Kinetics for the hydrolysis of Ti(OC₃H₇)₄: A molecular dynamics simulation study

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Abstract

Using molecular dynamics (MD) simulations in conjunction with a reactive force field method, the chemical kinetics of the hydrolysis of titanium tetraisopropoxide (Ti(OC₃H₇)₄, TTIP) at high-temperature conditions is investigated. The MD simulations allow for presenting the complete dynamic process of the TTIP conversion at the atomic level. The rate constant of TTIP hydrolysis at 1 atm is estimated to be \( k = 1.23 \times 10^{14} \exp(-11.323/T(K)) \) mol\(^{-1}\) cm\(^3\) s\(^{-1}\) using a second-order reaction model. On the basis of Ti-containing intermediate species profiles, the evolutions of the main decomposition products during the TTIP hydrolysis are identified and key reaction pathways are elucidated. The results show that the clusters are formed before TiO\(_2\) molecules are observed. During the decomposition, Ti-containing species with one or two C–O bonds and carbon-free species with more than two Ti–O bonds are formed and undergo two separate pathways. One is the combination via the formation of Ti–O–Ti bridges, forming early clusters that serve as precursors for large TiO\(_2\) nanoparticles. The other is the further decomposition to smaller molecules such as TiO\(_2\) that participate in the subsequent cluster formation. Interactions between Ti and O atoms in the cluster stabilize the large structure through the abstraction of water and \(-\text{C}_x\text{H}_y\) groups.

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1. Introduction

Titanium dioxide (TiO\(_2\)) nanoparticles are encountered in a wide range of industrial applications that include photocatalysis, pigments, semiconductors and gas sensors [1]. The chemical and physical properties of nanomaterials are strongly influenced by the size, shape and crystalline phase. Therefore, understanding the reaction mechanism and nucleation behavior is essential toward enabling the control of the particle growth during the synthesis process.

Gas-phase flame synthesis, one of the most scalable and economical technologies for producing well-controlled nanomaterials, combines advantages of a continuous single-step synthesis process with high throughput and fast processing time [2,3]. In this process, the high-temperature flame environment can be controlled to cover a wide range of operating conditions (e.g., temperature,
reactant concentration, residence time, etc.) [4]. Over recent years, several studies have been carried out to experimentally examine the synthesis of TiO$_2$ in flames focusing on the influence of pressure, temperature, and flame geometry [5–7]. However, due to the fact that chemical reactions and particle nucleation proceed on extremely short time-scales in typical flame environments, only a few experimental studies reported the detailed evolution from precursors to small clusters [3]. Therefore, the gas-phase kinetics and precursor reaction mechanisms at the early stage of the particle formation remain incompletely understood and require further investigations [8].

Titanium tetraisopropoxide (TTIP, Ti(OC$_3$H$_7$)$_4$) is commonly used as precursor for the production of TiO$_2$ in flames with chlorine-free byproducts and is safer in handling compared to titanium tetrachloride (TiCl$_4$). While the detailed kinetics of TiCl$_4$ oxidation has been extensively studied both theoretically [9,10] and experimentally [11], the detailed reaction process leading to the TiO$_2$ formation from TTIP is less explored. Two main global chemical pathways have been suggested for the TTIP conversion, namely thermal decomposition and hydrolysis. Thermal decomposition takes place above 573 K and hydrolysis occurs at a temperature as low as 380 K [12]. The overall reaction of the thermal decomposition was reported as [13],

$$\text{TTIP} \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_6 + 2\text{H}_2\text{O},$$

and a first-order rate constant was estimated from measuring the temperature-dependent propylene formation with a value of $k = 3.96 \times 10^7 \times \exp(-8479.7/T(\text{K}))$ s$^{-1}$. A reaction rate value derived from the measurement of the size distribution of sub-2 nm TiO$_2$ particles formed through the thermal decomposition of TTIP showed good agreement with these results [14].

