



# Theoretical study of hydrolysis reactions of tetravalent thorium ion

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## Abstract

The hydrolysis reaction of the tetravalent thorium ( $\text{Th}^{4+}$ ) ion was investigated by ab initio theoretical calculations on hydration complex models. The transition state structure was optimized, and the intrinsic reaction coordinate was traced. The results showed that the hydrolysis is highly exothermic and the transition state is close to the reactant. Reaction dependency upon the number of non-reactive water molecules was examined.

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## 1. Introduction

Recently, we have reported a series of theoretical studies on the hydration of tetravalent thorium ( $\text{Th}^{4+}$ ) as an archetypal of highvalent actinide ions [1–5]. The structure and dynamics of its hydration have been systematically calculated by the Stuttgart relativistic effective core potential (RECP) [6] and the so-called B3LYP hybrid density-functional theory [7] with the GAUSSIAN 98

code [8]. The calculated results have been compared with experimental observations [9–13]. The hydration number has been confirmed to be 9 or 10, and the importance of including the bulk solvent effect via the polarizable continuum model (PCM) [14] or its conductive variant (CPCM) [15] was demonstrated to estimate the Th–O distances in a good agreement with experiments in [3,5]. The electronic structure of the hydrated  $\text{Th}^{4+}$  was investigated by using all-electron Dirac–Hartree–Fock relativistic calculations implemented in the DIRAC code [16], and the nature of its coordinate bond, which is characterized by the electrostatic attraction of positive charge on the central metal atom and the electron donation from the water molecules, was revealed in detail in [3]. It was found that the O–H bond in the water molecule is weakened to enhance the electron donation

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through the reorganization induced by the interaction with the 6p semivalence shell of Th.

It has been well known that the  $\text{Th}^{4+}$  ion easily causes the hydrolysis reaction which is formally written as  $\text{Th}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{Th}(\text{OH})_2^{2+} + 2\text{H}_3\text{O}^+$  [17]. Tsushima et al. [5] calculated the hydration structures of the hydrolysis products  $\text{Th}(\text{OH})_n^{4-n}$  ( $n = 1-4$ ). However, the details of the reaction itself, such as the activation energy (AE) and the transition state (TS) structure, remained to be elucidated. As denoted above, the O–H bond in the coordinating water molecule should be weaker than in the free molecule, and the H atom has a more protonic character to which the other water molecule can easily attack to form the oxonium ion  $\text{H}_3\text{O}^+$  and the Th–OH bond. This consideration leads not to the simultaneous formation of two Th–OH bonds but to stepwise formations. As the thorium ion is surrounded by water molecules (or hydrated), this situation should be taken into account when one wishes to model the hydrolysis reactions.

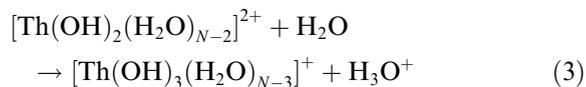
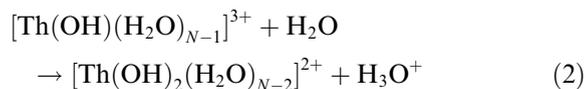
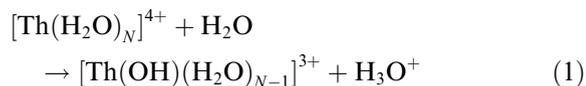
In this Letter, we report ab initio molecular orbital calculations on the thorium hydrolysis reactions in a stepwise way, by using hydration complex models. The high ionicity of the reaction system suggests that the reaction is highly exothermic and the TS is close to the reactant according to Hammond's rule. These predictions were verified by the optimized TS structure and the associated intrinsic reaction coordinate (IRC) [18]. We also discuss the dependency upon the number of non-reactive water molecules, and address the relation between the Mulliken net charges and AE values.

## 2. Computational method

All calculations reported in this Letter were carried out with the GAUSSIAN 98 program [8]. The hybrid density-functional theory (DFT) was used in the calculations. Namely, Becke's three-parameter hybrid method was employed with the LYP correlation functional (B3LYP) as the exchange-correlation functional [7,19,20]. The valence triple-zeta plus polarization functions (6-311G(d,p)) were used as the basis sets of O and H atoms. For the Th atom, the Stuttgart small

core RECP was used, where 30 outermost electrons were treated explicitly [6].

We examined the following stepwise model reactions to simulate the hydrolysis of a  $\text{Th}^{4+}$  ion.



