Water Exchange Reactions and Hydrolysis of Hydrated Titanium(III) Ions. A Density Functional Theory Study

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The structure and water exchange mechanism of hexahydrated Ti(III), its hydrolysis, and the water exchange mechanism of analogous hydroxo–aqua complexes have been studied using density functional theory (DFT) calculations. Isolated metal–aqua and metal–hydroxo clusters corresponding to the gas-phase ($T = 0$ K) were used to approximate the model reactions. The structure of $[Ti(H_2O)_6]^{3+}$ was found to have C_i symmetry and Ti–O bond lengths of 2.094 Å. The water exchange reaction of this complex follows an (almost) limiting A mechanism with an energy of activation of 15.8 kcal mol^{-1}. The hydrolysis of hexahydrated Ti(III) was modeled by an in vacuo proton-transfer process between water molecules of the first and second coordination spheres of $[Ti(H_2O)_6]^{3+}\cdot H_2O$. This process was found to be activationless and leads to the unusually stable dication:cation pair $[Ti(H_2O)_5(OH)]^{2+}\cdot H_3O^+$, which is lower in energy than the reactant by 4.5 kcal mol^{-1}. Only a weak structural influence, indicated by a slight increase in the mean value of the Ti–O bond lengths of water molecules in the first coordination sphere, is observed when the hydroxo ligand is formed. The water exchange reactions of the corresponding hydroxo–aqua complexes $[Ti(H_2O)_5(OH)]^{2+}$ and $[Ti(H_2O)_5-(OH)]^{2+}\cdot H_2O$, respectively, were found to proceed via limiting D mechanisms. The energies of activation for the exchange of the water molecule in the trans-position to the hydroxo ligand were calculated to be only 9.8 and 7.2 kcal mol^{-1}, respectively. This, however, implies that the apparently weak influence of coordinated hydroxide still results in a significant reduction in the energy barrier for the water exchange reaction and also leads to a complete changeover in the preferred exchange pathway from A to D.

Introduction

On the basis of theoretical[1,2] and experimental[2,3] approaches, several structures for the hexahydrated complex $[Ti(H_2O)_6]^{3+}$ have been proposed in order to explain the characteristic bands in its absorption spectrum.[4,5] The hexaqua Ti(III) ion occurs in alums such as $CsTi(SO_4)_2\cdot 12H_2O$ and hydrolyzes to give the hydroxo–aqua complex $[Ti(H_2O)_5(OH)]^{2+}$.[6] The measured pK_{a1} value of $[Ti(H_2O)_6]^{3+}$ is between 1.8 and 2.5[7] and it therefore can be considered to be a relatively strong acid similar to $[Fe(H_2O)_6]^{3+}$, which has a pK_{a1} between 2.2 and 2.9,[7,8] implying that spontaneous deprotonation of $[Ti(H_2O)_6]^{3+}$ can be expected in aqueous solution.

Besides the structural clarification of the $[Ti(H_2O)_6]^{3+}$ ion, a more dynamic aspect, the water exchange reaction at Ti(III) is of great interest, especially in comparison to trivalent 3d-metal ions such as V(III),[9] Cr(III),[10] and Fe(III)[8] and other trivalent transition metal ions such as Ru(III), Rh(III), and Ir(III).[11] On the basis of a simplified gas-phase cluster approach, recent theoretical papers have successfully mimicked the water exchange behavior of di- and trivalent transition metal ions[12–15] and also demonstrated strong interest in studying these kinds of reactions, although the commonly applied mechanistic picture for solvent exchange and ligand-substitution processes based on volumes of activation[16] already provides a consistent and

distinct mechanistic scheme and notation for such mechanisms.[17] In addition, Merbach, Rotzinger and co-workers have revised the interpretation of the water exchange reactions of Al(III), Ga(III), and In(III) using new experimental data in conjunction with ab initio calculations of approximate gas-phase metal–aqua clusters.[18] By comparison of experimental *and* theoretical results the authors clearly showed that the use of such gas-phase models, which only account for a complete first coordination sphere, is justified in order to reproduce the water exchange reactions of metal ions in solution.

In this report we comment on the most favored gas-phase structure of hexahydrated Ti(III) and its preferred water exchange pathway. To cover the exchange behavior of this ion fully, the effect of base catalysis on the overall reaction mechanism was investigated by an in vacuo proton-transfer process between water molecules of the first and second coordination spheres. The water exchange reactions of the thus formed hydroxo–aqua species $[Ti(H_2O)_5(OH)]^{2+}$ and its more extended analogue $[Ti(H_2O)_5(OH)]^{2+}\cdot H_2O$ have been studied in more detail.
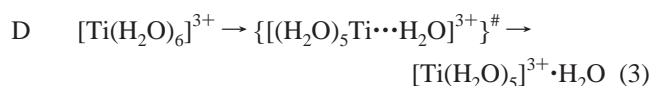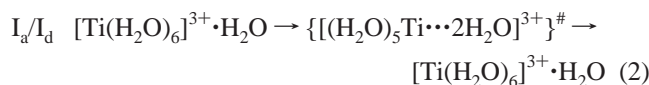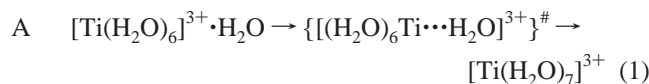
Methods and Levels of Theory

(a) Model Reactions. The water exchange mechanism of $[Ti(H_2O)_6]^{3+}$ was examined by using gas-phase clusters consisting of the metal ion surrounded by up to seven water molecules. All possible substitution modes, namely the limiting associative (eq 1), the associatively/dissociatively activated interchange (eq
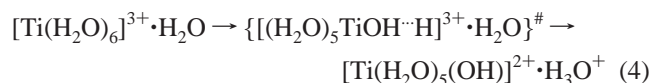

