

Reaction Mechanism for the Hydrolysis of Titanium Alkoxides

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Metal alkoxides have strong reactivities due to the difference of polarizabilities between metal and alkoxy groups. Hence, many kinds of metal alkoxides can be hydrolyzed with ease and transformed to metal oxide powder *via* a condensation-polymerization reaction of the hydrolyzed species. The hydrolysis reaction mechanisms of the metal alkoxides depend on the electron affinities, sizes and charges of metal ions and alkoxy groups.¹⁻³ In the case of alkoxides that have the same metal ions, the sizes and numbers of alkoxy groups play an important role in the hydrolysis reaction. Examples are found in silicon alkoxide where the reaction rates of hydrolysis decrease with increasing size of the alkoxy groups through steric effects.^{4,5} Reaction rates or mechanisms of metal alkoxides can be also changed by the kinds of metal ions. Particularly, the transition metal ions, which have different oxidation states, have different electron affinities, sizes and coordination numbers, so careful investigation of the hydrolysis of transition metal alkoxides is required.² The kinetic studies on the hydrolysis reactions of metal alkoxides, in general, have been carried out by spectroscopic methods⁶⁻⁸ such as NMR, Raman, Infrared, UV, etc. Extensive kinetic data for the silicon alkoxides^{9,10} have been obtained by the above methods, but very few kinetic results for the transition metal alkoxides have been reported.

In this study, the hydrolysis reaction rate and mechanism of the titanium tetra ethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) were investigated by the use of the UV spectroscopic method and the results were compared with those of the other titanium alkoxides reported in our previous works.¹¹⁻¹³

Experimental Section

4.5×10^{-3} M titanium tetra ethoxide [$\text{Ti}(\text{OEt})_4$] was hydrolyzed by adding 0.5-0.7 M H_2O dropwise. Ethanol was used as solvent to make these solutions and the reaction temperatures were adjusted in the range of 25-35 °C. The concentration of H_2O was in excess compared to that of $\text{Ti}(\text{OEt})_4$. Therefore the hydrolysis reaction was estimated to proceed in a pseudo-first order reaction. The UV absorbance of the solution was measured at a certain wavelength during the course of reaction and its rate constant was calculated from the variation of UV absorbance with time. The wavelength used to measure the absorbance was selected where the absorbance varied regularly; 310 nm, which was 10 nm

longer than the wavelength of the maximum absorbance, 300 nm, of $\text{Ti}(\text{OEt})_4$ solution. The absorbance variations with time were measured in H_2O concentrations ranging from 0.5 M to 0.7 M and at temperatures of 25 °C, 30 °C and 35 °C. With these data, the rate constants of the pseudo-first order reaction (k_{obs}) were calculated by the following Guggenheim equation.¹¹

$$\ln(A_{t+\Delta t} - A_t) = -k_{\text{obs}} \cdot t + \text{constants}$$

Here, A_t is the absorbance at 310 nm, time t and $A_{t+\Delta t}$ is the absolute equilibrium absorbance which is an absorbance at a time 2-3 times longer than the half-life.

Results and Discussion

The reaction is thought to be composed of two stages. One is a hydrolysis stage where $\text{Ti}(\text{OEt})_4$ is hydrolyzed to form Ti-OH bonds. In this stage, UV absorbance of the solution increases gradually. The other stage is a condensation polymerization stage where Ti-O-Ti bonds form resulting in the creation of a three-dimensional structure, which precipitates out of solution. In this stage, the absorbance increases quickly. This rapid increase in absorbance makes it very difficult to determine the absolute equilibrium point of absorbance. Therefore, the hydrolysis reaction stage, where UV absorbance increases gradually, was used to determine the reaction rate constant. The absorbance measured just before precipitation began was chosen as the absolute equilibrium absorbance ($A_{t+\Delta t}$) and the half-life ($t_{1/2}$) was determined using the above equilibrium absorbance.

Figure 1 shows the absorbance changes with time at various temperatures (a) and H_2O concentrations (b). It can be seen from Figure 1 that the absorbance ($\ln(A_{t+\Delta t} - A_t)$) varies linearly with time at any temperatures and H_2O concentration, obeying Guggenheim's equation. This means that the absolute equilibrium absorbance chosen above coincides with the Guggenheim's equilibrium absorbance. It is also confirmed from Figure 1 that the slopes of the straight lines increase with increasing temperature (a) and H_2O concentration (b). The slope of the straight line of absorbance change corresponds to the 1st order reaction rate constant for the $\text{Ti}(\text{OEt})_4$ hydrolysis, k_{obs} , in the Guggenheim method. The increase in the slope, showed in Figure 1, indicates that the 1st order rate constants increase with increasing temperature and H_2O concentration.