We studied  $N = 1-4$  for reaction (1) and  $N = 4$  for reactions (2) and (3). These coordination numbers ( $N$ ) of Th ions in water are considerably smaller than the number suggested from our previous study, where  $N$  was considered to be 9–10 [1,4]. However, as is discussed below, we could not identify the TS at a larger coordination number ( $N \geq 5$ ) because the total-energy curve seemed to be too flat to determine the TS.

The total energy of the reactant must be subtracted from that of the TS (product) to compute the activation energy (reaction energy). If we define the sum of the total energy of an isolated hydrated Th ion and an isolated reagent  $\text{H}_2\text{O}$  molecule as the total energy of the reactant, this scheme corresponds to neglecting one dative bond formed between the hydrated Th ion and the reagent  $\text{H}_2\text{O}$  molecule. Thus, this scheme would result in high total energy for the reactant. To avoid this difficulty and to delete the ambiguity of the reactant, we used the IRC calculation. The IRC connects the TS both to the reactant and the product. We calculated that the IRC from the TS toward the reactant up to the molecular geometry was sufficiently close to the reactant. Since sizable forces still remained along the reaction coordinate in the geometry of the reactant obtained by the IRC calculation, we then fully relaxed the molecular geometry obtained by the IRC calculation and defined this geometry as that of the reactant. In reaction (1), the reactant determined through this procedure is substantially equivalent to the Th ion hydrated by  $N + 1$   $\text{H}_2\text{O}$  molecules.

On the other hand, to compute the product as a complex of hydrated Th ion and oxonium ion is difficult because of a repulsive interaction between these two positive ions. Thus, we used the sum of the total energy of hydrated Th ion and  $\text{H}_3\text{O}^+$  as the total energy of the product.

### 3. Results and discussion

We list the calculated results for reaction (1) in Table 1.  $\text{O}-\text{H}_a$ ,  $\text{O}-\text{H}_b$ ,  $\text{Th}-\text{O}_a$ , and  $\text{Th}-\text{O}_b$ , are bond distances at the TS, as is shown in Fig. 1 for  $N = 4$ . These bonds corresponded to breaking ones ( $\text{O}-\text{H}_a$  and  $\text{Th}-\text{O}_b$ ) and the forming one ( $\text{O}-\text{H}_b$ ) as the hydrolysis proceeded. The bonding character of  $\text{Th}-\text{O}_a$  was changed from a coordinate bond to a covalent but highly ionic bond as the reaction proceeded. All TS structures had only one imaginary frequency, which is shown in

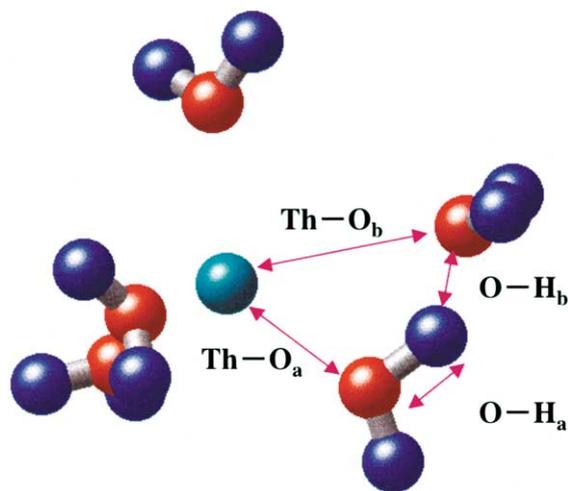


Fig. 1. Optimized geometry of the transition state of the reaction  $[\text{Th}(\text{H}_2\text{O})_4]^{4+} + \text{H}_2\text{O} \rightarrow [\text{Th}(\text{OH})(\text{H}_2\text{O})_3]^{3+} + \text{H}_3\text{O}^+$ .

Table 1. The imaginary frequency became softer as  $N$  increased. This result indicated that the total-energy curve became flatter around the TS as  $N$  increased. We found that the activation energy became lower and the  $\text{O}-\text{H}_a$  bond length became shorter as  $N$  increased. In addition, we noted that the length of  $\text{O}-\text{H}_a$  (1.076–1.146 Å) was quite close to that of the reactant (0.98 Å). According to Hammond's rule, these results suggest that the TS became closer to the reactant as the hydration number increased. Fig. 2a shows the result of IRC calculation for  $N = 4$ . We can clearly observe that the  $\text{O}-\text{H}_a$  bond breaks and the  $\text{O}-\text{H}_b$  bond forms as the reaction proceeds to form the  $\text{Th}-\text{O}_a$  bond and the oxonium ion. It should be noted that the elongating  $\text{Th}-\text{O}_b$  length in Fig. 2a means the increasing repulsion between the Th ion and the forming oxonium ion both of which are positively charged. The total-energy curve is flat around the TS is notable. We consider this is the reason why we could not identify the TS with a larger hydration number ( $N \geq 5$ ). We believe that a larger hydration number brings a flatter total-energy curve so that to determine the TS is difficult.