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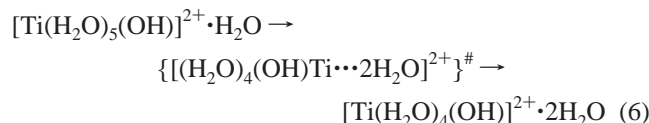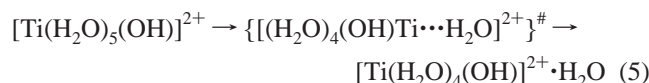[‡] Institut für Anorganische Chemie.
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A $[Ti(H_2O)_6]^{3+} \cdot H_2O \rightarrow \{[(H_2O)_6 Ti \cdots H_2O]^{3+}\}^{\#} \rightarrow$

$$[Ti(H_2O)_7]^{3+} \quad (1)$$

I_a/I_d $[Ti(H_2O)_6]^{3+} \cdot H_2O \rightarrow \{[(H_2O)_5 Ti \cdots 2H_2O]^{3+}\}^{\#} \rightarrow$

$$[Ti(H_2O)_6]^{3+} \cdot H_2O \quad (2)$$

D $[Ti(H_2O)_6]^{3+} \rightarrow \{[(H_2O)_5 Ti \cdots H_2O]^{3+}\}^{\#} \rightarrow$

$$[Ti(H_2O)_5]^{3+} \cdot H_2O \quad (3)$$

2), and the limiting dissociative (eq 3) mechanisms were analyzed before the most favorable reaction pathway was suggested. In contrast to the fundamental theoretical work on the water exchange reactions of 3d di- and trivalent transition metal ions by Rotzinger,[13] it was, however, not possible to verify a limiting D mechanism according to eq 3. On the chosen levels of theory, all attempts to locate transition state structures and intermediate complexes for this process invariably ended up in hydroxo–aqua complexes of Ti(III), in which the leaving water molecule initiates the deprotonation of a neighboring water molecule of the first coordination sphere. Therefore, a detailed study of the deprotonation of $[Ti(H_2O)_6]^{3+}$ was mandatory. In this respect, further calculations were carried out for the proton-transfer process between water molecules of the first and second coordination spheres (eq 4). This deprotonation involves the

$$[Ti(H_2O)_6]^{3+} \cdot H_2O \rightarrow \{[(H_2O)_5 TiOH \cdots H]^{3+} \cdot H_2O\}^{\#} \rightarrow$$

$$[Ti(H_2O)_5(OH)]^{2+} \cdot H_3O^+ \quad (4)$$

reaction with an *external* water molecule, initially located in the second coordination sphere, which accepts a proton from directly coordinated water to produce a H_3O^+ ion. Consideration of such "hydrolyzed" cations of the general type $[Ti(H_2O)_n-(OH)]^{2+} \cdot mH_2O$ with $n = 5$, $m = 0$ and $n = 5$ and $m = 1$, however, implies that the operation of a limiting D mechanism for the water exchange reaction of this ion is inevitably coupled to labilizing effects exerted by an OH^- ligand.[11] Consequently, eq 3 was modified by considering the corresponding hydroxo complex of Ti(III), thus leading to eqs 5 and 6, the latter

$$[Ti(H_2O)_5(OH)]^{2+} \rightarrow \{[(H_2O)_4(OH)Ti \cdots H_2O]^{2+}\}^{\#} \rightarrow$$

$$[Ti(H_2O)_4(OH)]^{2+} \cdot H_2O \quad (5)$$

$$[Ti(H_2O)_5(OH)]^{2+} \cdot H_2O \rightarrow$$

$$\{[(H_2O)_4(OH)Ti \cdots 2H_2O]^{2+}\}^{\#} \rightarrow$$

$$[Ti(H_2O)_4(OH)]^{2+} \cdot 2H_2O \quad (6)$$

including one additional water molecule as a *theoretically* possible entering ligand. The notation used to describe the complexes and the selected structural parameters abbreviates bond lengths between titanium and oxygen as $r(Ti-O)$ with the indices I and II, indicating water molecules in the first and second coordination spheres, respectively. Complexes of the general type $[Ti(H_2O)_n]^{3+} \cdot mH_2O$, where $n = 6$, $m = 0,1$ and $n = 7$ and $m = 0$, are abbreviated only by their coordination numbers in the first and second coordination spheres, thus leading to an (n,m) notation. In addition, hydroxo–aqua complexes of the general type $[Ti(H_2O)_n(OH)]^{2+} \cdot mH_2O$, where $n = 5$ and $m = 0,1$ are denoted in a similar way as (OH,n,m). Complexes involved in a proton-transfer reaction between water molecules of the first and second coordination spheres have the general form $[Ti(H_2O)_n(OH)]^{2+} \cdot H_3O^+$ and are written as
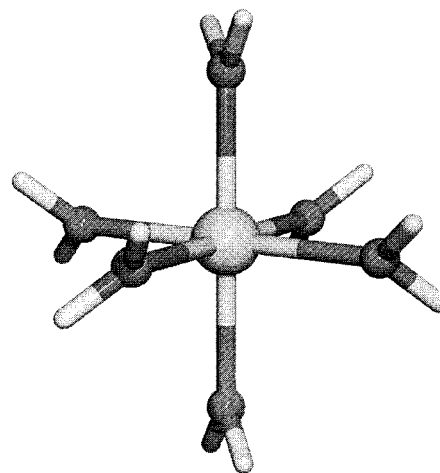
(6,0)

Figure 1. Molecular structure of $[Ti(H_2O)_n]^{3+}$.

(OH,n,H_3O) with $n = 5$. All transition states are further marked with a superscript pound sign (#).