The gas-phase hydrolysis of TTIP was studied by Seto et al. [15] by considering the global mechanism,

$$\text{TTIP} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_7\text{OH},$$

with a first-order rate constant given by $k = 3 \times 10^{15} \times \exp(-1013.9/T(\text{K}))$ s$^{-1}$ without providing further details on the evaluation of this rate constant in the original reference. Shmakov et al. [16] proposed a bimolecular reaction, TTIP + H$_2$O → Product, to describe the primary stage of the TTIP decomposition in H$_2$/O$_2$/Ar flames with a rate constant of $k = 2 \times 10^{12} \times \exp(-6140/T(\text{K}))$ mol$^{-1}$cm$^3$ s$^{-1}$. Their results support that the hydrolysis reaction pathway is the main contributor to the conversion of TTIP at high temperatures.

Most modeling work has been done by considering an overall one-step reaction without intermediate species [8,17]. However, detailed chemical mechanisms and rate constants of the elementary reactions are crucial towards the improved modeling of processes leading to the nanoparticle formation. Several attempts have been made focusing on the kinetic mechanisms underlying the TTIP decomposition. The decomposition of TTIP was assumed to proceed by successive $\beta$-hydride elimination of propene and the condensation polymerization for waterless atomic layer deposition [18]. Buerger et al. [19] derived a thermodynamically consistent chemical mechanism for the thermal decomposition of TTIP with Ti(OH)$_4$ taken as the final stable product.

While progress has been made on examining the thermal decomposition of TTIP, the hydrolysis mechanisms and nucleation kinetics of nanoclusters remain elusive. This is largely attributed to the absence of quantitative measurement techniques with high temporal resolution to resolve the ultrafast reaction rates. Previous classical molecular dynamics (MD) studies have explored the high-temperature dynamics of TiO$_2$ nanoparticles, including particle-particle interaction [20], collision [21], and coalescence [22]. By employing the ReaxFF reaction force field method, molecular dynamics simulations serve as a viable method to study the hydrolysis process prior to the nanoparticle formation at the atomic level.

The objective of this study is to obtain insight into the initial stage of the decomposition reaction of TTIP and the subsequent nanoparticle formation at high temperatures. For this purpose, ReaxFF MD simulations are performed for a range of temperatures and pressures to determine the rate constant and identify elementary reaction pathways. By analyzing the evolution of the main species and observing the cluster formation process, growth mechanisms are deduced. The remainder of this manuscript has the following structure. The MD simulation method and computational details are presented in Section 2. Simulation results are discussed in Section 3, and the paper finished by drawing conclusions for the kinetics of TTIP hydrolysis and cluster growth.

2. Computational method

The ReaxFF potential force-field [23], implemented in the LAMMPS package [24], is used for the MD simulations. The Ti/C/H/O ReaxFF force field in the present study has been employed to investigate MXenes (i.e., pristine Ti$_3$C$_2$(OH)$_2$) [25,26], and the interaction parameters of the Ti/O/H system were originally developed and validated for modeling the reaction of water with TiO$_2$ surfaces [27]. Here, the force field was validated by calculating the enthalpy of formation, $\Delta H_f$, 298.15 K, for TTIP by considering the unimolecular reaction (1), and all standard enthalpies of formation

$\text{TiO}_2 + 4\text{C}_3\text{H}_6 + 2\text{H}_2\text{O}$

$\rightarrow \text{TTIP}$
of the reference species are taken from the NIST database [28]. The computed value of $\Delta H_{f,298.15 K}$ is $-1497$ kJ/mol, which is in good agreement compared to the literature value of $-1509 \pm 3.3$ kJ/mol [19].