Although Table 1 shows the trend that the activation energy became lower as the hydration number increased, the current values (0.73–1.49 eV) are much too high when we consider that the reaction occurs easily at room temperature. Therefore, we should estimate an activation energy that corresponds to a large coordination number as is explained in more detail below.

Next, in Table 2, we show that the calculated results of the reactions (2) and (3) correspond to successive hydrolysis of reaction (1). We noted that the activation energy became lower and the  $\text{O}-\text{H}_a$  bond length became shorter as the number of OH that bonds to the Th ion increased. This result suggests that hydrolysis occurs more easily

Table 1

Activation (AE) and reaction (RE) energies (in eV), four bond lengths ( $\text{O}-\text{H}_a$ ,  $\text{O}-\text{H}_b$ ,  $\text{Th}-\text{O}_a$ ,  $\text{Th}-\text{O}_b$ ; in Å), and imaginary frequency ( $\nu_i$ ; in  $\text{cm}^{-1}$ ) at the transition state for  $N = 1-4$  cases of the first reaction (1)

Reaction	AE	RE	$\text{O}-\text{H}_a$	$\text{O}-\text{H}_b$	$\text{Th}-\text{O}_a$	$\text{Th}-\text{O}_b$	$\nu_i$
$[\text{Th}(\text{H}_2\text{O})_4]^{4+} + \text{H}_2\text{O}$	0.735	9.053	1.076	1.472	2.245	3.138	289.2
$[\text{Th}(\text{H}_2\text{O})_3]^{4+} + \text{H}_2\text{O}$	1.135	9.366	1.112	1.429	2.192	2.973	549.5
$[\text{Th}(\text{H}_2\text{O})_2]^{4+} + \text{H}_2\text{O}$	1.290	10.149	1.132	1.426	2.156	2.855	796.0
$[\text{Th}(\text{H}_2\text{O})]^{4+} + \text{H}_2\text{O}$	1.494	10.158	1.146	1.448	2.115	2.746	1014.6

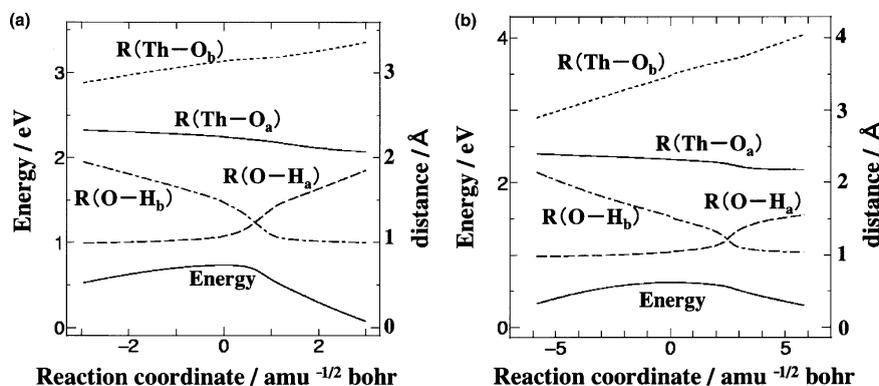


Fig. 2. (a) IRC of the first reaction  $[\text{Th}(\text{H}_2\text{O})_4]^{4+} + \text{H}_2\text{O} \rightarrow [\text{Th}(\text{OH})(\text{H}_2\text{O})_3]^{3+} + \text{H}_3\text{O}^+$  (refer also to Table 1). (b) IRC of the second reaction  $[\text{Th}(\text{OH})(\text{H}_2\text{O})_3]^{3+} + \text{H}_2\text{O} \rightarrow [\text{Th}(\text{OH})_2(\text{H}_2\text{O})_2]^{2+} + \text{H}_3\text{O}^+$  (refer also to Table 2).