To follow the changes in bond lengths occurring during the reactions, a measure that parallels the volume of activation is required. For this purpose, all the Ti–O bond lengths in the reactant and in the transition state complexes are summed. The difference Δ obtained by subtracting the latter from the former value gives the structural change associated with the activation process during the water exchange process.[13,15]

(b) Computational Details. All calculations used the program packages Gaussian 94[19a] and Gaussian 98[19b] and the B3LYP[20,21] combination of functionals. A combination of an augmented Schäfer, Horn, Ahlrichs basis set[22] for Ti and standard triple-split valence basis sets, 6-311G(d)[23] and 6-311+G(d,p)[24] for O and H were used for all the calculations. The first combination of basis sets is referred to as SHA+6-311G(d) and the latter as SHA+6-311+G(d,p) in the following.

Minimizations and optimizations to transition states both used the Berny algorithm together with redundant internal coordinates.[25,26] Frequency analyses were performed on both the B3LYP/SHA+6-311G(d)//B3LYP/SHA+6-311G(d) and B3LYP/SHA+6-311+G(d,p)//B3LYP/SHA+6-311+G(d,p) levels of theory and zero-point vibrational energies (ZPE), obtained at these levels were used to correct the total energies (for further details see the Supporting Information).

Unless otherwise noted, all values given in the text are those obtained at the highest level of theory, B3LYP/SHA+6-311G+-(d,p)//B3LYP/SHA+6-311G+(d,p).

Results and Discussion

(a) Hexahydrated Ti(III). The most favored gas-phase structure found for hexahydrated Ti(III) is shown in Figure 1. Table 1 summarizes all (6,0) structures characterized together with their point group assignments, Ti–O bond lengths, electronic states and number of imaginary vibrations. Structures for hexaquatitanium complexes that are local minima with respect to the potential hypersurface have either C_i or C_1 symmetry. Calculations on both levels of theory suggest that the energy difference between these two complexes is negligible and the $r(Ti-O)$ bond lengths differ by only 0.003 Å. Therefore, these structures can be considered to be the same. Further structures for this (6,0) complex were found using C_{2h} and D_{2h} symmetries. The former was clearly verified as transition state, whereas the latter turned out to be a second-order saddle point. Rotzinger[13] suggested the $[Ti(H_2O)_6]^{3+}$ complex to have D_{2h}

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TABLE 1: Point Group Assignment, Ti–O Bond Lengths (Å), Electronic State, and Number of Imaginary Vibrations (Nimag) of $[Ti(H_2O)_6]^{3+}$

PG	r(Ti–O)	state	nimag
D_{3d}	2.094[a]	$^2A_{1g}$	1
	2.083[b]		
D_{2h}	2.061, 2.063, 2.063, 2.134[b]	$^2B_{1g}$	2
C_{2h}	2.067, 2.091, 2.094[b]	^2B_g	1
C_i	2.094[a]	^2A_g	0
	2.083[b]		
C_1	2.080, 2.080, 2.084, 2.084, 2.085, 2.085[b]		0

[a] B3LYP/SHA+6-311+G(d,p)//B3LYP/6-311+G(d,p). [b] B3LYP/SHA+6-311G(d)//B3LYP/6-311G(d).

symmetry and Ti–O bond lengths between 2.09 and 2.17 Å on a CISD level of theory and between 2.11 and 2.16 Å using DFT.

On the basis of ab initio CI calculations on the $[Ti(H_2O)_6]^{3+}$ cation[1] and ESR and electron-spin echo (ESE)[2,3] studies on the hydrated Ti(III) ion in the Cs-alum $[CsTi(SO_4)_2]\cdot12H_2O$, the groups of Ichikawa and Tachikawa have suggested a geometry for the hexahydrated Ti(III) that is slightly distorted from O_h symmetry by the Jahn–Teller effect to give a D_{3d}-symmetric structure. They calculated the Ti–O bond length to be 1.966 Å, which differs significantly from the experimental bond length of 2.20 Å. Further computations of Tachikawa and Murakami using more extensive basis sets gave Ti–O bond lengths of 1.995 and 2.053 Å.[2] Within the levels of theory used in this work, such a D_{3d}-symmetric complex was found to be a transition state rather than a local minimum. However, the energy difference between this complex and the most stable C_i-symmetric structure is less than 1 kcal mol^{-1} favoring the latter. In addition, the Ti–O bond lengths of both of these two structures were calculated to be 2.094 Å, in reasonable agreement with the experimental values.[2,3,6] Although the subsequent discussion of the water exchange mechanism will be based on the local minimum structure in C_i symmetry, one should keep in mind that this complex represents a time-averaged D_{3d}-symmetric structure in terms of structure and energy.

(b) Associative Water Exchange on Hydrated Ti(III) Ions. The water exchange reaction of hydrated Ti(III) has been studied thoroughly by experimental[27] and theoretical[13] techniques. In general, volumes of activation $\Delta V^{\#}$ suggest a trend for the water exchange mechanisms of di- and trivalent transition 3d-metal ions.[28] The increasingly positive values of $\Delta V^{\#}$ on going from hydrated V(II) to Ni(II) indicate an increasingly dissociative mode of substitution, whereas the negative values of $\Delta V^{\#}$ for the water exchange reactions of trivalent 3d-metal ions generally suggest associative substitution modes. The volume of activation for the water exchange reaction of hydrated Ti(III) was measured to be −12.1 cm^3 mol^{-1},[27] close to the value of −13.5 cm^3 mol^{-1} suggested for a limiting A mechanism,[29] implying a pronounced tendency of $[Ti(H_2O)_6]^{3+}$ to exchange water via a limiting or almost limiting A mechanism.[27] Comparison with the volumes of activation for other water exchange reactions involving trivalent 3d-metal ions, like V(III), Cr(III), and Fe(III), which are −8.9,[9] −9.6,[10] and −5.4 cm^3 mol^{-1},[8] respectively, shows the operation of an associatively activated I_a rather than a limiting A exchange mechanism.[28]