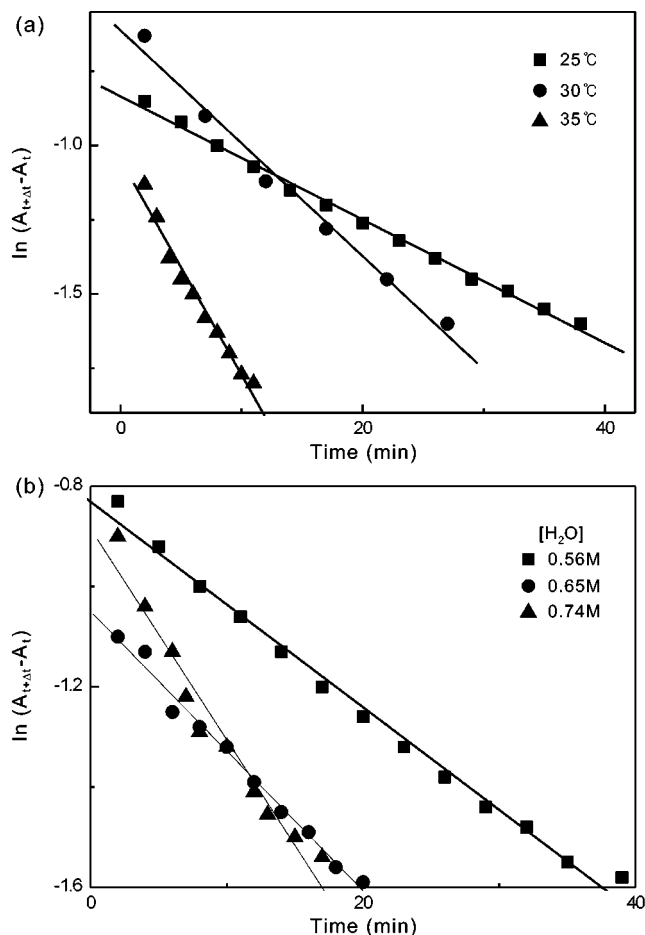


Figure 1. Plots of $\ln(A_{t,31} - A_t)$ vs. time for the hydrolysis of $\text{Ti}(\text{OEt})_4$ at various temperatures (a) and various concentration of H_2O (b).

Kivinen¹⁵ explained the relationship between the rate constants and H_2O concentrations in the following equation, with assumption that n molecules of H_2O participate in the initial hydrolysis reaction to form the transition state.

$$\ln k_{\text{obs}} = n \cdot \ln[\text{H}_2\text{O}] + \ln k_{\text{exp}}$$

By Kivinen's equation, a linear relationship exists between the log values of H_2O concentration and rate constant of the pseudo-first order reaction. In this plot, the slope of a straight line indicates the number of H_2O (n -value) which participates in the initial hydrolysis reaction and the intercept implies the second order rate constant (k_{exp}). In addition, Kivinen interpreted the reaction to proceed *via* a bimolecular path when the slopes of the straight line, n -value, were 2-3, while in the case of n -value of 6-7, the reaction occurred *via* a unimolecular path.¹⁵

The plot of Kivinen's equation for the hydrolysis of $\text{Ti}(\text{OEt})_4$ is shown in Figure 2. This plot gives straight lines at various temperatures and we can estimate that the hydrolysis of $\text{Ti}(\text{OEt})_4$ obeys Kivinen's equation. Moreover, it can be seen from Figure 2 that the slope of the straight lines, the numbers of H_2O molecules (n), increase with increasing temperature. n -values calculated from the slopes

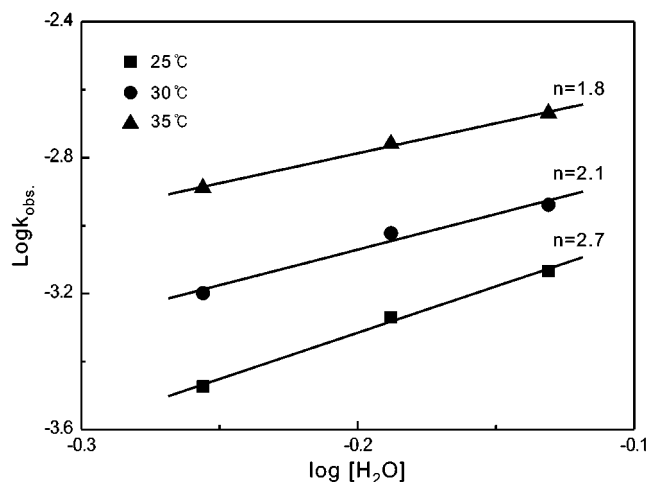


Figure 2. Plots of $\log[\text{H}_2\text{O}]$ vs. $\log k_{\text{obs}}$ for the hydrolysis of $\text{Ti}(\text{OEt})_4$ at various temperatures (n : the number of H_2O molecules).

of the straight lines in Figure 2 were 1.8-2.7. The second order rate constants, k_{exp} , were also determined from the intercept of straight lines. By Kivinen's n -value criterion, the reaction path to the transition state for the hydrolysis of $\text{Ti}(\text{OEt})_4$ is bimolecular from the above n -values. The temperature dependence of the rate constant can be discussed using the well known Arrhenius equation ($\ln k = \ln A - (E_a/RT)$). This equation was applied to the temperature dependence of the second order rate constant, k_{exp} , for the hydrolysis of $\text{Ti}(\text{OEt})_4$ and the activation energy (E_a) was calculated from slope of the straight line in the $\ln k_{\text{exp}}$ vs. $1/T$ plot. Activation enthalpy (ΔH^\ddagger) and activation entropy (ΔS^\ddagger) were also determined by the transition state theory using the calculated activation energy (E_a).