In the present study, 410 water molecules and 27 TTIP molecules in the gas phase with an initial water/TTIP ratio of 15 are simulated inside three-dimensional cubic periodic systems to study the hydrolysis reaction. For the simulations discussed here, three pressures with $P = \{1, 7, 238\}$ atm are considered as the initial system pressure. The initial pressure of 238 atm is high enough to ensure that the complete process takes place within a nanosecond timescale. The size of the simulation box for each temperature and pressure is calculated based on the ideal gas law. To delineate hydrolysis from thermal decomposition, separate simulations are conducted in which all water molecules are replaced by 27 TTIP molecules to maintain the total atom numbers at 1 atm.

All MD simulations are performed under NVT conditions (constant number of atoms, volume, and temperature) to study the hydrolysis of TTIP with fixed temperatures between 1500 K and 3000 K for each pressure. The NVT ensemble is employed to examine the influence of temperature on the reaction rate and obtain rate constants of the primary reaction. Every simulation begins with an energy minimization using a conjugate gradient algorithm to eliminate artifacts of the initialization. For each case, the atomic configuration is equilibrated at target temperatures in the NVT ensemble. The system temperature is controlled by the Nosé–Hoover thermostat with a damping constant of 10 fs. For ReaxFF simulations, a smaller time step is preferred because the atom charges and bond orders can change at every time step [29]. Here, a time step of 0.1 fs is adopted to ensure that collisions and reactions evolve smoothly. ReaxFF allows for bond formation and dissociation during MD simulations by employing a bond-order/bond-energy relationship [30]. A 0.3 bond-order cutoff is employed to identify molecules and analyze the species formed during the simulation.

## 3. Results and discussions

### 3.1. Global kinetic parameters

Fixed-temperature NVT MD simulations between 1500 K and 3000 K are performed for three different pressures to study the reaction pathways of TTIP hydrolysis. Figure 1a illustrates the initial configuration of the system inside an 8.55 nm periodic cube from a simulation at 2500 K and 238 atm. All molecules are randomly placed and energy minimized subsequently. Figure 1b and c shows snapshots at the simulation time of 500 ps and 1000 ps, respectively. At 500 ps, the TTIP molecules are fully consumed and Ti-containing intermediates are formed. The inset depicts the structure of a representative Ti-containing species from each snapshot. A cluster containing 26 Ti atoms is observed in Fig. 1c. We proceed with our discussion by focusing on the formation process of clusters, including the detailed analysis of the chemical reaction pathways and subsequent nucleation.

Figure 2 represents the number of TTIP ($N_{TTIP}$) and water ($N_{H_2O}$) molecules as a function of the simulation time obtained from NVT-MD simulations at a pressure of 238 atm and temperature ranging from 1500 K to 3000 K. The decomposition of TTIP occurs first, followed by the absorption of water with decomposition products. Here, these two processes are combined into one primary reaction path. The ratio of the consumed TTIP and water molecules is approximately unity, which supports an overall second-order reaction model during the primary stage. The kinetic parameters of the Arrhenius equation were calculated using the temperature dependence of the concentration profiles of TTIP and water following the second-order reaction model,

\[
  k = \frac{1}{(\text{H}_2\text{O}) - [\text{TTIP}]_0} \ln \left( \frac{[\text{TTIP}]_0\text{H}_2\text{O}}{[\text{H}_2\text{O}]_0[\text{TTIP}]} \right)
\]

where [TTIP] and [H$_2$O] denote the concentration of TTIP and H$_2$O at time $t$ and the subscript 0 refers to initial conditions. For each simulation point, three MD simulations are performed. From the Arrhenius plot in Fig. 3, Arrhenius parameters are determined through the linear equation, $\ln k = \ln A - \left(\frac{E_a}{RT}\right)$, where $A$ is the pre-exponential factor, $E_a$ is the activation energy and $R$ is the gas constant. The calculated activation energy is consistent at the three pressures with the standard deviation of 0.24 kJ/mol. At the ambient pressure of 1 atm, the rate constant has a value of $k = 1.23 \times 10^{14} \times \exp(-11, 323/T(K))$ mol$^{-1}$cm$^3$s$^{-1}$ with a corresponding activation energy of $E_a = 94.1$ kJ/mol. The result shows good agreement for the high-temperature regime with experimental results by Shmakov et al. [16] (black dashed line in Fig. 3) and is also consistent with the rate parameters from the water-assisted surface deposition of TTIP vapor [31]. In comparison with thermal decomposition, the first-order rate constant for hydrolysis is also calculated from $k = -(1/\tau)\ln([\text{TTIP}]/[\text{TTIP}]_0)$ (see Fig. S3 in the Supplementary Material).