To model the water exchange reaction of $[Ti(H_2O)_6]^{3+}$, the reaction mechanisms shown in eqs 1 and 3 were studied using DFT calculations. The interchange mechanism (eq 2) was not investigated explicitly, since if such a mechanism is operative in the water exchange reaction of Ti(III), it will be recognized from the relative energies of the complexes involved in eq 1 and also from the changes in the Ti–$O_{I/II}$ bond lengths (i.e.,
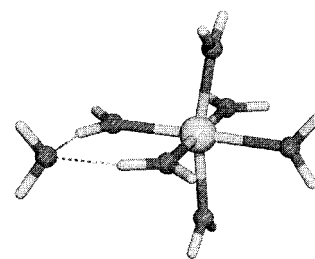
(6,1)
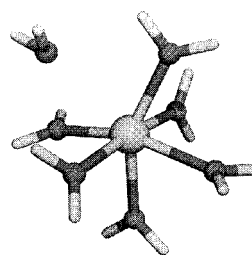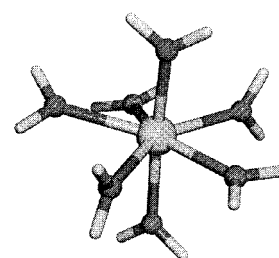
(6,1)$^{\#}$ **(7,0)**

Figure 2. Reactant (6,1), transition state (6,1)$^{\#}$, and intermediate (7,0) according to eq 1.

TABLE 2: Selected Structural Parameters r(Ti–O_I) and r(Ti–O_{II}) (Å), Relative Energies ΔE (kcal mol^{-1}), and Point Group Assignment for the Water Exchange Reaction of Ti^{3+} According to Eq 1

	r(Ti–O_I)	r(Ti–O_{II})	ΔE	Σr(Ti–O)	PG
(6,1)	2.042, 2.049, 2.088, 2.088, 2.105, 2.172	3.800		16.344	C_s
(6,1)$^{\#}$	2.072, 2.073, 2.111, 2.134, 2.153, 2.157	2.686	15.8[a]	15.386	C_1
(7,0)	2.246, 2.224, 2.182, 2.164, 2.129, 2.121, 2.086		14.5[b]	15.152	C_1

[a] Energy of activation (6,1) → (6,1)$^{\#}$. [b] Reaction energy (6,0) → (7,0). All values shown are based on B3LYP/SHA+6-311+G(d,p)//B3LYP/SHA+6-311+G(d,p).

the distances of the entering and leaving water molecules to the metal center) on going from the reactant to the transition state during the study of eq 1. For this purpose, the reaction sequence (6,1) → (6,1)$^{\#}$ → (7,0) (Figure 2) in which the water molecule is initially part of the second coordination sphere of the metal ion, was studied. Table 2 summarizes selected structural parameters, point group assignments and relative energies for this reaction. The seventh water molecule of reactant (6,1) is bound to water molecules of the first coordination sphere by two hydrogen bonds. The Ti–O_{II} distance was calculated to be 3.800 Å, whereas the Ti–O_I bond lengths are between 2.042 and 2.172 Å. The overall structure of this complex is of C_s symmetry. A shortening of the Ti–O_{II} bond length results in the formation of transition state (6,1)$^{\#}$. The Ti–O_{II} bond distance is now 2.686 Å, whereas the Ti–O_I bond lengths are between 2.072 and 2.157 Å. This, however, implies that in the transition state the entering water molecule rather belongs to the first than to the second coordination sphere and that no water molecule of the first coordination sphere shows any tendency to leave its location during the approach of the seventh water molecule. In the intermediate complex (7,0) the Ti–O bond lengths are between 2.086 and 2.246 Å, giving a mean value of 2.165 Å. These results are in agreement with those obtained from ab initio

TABLE 3: Selected Structural Parameters (Å) for the Complexes of Eq 4 and Relative Energies (kcal mol^{-1})^a

	r(Ti−O$_I$)	r(Ti−O$_d$)	r(Ti−O$_{II}$)	r(Ti−OH··H)	r(H···OH$_2$)	ΔE
(6,1)	2.052, 2.088, 2.088, 2.105, 2.172 (2.101)^b	2.049	3.800	1.003	1.724	
(OH,5,H$_3$O)$^{\#}$	2.093, 2.097, 2.105, 2.124, 2.137 (2.112)^b	1.990	3.928	1.085	1.391	1.3^c
(OH,5,H$_3$O)	2.104, 2.124, 2.170, 2.170, 2.179 (2.149)^b	1.881	4.277	1.608	1.030	−4.5^d

^{a} All values are based on B3LYP/SHA+6-311+G(d,p)//B3LYP/SHA+6-311+G(d,p). ^{b} Mean value of all r(Ti−O$_I$) bond lengths given in brackets. ^{c} Energy of activation (6,1) → (OH,5,H$_3$O)$^{\#}$ *without* ZPE. Consideration of this correction results in a relative energy of −0.1 kcal mol^{-1} using the SHA+6-311G+(d,p) basis set and 1.3 kcal mol^{-1} using the SHA+6-311G(d) basis set. ^{d} Reaction energy (6,1) → (OH,5,H$_3$O) including ZPE.

