled with color, and "yl"-oxygens are in bold font and with color to allow tracking them throughout the entire pathway. In this scheme, the primary route is via complex **IV** even if the alternative route cannot be excluded. Gibbs energies (and activation enthalpies in parentheses) relative to the respective precursor are given in kJ mol^{-1}.

Table 2. Major Bond Distances of All Complexes in Scheme 2[a]

	U−O_{oxo}[b]	U−U
I	1.767, 1.767, 1.767, 1.768	3.835
II	1.761, 1.763, 1.780, 1.780	4.322
III	1.762, 1.763, 1.779, 1.781	4.354
IV	1.761, 1.762, 1.775, 1.846, 2.498	3.706
V	1.769, 1.771, 1.771, 1.819, 2.586	4.267
VIa	1.761, 1.761, 1.800, 1.899, 1.924, 2.315	4.153
VIb	1.768, 1.768, 1.812, 1.853, 2.008, 2.160	4.165
VIc	1.776, 1.776, 1.780, 1.780, 2.078, 2.130	4.198
VII	1.776, 1.776, 1.779, 1.781, 2.078, 2.129	4.200
VIII	1.774, 1.774, 1.777, 1.824, 2.064, 2.175, 2.662	3.554
IX	1.761, 1.761, 1.778, 1.779	4.419

[a]Unit is in Ångström. [b]The U−O_{oxo} bond was defined by a distance of less than 3.0 Å between uranium and oxygen atoms that are not bound to any hydrogen.

transition. It was not possible to identify the transition state between **VIa** and **VIc**. In principle, molecular reorganization involving uranyl bonds, which is the case in **VIa** → **VIc**, may have relatively high activation barrier. However, complex **VIc** is much more stable than **VIa** with Gibbs energy difference of 60.5 kJ mol^{-1}. Large stabilization by the transition **VIa** → **VIc** is indicative of relatively low activation barrier but this step may have $\Delta^{\ddagger}H$ greater than 94.7 kJ mol^{-1} relative to complex **I** and may slightly increase the overall activation barrier. A direct proton transfer from OH to the oxo bridge (**V** → **IX**) may seem to be also possible, but such a reaction has a much higher activation barrier than the two step proton transfer (**V** → **VIa** → **VIc** → **IX**), and it was not possible to identify the transition state in **V** → **IX**.

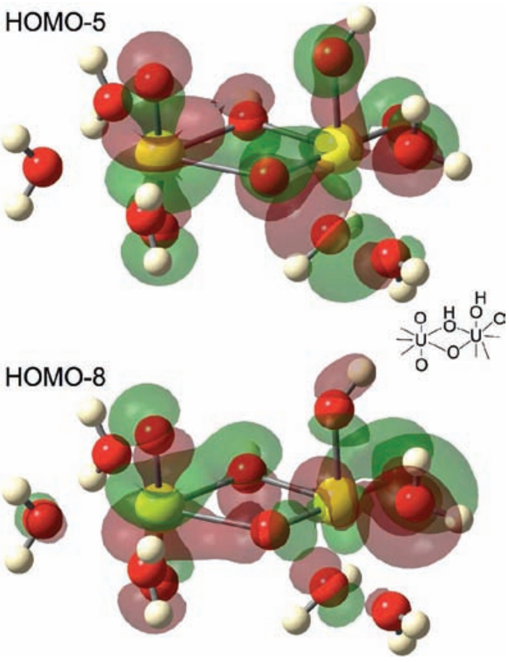


Figure 1. Two molecular orbitals in complex **IV** which are representative of the interaction between two uranyl centers (U−O_{yl}−U bridge formation). The HOMO-5 (upper MO) describes an antibonding interaction between uranyl σ_u orbital and O_{yl} 2p orbital whereas the HOMO-8 (lower MO) describes a bonding interaction between uranyl σ_u orbital and O_{yl} 2p orbital.

Finally, complex **I** follows the following reaction:

$$(UO_2)_2(OH)_2^{2+} + 2H^+ \Leftrightarrow 2UO_2^{2+} + 2H_2O \quad (1)$$

The reaction 1 is known to be a rapid equilibrium,[40] and there is a fast exchange of oxygen in OH of $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ and that in solvent water.

The "yl"-oxygen exchange mechanism in Scheme 2 is consistent with the previous experiments of Szabó and Grenthe. The activation enthalpy of 94.7 kJ mol^{-1} agrees with their value of 80 ± 14 kJ mol^{-1}. As discussed in the Introduction, various studies have suggested that a discrepancy of 15 kJ mol^{-1} (94.7 versus 80 kJ mol^{-1}) is acceptable between theory and experiment. Schreckenbach et al.[5] studied the "yl"-oxygen exchange in $UO_2(OH)_4^{2-}$ and concluded that the activation energy obtained by DFT calculations (B3LYP and PBE) is slightly overestimated (8−12 kJ mol^{-1}). Other studies on uranyl(V) complexes also suggested that the accuracy of this type of energy calculation is ±20 kJ mol^{-1}. Bühl and Wipff point out the "intrinsic DFT deficiencies" in calculating reaction energies where the complexes with different coordination numbers are involved.[41] This does not apply to the present case because the rate determining step is proton transfer between the ligands where the coordination number of uranium remains a constant value.