### 3.2. Time evolution of main species

Simulation results at 2500 K and 238 atm are considered to examine the kinetics of the TTIP decomposition. In addition, simulation of a large system containing 216 TTIP and 3280 water molecules at the same condition is performed to conduct statistical analysis for the species evolution. The species involved in the formation pathways of TTIP...
hydrolysis are complicated and only major Ti-containing species are considered here. Based on the structure of TTIP, the hydrolysis reaction of TTIP can be divided into four stages, each involving the decomposition of one $\text{O}_x\text{C}_7\text{H}_{17}$ ($x = \{0, 1\}$) branch. The consumption of TTIP and the yields of major Ti-containing species during the reaction are shown in Fig. 4.

Over the duration of the simulation, the primary species is $\text{Ti}(\text{O})\text{(OC}_3\text{H}_7)_3$, due to the dissociation of one C–O bond at the first stage. Previous DFT calculations have shown that the energy barrier for the reaction via the C–O bond dissociation is lower by 2.8 kcal/mol compared to that for Ti–O bond dissociation [16], which supports our observation. This initial hydrolysis step is followed by a second stage that involves either the breaking of a Ti–O bond forming $\text{TiO(OC}_3\text{H}_7)_2$ or the breaking of a C–O bond forming $\text{Ti(O)(OH)(OC}_3\text{H}_7)_2$. The transfer of primary or secondary hydrogen from carbon to oxygen can lead to the release of a propylene molecule instead of iso-propyl during the reaction, generating hydroxyl rather than $\text{O}$ radicals. At the third stage, the dissociation of the C–O bond is thermodynamically preferred for $\text{TiO(OC}_3\text{H}_7)_2$ leading to the formation of $\text{TiO(OH)(OC}_3\text{H}_7)$ and $\text{TiO(O)(OH)(OC}_3\text{H}_7)$. While for $\text{Ti(O)(OH)(OC}_3\text{H}_7)_2$, the cleavage of Ti–O or C–O leads to the formation of three species as shown in Fig. 4c. The molar fraction of $\text{TiO(OH)(OC}_3\text{H}_7)$ increases slightly around 100 ps due to the decomposition of species from the second stage and the transfer of one hydrogen atom from a nearby $\text{H}_2\text{O}$ to $\text{TiO(O)(OC}_3\text{H}_7)$. 

![Fig. 1. Snapshots from an MD simulation at 2500 K and 238 atm containing 27 TTIP molecules and 410 water molecules showing (a) initial energy-minimized configuration, (b) $t = 500$ ps, and (c) $t = 1000$ ps (for color figure, gray = titanium, red = oxygen from TTIP, blue = carbon, white = hydrogen from TTIP, yellow = oxygen from water).](image)

![Fig. 2. Temporal evolution of TTIP and water molecules at a pressure of 238 atm and temperature ranging from 1500 K to 3000 K.](image)

![Fig. 3. Arrhenius plot from MD simulations showing the temperature dependence of the reaction rate constant for hydrolysis (open symbols). Experimental results from Shmakov et al. [16] are included for reference (solid symbols). Solid lines correspond to fitting formulas while the black dashed line fits the literature data above 1000 K.](image)
clude TiO(OH)$_2$, TiO(O')(OH), Ti''(OH)$_2$, TiO$_2$, Ti'(OH)$_2$ and Ti'O(OH), as shown in Fig. 4d.