HF and CI approaches, which result in r(Ti−O) values between 2.13 and 2.25 Å.[13] Sandström and co-workers[12c] reported a bond length of 2.207 Å for the seventh, "exchanging" water molecule, which is equivalent to the r(Ti−O) value of 2.246 Å found in this work. In conclusion, these structural considerations imply the operation of a limiting A mechanism. Further verification of this is given by the Δ value, which parallels the volume of activation[13,15] and is found to be as negative as −0.958 Å. The energy of activation $\Delta E^{\#}$ is 15.8 kcal mol^{-1} and thus significantly larger than the experimental enthalpy of activation $\Delta H^{\#}$ of 10.3 kcal mol^{-1}.[27] This might be due to the neglect of solvent contributions from the second coordination sphere and must thus be treated with caution. However, frequency analysis of complex (6,1)$^{\#}$ clearly characterizes it as a transition state with only one imaginary vibration involving only the movement of the incoming water toward the metal center. The reaction energy for the overall formation of complex (7,0) from reactant (6,1) is 14.5 kcal mol^{-1}, confirming that complex (7,0) is an intermediate in the water exchange reaction of [Ti(H$_2$O)$_6$]$^{3+}$, since such an intermediate may not be more stable than its preceding reactant but must be a local minimum with respect to the potential hypersurface in order to be experimentally "detectable". The energy difference between transition state (6,1)$^{\#}$ and intermediate (7,0), however, is only 1.3 kcal mol^{-1}. Therefore, whereas structural considerations (e.g., Ti−O bond lengths and Δ value) unequivocally imply a limiting A substitution mode, this small energy difference suggests a mechanism with more I_a character (i.e., a *concerted* interchange of the water molecules). A limiting A mechanism should form a true intermediate, which, although less stable than the reactant, should be energetically clearly distinguishable from the transition state.

(c) Proton-Transfer Process. To estimate the energy required for the deprotonation of a water molecule coordinated directly to Ti(III), an in vacuo ($T = 0$ K) proton-transfer process between the first and second coordination sphere water molecules according to eq 4 was examined further. This gas-phase approach to the hydrolysis of hexahydrated Ti(III) leads to an uncommon but surprisingly stable dication:cation pair [Ti(H$_2$O)$_5$-(OH)]$^{2+}$·H$_3$O$^+$. The parameters used to characterize structural changes occurring during this process comprise the bond distance between titanium and the oxygens of water molecules in the first coordination sphere r(Ti−O$_I$), the bond distances between titanium and oxygen of the donor water molecule r(Ti−O$_d$), the distance between titanium and oxygen of the water molecule in the second coordination sphere r(Ti−O$_{II}$), the bond distance between oxygen and hydrogen of the donor water molecule r(Ti−OH···H), and the distance between oxygen and hydrogen of the acceptor water molecule r(H···OH$_2$). All of these structural parameters are summarized in Table 3, whereas Figure 3 sketches the structures of the transition state and the product involved in this proton-transfer process. The second sphere water of complex (6,1), which was discussed before (Figure 2, Table 2), now does not act as a potential entering group but rather is used as a base, prone to accept a hydrogen from a water molecule of the first coordination sphere. The bond
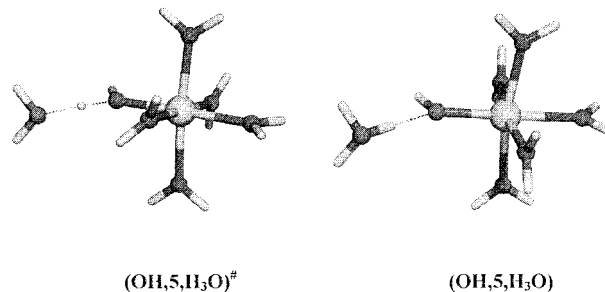

(OH,5,H$_3$O)$^{\#}$ **(OH,5,H$_3$O)**

Figure 3. Transition state (OH,5,H$_3$O)$^{\#}$ and product complex (OH,5,H$_3$O) according to eq 4. The corresponding reactant (6,1) is shown in Figure 2.

distance between hydrogen and oxygen of the donor water molecules is 1.003 Å, whereas the distance between this hydrogen and the oxygen of the water molecule located in the second coordination sphere is 1.724 Å. On lengthening the former bond, transition state (OH,5,H$_3$O)$^{\#}$ is reached. The r(Ti−OH···H) value for the donor water molecule is slightly elongated to 1.085 Å, whereas the r(H···OH$_2$) distance is shortened to 1.391 Å. The distance between titanium and the oxygen of the water molecule in the second coordination sphere is 3.928 Å, whereas the bond distance from the metal center to the oxygen of the donor water is shortened to 1.990 Å. This, however, shows that the more the proton transfer evolves, the more pronounced will the hydroxo character of the donor water ligand of the first coordination sphere be and the more obvious is the resemblance of the water molecule in the second coordination sphere with an oxonium ion. Passing through this transition state results in the formation of the product complex (OH,5,H$_3$O), which shows small but nevertheless significant changes in the Ti−O bond lengths of the water molecules directly coordinated to the metal ion compared to the starting complex (6,1) and the transition state (OH,5,H$_3$O)$^{\#}$. The bond distance between titanium and the oxygen of the water molecule in the second coordination sphere is as large as 4.227 Å, thus resembling the repulsion between the two positively charged molecular fragments [Ti(H$_2$O)$_5$-(OH)]$^{2+}$ and H$_3$O$^+$. However, despite this repulsion, the product complex is surprisingly more stable than the reactant by 4.5 kcal mol^{-1}. The bond length between titanium and the oxygen of the donor water molecule is only 1.881 Å, whereas the mean value of the r(Ti−O$_I$) bond lengths increases from 2.101 Å in the starting complex (6,1), to 2.112 Å in the transition state (OH,5,H$_3$O)$^{\#}$, and finally to 2.149 Å in the product complex (OH,5,H$_3$O). The overall difference of this mean bond length is 0.048 Å and can be interpreted as bond weakening induced by the OH$^-$ ligand. The difference between the Ti−O bond lengths of the water molecule in the trans-position to the OH$^-$ ligand and the largest Ti−O bond lengths of coordinated water is, however, as small as 0.009 Å, which does not account for a very pronounced trans influence.