Table 2

Activation (AE) and reaction (RE) energies (in eV), four bond lengths (O–H<sub>a</sub>, O–H<sub>b</sub>, Th–O<sub>a</sub>, Th–O<sub>b</sub>; in Å), and imaginary frequency ( $\nu_i$ ; in  $\text{cm}^{-1}$ ) at the transition state for  $N = 4$  case of the second reaction (2) and third reaction (3)

Reaction	AE	RE	O–H <sub>a</sub>	O–H <sub>b</sub>	Th–O <sub>a</sub>	Th–O <sub>b</sub>	$\nu_i$
$[\text{Th}(\text{OH})(\text{H}_2\text{O})_3]^{3+} + \text{H}_2\text{O}$	0.619	4.682	1.041	1.524	2.321	3.480	129.7
$[\text{Th}(\text{OH})_2(\text{H}_2\text{O})_2]^{2+} + \text{H}_2\text{O}$	0.489	0.517	1.011	1.598	2.428	3.705	72.2

in terms of kinetics as the number of OH bonds increases. On the other hand, exothermicity of reaction (3) was significantly smaller than that in reactions (1) and (2), which means that the reaction becomes less favorable in terms of thermodynamics as the number of OH bonds increases. At a large hydration number, where the activation energy is expected to be significantly low, thermodynamics may be more relevant to explain the reactivity of the hydrolysis of a Th ion.

Fig. 2b shows the result of IRC calculation for reaction (2). The total-energy curve is flatter around the TS than that of Fig. 2a. From the behavior of breaking bonds (O–H<sub>a</sub> and Th–O<sub>b</sub>) and the forming bond (O–H<sub>b</sub>), the calculated TS correctly described the hydrolysis of the Th ion.

We are now in a position to estimate the activation energy of hydrolysis at a large hydration number. The results obtained thus far showed two characteristics: (i) The activation energy decreased as the hydration number increased. (ii) The activation energy decreased as the number of OH bond increased. We consider that the charge of the Th ion is more effectively shielded when the hydration number is large. Moreover, the charge of

the Th ion is reduced when the bond with an OH<sup>−</sup> ion forms. Therefore, the interaction between the Th ion and the reagent H<sub>2</sub>O molecule becomes weak as the hydration number or the number of OH bonds increases. This brings about the situation that the reagent H<sub>2</sub>O molecule more easily causes a nucleophilic attack to a hydrated H<sub>2</sub>O molecule than to the Th ion itself.

The arguments above suggest that the activation energy of the hydrolysis is related to the charge of Th. We found that there is an almost linear relation between the Mulliken charge of Th at the TS and the activation energy. We also found that the Mulliken charge of Th at the TS was larger than that at the reactant by about 0.03 at most. Thus, by using the Mulliken charge of the Th in the reactant, we could estimate the activation energy of hydrolysis with a large hydration number from the regression line in Fig. 3. When the hydration number of the reactant ( $N + 1$ ) equaled 10, the Mulliken charge of the Th was 2.02. This corresponds to an activation energy of 0.31 eV. Although this value may be a bit large considering that the reaction proceeds at room temperature, we consider this extrapolation

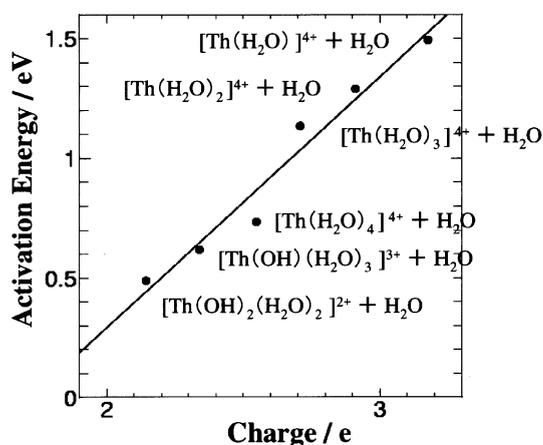


Fig. 3. Mulliken charge of Th atom at the reactant versus the activation energy for reactions (1)–(3).

procedure gives valuable information concerning the reactivity of Th ion in water, which is difficult to calculate directly.

#### 4. Summary

We performed ab initio molecular orbital calculations to investigate the hydrolysis of  $\text{Th}^{4+}$  ion. We found two characteristic points concerning the reactivity of the hydrolysis: (i) The activation energy decreases as the hydration number increases. (ii) The activation energy decreases as the number of OH bonds to Th increases. These findings suggest that the activation energy of the hydrolysis is related to the charge of Th. We also estimated the activation energy at a high coordination number, where the direct calculation was difficult.

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