It is worth noting that clusters, containing more than one Ti atom, appear before the first TiO$_2$ molecule is formed, as depicted in Fig. 4e. These nascent clusters contain propyl groups that are released during the subsequent nucleation. In order to examine the cluster formation and growth process completely, we consider the smaller system with 27 TTIP molecules in the next section in more detail.

3.3. Formation of nanoclusters

The conversion from precursors to TiO$_2$ nanoparticles is usually separated into two processes, namely the chemical reaction from precursors to TiO$_2$ molecule and the subsequent nucleation of single TiO$_2$ molecules to (TiO$_2$)$_n$ clusters. A semi-empirical reaction scheme was proposed earlier to describe the decomposition of TTIP, leading to the formation of Ti(OH)$_4$ as a stable intermediate and ultimately to a TiO$_2$ molecule [16]. Extensive computational studies on (TiO$_2$)$_n$ clusters have been performed, starting with TiO$_2$ monomers [33]. By measuring charged clusters with an atmospheric pressure interface time-of-flight (API-TOF) during flame synthesis using TTIP as the precursor, Fang et al. [1] observed the formation of intermediate organic species in the form of Ti$_x$C$_y$O$_w$H$_z$ prior to complete conversion to TiO$_2$. Here, by performing ReaxFF simulations, we are able to consider the conversion process as a whole and gain insight into the underlying mechanisms.

The initial steps of TiO$_2$ formation after TiCl$_4$ hydrolysis have been studied [9,34]. Partially oxygenated Ti-containing molecules (Ti$_x$O$_y$Cl$_z$(OH)$_w$) are formed that serve as precursors to TiO$_2$ nanoparticles. Energy analysis of hydrated (TiO$_2$)$_n$ clusters has shown that the dehydration reaction of two spatially available Ti(OH) groups is thermodynamically favored and enables further aggregation of clusters, which can be expressed as 2(Ti(OH)) $\rightarrow$ TiOTi + H$_2$O [35]. A similar reaction pathway is observed from our MD simulation for TTIP hydrolysis. Figure 5 illustrates one example of the formation of a Ti$_2$O$_4$ cluster with TiO(OH) and TiO(OCH$_2$H)$_2$ as initial species. The reaction is initiated by forming the Ti-O-Ti bridge to combine the two molecules. Subsequently, Ti and O atoms tend to interact with nearby O or Ti atoms, resulting in the distortion and reconstruction of the whole molecule [36]. After releasing two $\mathrm{C}_3\mathrm{H}_7$ groups and one water molecule, Ti$_2$O$_4$ is generated having a thermodynamically stable structure.

The detailed formation process of the large cluster, shown in Fig. 1c, is illustrated through the atomistic snapshots in Fig. 6. Each row starts with an early cluster containing two Ti atoms and only the stable structure of the cluster is shown.
Fig. 5. Ti$_2$O$_4$ formation pathway observed from the ReaxFF NVT-MD simulation at 2500 K and 238 atm.

Fig. 6. Snapshots of cluster formation over 1000 ps.

with the corresponding formula at each step. At the early stage of the cluster formation, the cluster grows slowly and subsequently combines with nearby small Ti-containing molecules one after another. The intermediates produced from TTIP hydrolysis aggregate into large clusters, showing good agreement with previous experimental results [1]. It is noted that small species containing Ti=O and Ti–OH play an important role. For species with Ti=O, e.g., TiO$_2$, the double bond breaks and forms Ti–O–Ti to combine two molecules. For species involving a Ti–OH group, e.g., Ti$^{2+}$(OH)$_2$, the molecule has one or more radical sites and tends to form stable bonds through recombination.