The energy of activation for the reaction sequence (6,1) → (OH,5,H$_3$O)$^{\#}$ → (OH,5,H$_3$O) is 1.3 kcal mol^{-1} using the SHA+6-311+G(d,p) basis set *without* consideration of the ZPE and −0.1 kcal mol^{-1} with the inclusion of ZPE corrections.

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This, however, indicates an extremely small activation barrier for the proton transfer between water molecules of the first and second coordination spheres and implies that the energy barrier for the "hydrolysis" of $[Ti(H_2O)_6]^{3+}$ to form $[Ti(H_2O)_5(OH)]^{2+}$ is almost zero within this gas-phase approach. Although it is not justified to transfer these results rigorously to solution, they are in agreement with a low pK_{a1} value for hexahydrated Ti-(III) ions,[8] and thus a base-catalyzed D or I_d mechanism for its water exchange reaction should in principle be possible and comparable to the analogous mechanistic changeover found for other trivalent transition metal ions[11] and even for hydrated Al-(III).[30] In addition, the complexes discussed in this section are shown to be reasonable by comparing them to the results of Martin and co-workers,[31] who investigated the general mechanism of hydrolysis of Fe(III) ions in aqueous solution using DFT approaches. They calculated the $r(Fe-O)$ distances of the hydroxo–aqua complex $[Fe(H_2O)_5(OH)]^{2+}$ to be in the range of 2.103–2.150 Å, with an Fe–OH bond length of 1.760 Å.[31]

(d) Dissociative Water Exchange of Ti(III) Ions. To cover the water exchange reaction of hydrated Ti(III) fully, all theoretically possible exchange pathways must be investigated. Rotzinger has shown[13] that at an ab initio HF level of theory, the limiting D-mechanism should in principle be possible for the water exchange reaction of $[Ti(H_2O)_6]^{3+}$, but can be ruled out because of its relatively high energy of activation compared to the limiting A mechanism. In the present DFT calculations, however, no suitable structures representing a transition state or intermediate complex involved in eq 3 could be found. Instead, any approach to the limiting D mechanism invariably led to structures suggesting that the leaving water molecule deprotonates a neighboring water molecule before it enters the second coordination sphere completely as an H_3O^+ ion, leaving behind a hydroxo–aqua complex of Ti(III). Consequently, a limiting D (eq 3) or a dissociative interchange I_d (eq 2) mechanism may not be possible for this trivalent metal ion unless deprotonation, and thus the appropriate hydroxo–aqua complexes of Ti(III), are considered. This behavior, although new for hydrated Ti(III), is well-known in inorganic reaction kinetics and resembles the known water exchange mechanisms of complexes of the general type $[M(H_2O)_6]^{3+}$ with M = Cr,[10] Fe,[8] Ru.[32] These undergo water exchange via an I_a mechanism, whereas the analogous reactions of the corresponding hydroxo–aqua complexes $[M(H_2O)_5(OH)]^{2+}$, with M = Cr,[10] Fe,[8] Ru[32] are of a dissociatively activated I_d character. The exchange rate, presumably with respect to the water molecule in the trans-position to the hydroxo ligand, is generally enhanced by a factor of 10^2–10^3, by labilizing effects of the coordinated OH^-.[10,11,28,32] Therefore, to account for "hydrolyzed" Ti(III) species, the D mechanism shown in eq 3 must be slightly modified to eqs 5 and 6.

Structural presentations of the complexes found for the reaction (OH,5,0) → (OH,4,1)# → (OH,4,1) (eq 5) are shown in Figure 4. Table 4 summarizes selected structural parameters. At the start of the reaction, the $r(Ti-O_{tr})$ value represents the distance between titanium and the oxygen of the water ligand in the trans-position to the hydroxo ligand. As the reaction proceeds, this value is changed to the $r(Ti-O_{II})$ value introduced earlier in order to describe the reaction path of the entering/leaving water molecule.

The reactant complex (OH,5,0) has a Ti–OH bond length of 1.742 Å. The bond length between titanium and oxygen of the water molecule in the trans-position to the OH^- ligand is 2.205 Å and therefore elongated compared to the $r(Ti-O_I)$ values of the remaining water molecules, which lie between 2.157 and

(OH,5,0)

(OH,4,1)#   **(OH,4,1)**

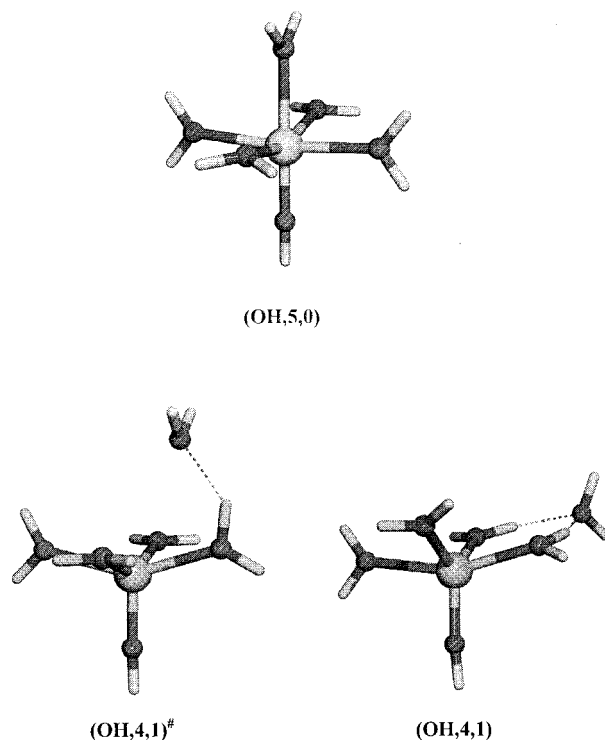**Figure 4.** Reactant (OH,5,0), transition state (OH,4,1)#, and intermediate (OH,4,1) according to eq 5.