In both present DFT calculations and NMR work by Szabó and Grenthe,[4] there is no indication of the direct or indirect involvement of the outer sphere solvent to the "yl"-oxygen exchange. This, however, does not necessarily imply that the outer sphere solvent do not play any role. Adding second solvation waters may give lower activation barrier because of the formation of hydrogen-bond network as demonstrated by Bühl and Schreckenbach in DFT-based molecular dynamics simulation.[5b] Such calculation, however, was not attempted in the present investigation.

Two other DFT functionals (PBE and M06) have been tested on several isomers in Scheme 2 and their energies are given in Table 3. The B3LYP and PBE give similar energetics, whereas M06 tends to give noticeably higher or lower energies as compared to B3LYP. There are different views on the accuracy, when using M06 functionals for the calculation of uranyl(VI) complexes. Bühl and Schreckenbach[5b] found M06 to give 4.2 kcal mol^{-1} higher energy than B3LYP for oxygen exchange reaction in uranyl(VI) hydroxide and conclude that M06 give "noticeably higher number" than B3LYP. Burton et al.[42] claims that the deviation of B3LYP and M06 for calculating uranyl(VI) systems is "at most" 4 kcal mol^{-1}. Hillier et al.,[43] on the other hand, argue that M06 performs even better than B3LYP as far as water exchange energetics and redox potentials are concerned.

Table 3. Relative Gibbs Energies (in kJ mol^{-1}) of the Complexes in Scheme 2 Calculated Using Different DFT Functionals

	I	VIa	VII	IX
B3LYP	0.0	96.0	28.4	83.3
PBE0	0.0	100.8	34.9	79.4
M06	0.0	115.0	51.4	49.5

In Scheme 2, there is no direct involvement of the coordinating water to the "yl"-oxygen exchange in the entire pathway. A proton is transferred only between the oxygen atoms in OH and O_{yl}. At first glance, this appears to contradict the results of Szabó and Grenthe[4] who could not detect an "yl"-oxygen exchange in $(UO_2)_2(\mu\text{-}OH)_2(F)_2(oxalate)_2^{4-}$ and concluded that "it is necessary to have coordinated water in the first coordination sphere of the binuclear complex, for exchange to take place". This, however, does not necessarily mean that coordinating water itself does participate in the "yl"-oxygen exchange. In Scheme 2, there is significant rearrangement of equatorial water molecules whereas such reorientation is sterically inhibited when chelating oxalate is coordinated to the equatorial plane. The absence of "yl"-oxygen exchange in $(UO_2)_2(\mu\text{-}OH)_2(F)_2(oxalate)_2^{4-}$ is presumably due to its sterical inflexibility and not to the lack of coordinating water.

It remains an open question, whether the pathway with the lowest activation barrier has truly been identified here by DFT. Various other pathways (including Scheme 1) have been investigated but were all found to have activation enthalpies larger than 94.7 kJ mol^{-1}, that is, much higher barriers than that in Scheme 2. The pathway with the second and the third lowest activation enthalpy is depicted in Schemes S1 and S2 in the Supporting Information, where the activation enthalpies are found to be 118.7 and 139.0 kJ mol^{-1}, respectively. The Scheme S2 describes only half of the "yl"-oxygen exchange pathway so that the activation enthalpy is even higher than 139.0 kJ mol^{-1}. No other pathway seems to have an activation barrier lower than that in Scheme 2.

The present study confirms the oxygen exchange mechanism via the binuclear $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ complex proposed by Szabó and Grenthe[4] and also by Suglobov et al.[10] It remains unclear, whether the original exchange mechanism involving the UO_2OH^+ proposed by Gordon and Taube[9] is still valid. Szabó and Grenthe cast doubts about the reliability of the analytical procedure by Gordon and Taube, thereby, questioning their data in general. It is possible that the species present in the experiments of Gordon and Taube is not UO_2OH^+ as claimed, but other hydrolysis species such as binuclear $(UO_2)_2OH^{3+}$. Such species is likely to be present because the experiments were carried out under much higher uranium concentration (~1M) than those by Szabó and Grenthe. The structure of $(UO_2)_2OH^{3+}$ as studied previously[25] is very similar to the intermediate state with a single OH bridge (complex **III** in Scheme 2) indicating that the "yl"-oxygen exchange can also take place in $(UO_2)_2OH^{3+}$ via oxo bridge formation. However, this assumption remains hypothetical and needs to be carefully examined both by theory and experiment.

■ CONCLUSIONS

The "yl"-oxygen exchange mechanism involving the binuclear $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ complex was studied here by density functional theory (DFT) calculations. DFT calculations confirm the mechanism via the $(UO_2)_2(\mu\text{-}OH)_2^{2+}$ complex as proposed earlier based on spectroscopic studies.[4,10] The "yl"-oxygen exchange takes place via two proton transfer reactions. It involves an intermediate species with a single oxo bridge between two uranyl centers. The analysis suggests that species with a stable oxo bridge, such as $(UO_2)_3(\mu_3\text{-}O)(OH)_3^+$, may have even lower activation barriers and could undergo even more rapid "yl"-oxygen exchange reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Alternative pathways for the "yl"-oxygen exchange. Coordinates of complexes in Scheme 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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