To stabilize the structure, the unsaturated Ti and O atoms on the outer surface of the cluster either continue to aggregate with other Ti-containing species from the surrounding or restructure the surface. In the meantime, the abundant water molecules in the surrounding environment will adsorb on the clusters molecularly or dissociatively. For molecular adsorption, the oxygen atom of the water molecule binds to an under-coordinated Ti atom, as seen from the structure of Ti$_{26}$O$_{31}$H$_6$ in Fig. 6. While in dissociative adsorption, the water molecule forms a hydrogen bond with a surface O atom forming a hydroxyl group, which can be observed for the formation of Ti$_3$O$_6$H$_3$ in the second row of Fig. 6.

For bulk TiO$_2$, the coordination number of Ti atoms in anatase, rutile, and brookite is 6 and that of O atoms is 3. While for amorphous titanium dioxide of small size, the averaged Ti–O coordination number reduces to around 5 mainly because most Ti atoms are located in the outer shell and the lattice is contracted in the core [37]. Here, we tracked the averaged Ti–O bond number for all the Ti and O atoms that have contributed to the formation of the large cluster (Ti$_{26}$O$_{31}$H$_6$), as shown in Fig. 7. From the beginning to around 100 ps, the
main Ti–O bond number drops from 4 to approximately 3 for Ti atoms due to the decomposition of TTIP, while the coordination number remains almost constant for O atoms that originate from TTIP and water. The coordination number of Ti–O bonds continually increases and reaches a value of 3 for O atoms due to cluster formation, which is consistent with the theoretical value. Since most Ti atoms are still unsaturated, the value of the average number of Ti–O bonds increases to 3.8 for Ti with an increasing trend at 1000 ps. This result indicates that generally only one Ti–O bond breaks during the whole conversion process for TTIP molecules. Compared with the breaking of two Ti–O bonds to obtain TiO2 and the formation of one Ti–O bond to build clusters, this is an energetically more favorable pathway. High resolution and ultrafast measurements are necessary to experimentally validate these findings.

4. Conclusions

In this work, the kinetics of the TTIP hydrolysis reaction is investigated by performing ReaxFF molecular dynamics simulations at temperatures ranging from 1500 K to 3000 K. The simulation results are used to identify chemical reactions, important intermediate species, and cluster formation pathways during the conversion process from the gas-phase precursor TTIP to small clusters. Knowledge of the nascent particle formation and growth can bridge the gap between chemical reactions and further particle growth at the nanometer scale, providing guidance for nanomaterial production.

The following conclusions are drawn from this study:

(1) Kinetic parameters for TTIP hydrolysis are estimated from simulations over a wide range of temperature and pressure conditions. Using a second-order reaction model, the determined rate constant at a pressure of 1 atm is $k = 1.23 \times 10^{14} \times \exp(-11, 323/T(\text{K}))$ mol$^{-1}$cm$^3$ s$^{-1}$.

(2) The species analysis indicates that the main reaction scheme of TTIP hydrolysis at high temperatures proceeds through the following stages: dissociation of a C–O bond to form Ti(O')(OC$_3$H$_7$)$_2$; breakage of a Ti–O bond or a C–O bond to form TiO(OC$_3$H$_7$)$_2$ or Ti(O')OH(OC$_3$H$_7$)$_2$; and C–O cleavage preferred for TiO(OC$_3$H$_7$)$_2$ leading to the formation of TiO(OH)(OC$_3$H$_7$) and TiO(O')(OC$_3$H$_7$) at the third stage. Then the species directly combine to form clusters or continue to release the remaining –O, C$_3$H$_7$ groups to create small intermediates, such as TiO(OH)$_2$, TiO(OH)$_2$, Ti'O(OH)$_2$.

(3) Early clusters are observed before the first TiO$_2$ molecule appears in the simulation. The cluster formation is initiated by forming a Ti–O–Ti bridge to combine two molecules, which is followed by the interactions between Ti and O atoms, resulting in the restructuring and release of water or –C$_3$H$_7$ groups. Further work is necessary to experimentally validate the mechanism proposed from the simulations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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