2.190 Å. The difference between the $Ti-O_{tr}$ and the longest $Ti-O_I$ bond lengths is only 0.015 Å, thus implying only a slight trans influence by the hydroxo ligand. However, comparison of the mean value of all $Ti-O_I$ bond lengths of 2.174 Å with the $r(Ti-O_{tr})$ value of 2.205 Å, reveals a more pronounced effect, of 0.031 Å, which can be interpreted as a general structural labilization by the OH^- ligand exerted on all water molecules in the first coordination sphere.
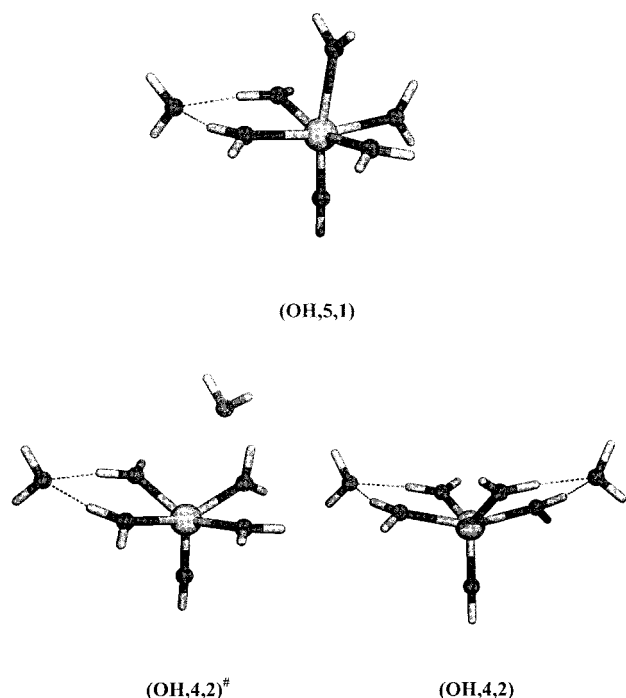
For reproducing the water exchange reactions according to eqs 5 and 6, the respective water molecules in the trans-position to the hydroxo ligand were used. Within the reaction scheme (OH,5,0) → (OH,4,1)# → (OH,4,1) (Figure 4, eq 5) a lengthening of the $Ti-O_{tr}$ bond leads to the C_s-symmetric transition state (OH,4,1)#. Now the $Ti-O_{tr}$ bond length is as large as 3.243 Å and implies a strong dissociative character compared to the other $Ti-O_I$ bond lengths. The Δ value[13,15] is 0.877 Å and therefore even larger than the analogous value obtained for the water exchange reaction of Zn(II), which was found to follow a limiting D mechanism.[15] Passing through this transition state gives intermediate (OH,4,1), in which the leaving water molecule is now completely located in the second coordination sphere of the hydroxo–aqua titanium complex and bound to two water molecules of the first coordination sphere via hydrogen bonds. The $Ti-O_{tr}$ (viz. $Ti-O_{II}$) bond length is 3.886 Å, whereas the Ti–OH bond is 1.728 Å. The overall energy of activation for this reaction was calculated to be 9.8 kcal mol^{-1}. Reactant (OH,5,0) is more stable than complex (OH,4,1) by 2.3 kcal mol^{-1}, which makes the latter complex an intermediate for this reaction. In addition, the relative energy between transition state (OH,4,1)# and intermediate (OH,4,1) is as large as 7.5 kcal mol^{-1}, favoring the intermediate, and therefore further justifies the assignment of a limiting D mechanism for this reaction. The energy barrier of the limiting D mechanism is thus 6.0 kcal mol^{-1} smaller than for the limiting A mechanism.

Consideration of an activationless deprotonation of hexahydrated Ti(III) further implies that the operation of a base-

TABLE 4: Selected Structural Parameters r(Ti−O$_I$), r(Ti−O$_{II}$), and r(Ti−OH) (Å), Relative Energies ΔE (kcal mol^{-1}), and Point Group Assignment for Structures Involved in the Water Exchange Reactions According to Eqs 5 and 6^a

	r(Ti−O$_I$)	r(Ti−O$_{tr}$)/r(Ti−O$_{II}$)	r(Ti−OH)	ΔE	Σr(Ti−O/OH)	PG
(OH,5,0)	2.157, 2.158, 2.190, 2.190	2.205	1.742		12.642	C_1
(OH,4,1)$^{\#}$	2.118, 2.118, 2.121, 2.185	3.243	1.722	9.8^b	13.507	C_s
(OH,4,1)	2.078, 2.112, 2.112, 2.194	3.886	1.728	2.3^c	14.110	C_1
(OH,5,1)	2.130, 2.136, 2.177, 2.205,	2.223, 3.909	1.746		16.526	C_1
(OH,4,2)$^{\#}$	2.103, 2.110, 2.135, 2.139	3.185, 3.902	1.727	7.2^d	17.301	C_1
(OH,4,2)	2.135, 2.135, 2.089, 2.089	3.921, 3.921	1.732	−0.2^e	18.022	C_2

^{a} The sum of all titanium−oxygen bond lengths (i.e., r(T−O$_I$), r(T−O$_{tr}$)/r(Ti−O$_{II}$), and r(T−OH)) is given as Σr(Ti−O/OH). All values shown were obtained with B3LYP/SHA+6-311+G(d,p)//B3LYP/SHA+6-311+G(d,p). ^{b} Energy of activation (OH,5,0) → (OH,4,1)$^{\#}$. ^{c} Reaction energy (OH,5,0) → (OH,4,1). ^{d} Energy of activation (OH,5,1) → (OH,4,2)$^{\#}$. ^{e} Reaction energy (OH,5,1) → (OH,4,2).