In general, the mechanism of ligand substitution through the bimolecular reaction path depends on the behavior of the leaving group and entering group.¹⁶⁻²⁰ Two kinds of mechanisms have been proposed. One is an associative (A) mechanism in which entry of the entering group occurs first, then a detectable intermediate of expanded coordination number is formed. The other mechanism is an interchange associative (I_a) mechanism in which the transition state is reached mostly through formation of the bond of the entering group. In this mechanism, however, the character of the dissociative (D) mechanism is comprised, so that bond weakening of the leaving group also takes place to a certain extent in the course of reaching the transition state. Two

Table 1. ΔH^\ddagger , ΔS^\ddagger and n -values for the hydrolysis of some titanium alkoxides (at 298.15 K)

	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (kJ mol ⁻¹ · K)	$-T\Delta S^\ddagger$ (kJ mol)	n -values
$\text{Ti}(\text{OEt})_4^a$	56.1	-110×10^{-3}	32.8	2.7
$\text{Ti}(\text{O}^i\text{Pr})_4^{11}$	58.2	-83.7×10^{-3}	24.9	3.1
$\text{Ti}(\text{O}^n\text{Pr})_4^{12}$	25.5	-233×10^{-3}	69.5	3.4
$\text{Ti}(\text{O}^t\text{Bu})_4^{13}$	19.7	-207×10^{-3}	61.7	4.8

^athis work.

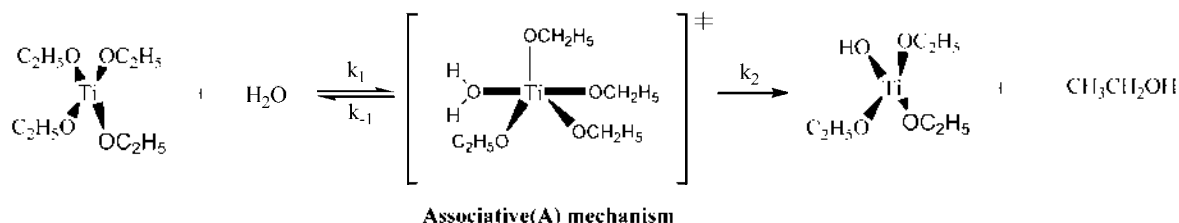


Figure 3. Proposed scheme of hydrolysis reaction mechanism for $\text{Ti}(\text{OEt})_4$.

terms that are components of activation free energy (ΔG^\ddagger), activation enthalpy (ΔH^\ddagger) and entropy ($-\text{T}\Delta S^\ddagger$), are thought to be related to the bond weakening of leaving group and the bond forming of entering group respectively. A high value for the activation enthalpy is associated with the difficulty of bond weakening of the leaving group, and a large activation entropy indicates that the bond for the entering group is formed with ease. ΔH^\ddagger , $-\text{T}\Delta S^\ddagger$ and n -values for the hydrolysis of some titanium alkoxides are given in Table 1.¹¹⁻¹³ In the case of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Ti}(\text{O}^i\text{Bu})_4$, it is obvious from Table 1 that $-\text{T}\Delta S^\ddagger$ values are much larger than ΔH^\ddagger values indicating that the bonds for the entering groups were easily formed. Moreover, it can be seen from the small value of ΔH^\ddagger that bond weakening of the leaving group also occurred in the path of transition state. Consequently, the transition states of the hydrolysis for $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Ti}(\text{O}^i\text{Bu})_4$ were reached through the interchange associative (I_a) mechanism described above.

However, ΔH^\ddagger of $\text{Ti}(\text{O}^i\text{Pr})_4$ in Table 1 is larger than $-\text{T}\Delta S^\ddagger$, which is opposite of what was observed for $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Ti}(\text{O}^i\text{Bu})_4$. We concluded in our previous work that the transition state of $\text{Ti}(\text{O}^i\text{Pr})_4$ hydrolysis was reached via the associative (A) mechanism in which a detectable intermediate with a coordination number of five was formed without bond weakening of the leaving group. In our present work for $\text{Ti}(\text{OEt})_4$ hydrolysis, ΔH^\ddagger (56.1 kJ/mol) shows a similar value to that of $\text{Ti}(\text{O}^i\text{Pr})_4$ (58.2 kJ/mol) and also, $-\text{T}\Delta S^\ddagger$ (32.8 kJ/mol) is less than ΔH^\ddagger as in the case of $\text{Ti}(\text{O}^i\text{Pr})_4$. According to these results, it is proposed that an associative (A) mechanism is most appropriate for the hydrolysis of $\text{Ti}(\text{OEt})_4$ (Figure 3).

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