(OH,5,1)

(OH,4,2)$^{\#}$ **(OH,4,2)**

Figure 5. Reactant (OH,5,1), transition state (OH,4,2)$^{\#}$, and intermediate (OH,4,2) according to eq 6.

catalyzed D or I$_d$ mechanism for the water exchange reaction should be considered as an alternative for the water exchange mechanism of hydrated Ti(III). To study this exchange behavior further, the model cluster was extended by an additional water molecule in the second coordination sphere, which may act as an entering ligand and thus enables the simulation of a theoretically possible interchange mechanism (I$_d$). The overall reaction sequence (OH,5,1) → (OH,4,2)$^{\#}$ → (OH,4,2) (Figure 5, eq 6), however, clearly indicates that this additional water molecule shows no tendency to penetrate the first coordination sphere when the water molecule in the trans-position to the hydroxo ligand is removed. In reactant (OH,5,1) a water molecule located in the second coordination sphere is bound via hydrogen bonds to water molecules of the first coordination sphere. The distance between this water molecule and titanium is 3.909 Å. On approaching the transition state (OH,4,2)$^{\#}$, the Ti−O$_{tr}$ bond is lengthened from 2.223 Å in (OH,5,1) to 3.185 Å, whereas the distance between the second sphere water molecule and titanium remains almost unchanged at 3.902 Å. This, however, clearly shows that there is no tendency for a penetration of the first coordination sphere during the water exchange reaction and thus rules out the operation of an I$_d$ mechanism within this gas-phase cluster approximation. This is also supported by the relative structural difference between (OH,4,2)$^{\#}$ and (OH,5,1) (Δ value), which is 0.775 Å and, although smaller than the one reported for the reaction (OH,5,0)

→ (OH,4,1)$^{\#}$ → (OH,4,1) (Figure 4, eq 5), can be considered as a reasonable value for a limiting D mechanism.[15] The final intermediate (OH,4,2) has two water molecules in its second coordination sphere with r(Ti−O$_{II}$) distances of 3.921 Å. The energy of activation for this reaction was calculated to be 7.2 kcal mol^{-1}, thus clearly implying that deprotonation of a first sphere water molecule enhances the water exchange reaction considerably when compared to the water exchange reaction for [Ti(H$_2$O)$_6$]$^{3+}$. In addition, this also leads to a changeover in the preferred exchange mechanism. Surprisingly, intermediate (OH,4,2) is almost as stable as reactant (OH,5,1), which is shown by a very small reacton energy of −0.2 kcal mol^{-1}. However, taking into account the limitations of the model clusters used, which do not consider additional interactions with second and/or third sphere water molecules, the stability of intermediate (OH,4,2) might be an artifact.

Conclusions

Within the presented in vacuo approach to the hydration and water exchange mechanism of hydrated and hydrolyzed Ti(III) ion, we suggest the energetically most favorable conformer of hexahydrated Ti(III) to be of C_i symmetry. Structural parameters such as the Ti−O bond length (2.094 Å) closely resemble those obtained using D_{3d} symmetry. In addition, the energy difference between the C_i and the D_{3d} complexes is less than 1.0 kcal mol^{-1}, favoring the former. Therefore, we conclude that a time-averaging between the C_i structures results in a D_{3d}-symmetric structure (electronic state ^{2}A$_{1g}$), which is most likely the gas-phase description of the [Ti(H$_2$O)$_6$]$^{3+}$ complex. The water exchange reaction of the hydrated Ti(III) ion was studied using both the [Ti(H$_2$O)$_6$]$^{3+}$ complex and its hydrolyzed analogues [Ti(H$_2$O)$_5$(OH)]$^{2+}$ and [Ti(H$_2$O)$_5$(OH)]$^{2+}$·H$_2$O. On the basis of structural considerations, a limiting A mechanism was found for the water exchange reaction of [Ti(H$_2$O)$_6$]$^{3+}$. The small energy difference of 1.3 kcal mol^{-1} between transition state and intermediate, however, also implies that an I_a mechanism should in principle be possible. The energy of activation was calculated to be 15.8 kcal mol^{-1}, significantly higher than the experimental enthalpy of activation. The water exchange reactions of the latter two complexes, however, were found to follow limiting D mechanisms. The energy of activation was calculated to be 9.8 and 7.2 kcal mol^{-1}, respectively The effect exerted from the OH$^-$ ligand to the other water molecules in the first coordination sphere, especially to the water molecule in the trans-position to the hydroxo ligand, is small but nevertheless significant, as it could be shown by the decrease in the activation energy for the water exchange processes of this ion.

To compare the water exchange mechanisms found for [Ti(H$_2$O)$_6$]$^{3+}$ and [Ti(H$_2$O)$_5$(OH)]$^{2+}$ and [Ti(H$_2$O)$_5$(OH)]$^{2+}$·H$_2$O, respectively, with each other, a proton-transfer process leading to such hydroxo−aqua species was studied in more detail. Within this approach a water molecule of the first coordination

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sphere acts as the H-donor, whereas the water molecule in the second coordination sphere acts as the H-acceptor. In the present case, such a proton-transfer process can be expected to be activationless and thus emphasizes the readiness of hydrated Ti(III) to deprotonate spontaneously in an aqueous medium, making it a relatively strong acid with strength ($pK_{a1} \sim 2.2$)[8] comparabl to that of $[Fe(H_2O)_6]^{3+}$.

Despite the limitations of the gas-phase cluster approximation used in our studies, this approach to the water exchange reaction of hydrated Ti(III) is sophisticated enough to indicate a mechanistic changeover in the water exchange mechanisms of $[Ti(H_2O)_6]^{3+}$ and $[Ti(H_2O)_5(OH)]^{2+}$, which can be expected on the basis of the available experimental data for the water exchange reactions of other trivalent metal ions.[8,10,11,30,32]

Supporting Information Available: A table including all of the total molecular energies and zero-point energy corrections (au) together with the archive entries produced by the programs. This material is available free of charge via the Internet at http://pubs.acs.org.

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