Hydrolysis Kinetic of New Laser Material $n$-$B_{18}H_{22}$

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Abstract: $n$-$B_{18}H_{22}$ is a potential blue laser material. In order to study the stability of $n$-$B_{18}H_{22}$ in aqueous solution, the hydrolytic reaction kinetic of $n$-$B_{18}H_{22}$ at various pH values and temperatures was studied by fluorescence spectroscopy. The results showed that $n$-$B_{18}H_{22}$ hydrolysis rate was accelerated by increasing temperature, and the trend showed that $n$-$B_{18}H_{22}$ hydrolyzed faster in low pH than in high pH solutions at the same temperature. The hydrolysis of $n$-$B_{18}H_{22}$ solution is second-order reaction at lower temperature (298.15K-323.15K), the activation energy is 52.37 kJ.mol$^{-1}$ and pre-exponential factor (A) is $7.9 \times 10^{10}$. The work described here is significant for future studies of the properties of $n$-$B_{18}H_{22}$ in aqueous solution.

1. Introduction
In recent years, borane materials have been widely used in catalysis, supramolecular coordination chemistry, hydrogen storage material and other material area, making more and more researchers into the study of the preparation and properties of the new functional borane materials. In particularly, the potential application of borane materials in medical science[1, 2] and new materials[3-6] have attracted more and more attention.

$n$-$B_{18}H_{22}$ is the only borane with fluorescence effect. In February 2015, the Czech scientists cooperated with the Spanish scientists to develop the first borane laser based on $n$-$B_{18}H_{22}$[7], which is an important milestone in the field of laser. This kind of blue fluorescence material with highly efficient and resistant to damage has potential large-scale application in the fields of spectroscopy and material processing. Increasingly, scientists are interested in $n$-$B_{18}H_{22}$.

Like other boranes, $n$-$B_{18}H_{22}$ is unstable in aqueous solution and easily reacts with water to produce boric acid and hydrogen at room temperature. The instability of $n$-$B_{18}H_{22}$ greatly limits its application in aqueous solutions. The study of the interaction between $n$-$B_{18}H_{22}$ and water had great significance in many applications, such as liquid laser, biological probe and its derivatives. Currently, little information is known about the

$n$-$B_{18}H_{22}$ hydrolysis in aqueous solution[8,9], and still some aspects are not sufficiently understood in detail. Similar to diacid, the ionization equations of $n$-$B_{18}H_{22}$ in aqueous solution are shown in equations (1) and (2).

\[ n \cdot B_{18}H_{22} + H_{2}O \rightleftharpoons n \cdot B_{18}H_{22}^{+} + H_{2}O^{+} \] (1)
\[ n \cdot B_{18}H_{22} + H_{2}O \rightleftharpoons n \cdot B_{18}H_{22}^{+} + H_{2}O^{+} \] (2)

In this work, we conducted an investigation on the hydrolysis kinetic behavior of $n$-$B_{18}H_{22}$ in a water system. The objectives of this study were to determine the following: the effect of pH and temperature on the hydrolysis of $n$-$B_{18}H_{22}$ in water. In this paper, the hydrolysis kinetic equation was obtained and...
related parameters were calculated. The work described here is significant for future studies of the properties of $n$-$B_{18}H_{22}$ in aqueous solution.

2. Experimental Part

2.1 Reagents and instruments

$n$-$B_{18}H_{22}$ was synthesized in our laboratory according to reference[10,11]: Decaborane was purchased from Henan vientiane chemical Co., LTD; Ultrapure water meter obtained from ELGA; Ultrasonic cleaner was obtained from Kunshan ultrasonic instrument Co., LTD., PHSJ-5 pH meter was purchased from Shanghai INESA scientific instrument Co., LTD. All other reagents used were of guaranteed analytical grade. Ultrapure water was employed in the preparation of solutions. All working solutions of $n$-$B_{18}H_{22}$ and other tested solutions were prepared by standard procedures and appropriate dilution.

2.2 Photoluminescence instrument

Photoluminescence (PL): PL scans were obtained with Hitachi F-4600 fluorescence spectrometer. The sample molecules were excited at 360nm, and the emission spectra were recorded with 10 nm excitation and emission slits. The scan voltage was 700V at scanning interval of 0.5nm and scanning speed of 1500nm/min.

2.3 Test method

Preparation of standard curve: A certain amount of $n$-$B_{18}H_{22}$ was dissolved in water, and a series of $n$-$B_{18}H_{22}$ aqueous solutions of different concentrations were prepared to measure the fluorescence intensity under the same conditions, and the fluorescence intensity-concentration curve of $n$-$B_{18}H_{22}$ was obtained as the standard curve. In the experiment, $n$-$B_{18}H_{22}$ aqueous solution was obtained after ultrasonic stirring, and its fluorescence intensity was measured after a period of hydrolysis. The fluorescence intensity measured in solution with different pH value, different temperature and different decomposition time was compared with the standard curve to obtain the corresponding concentration.

3. Result and Discussion

3.1 Hydrolysis reaction kinetics of $n$-$B_{18}H_{22}$

3.1.1 The calibration plot. The hydrolysate of $n$-$B_{18}H_{22}$ has no fluorescence, therefore, the degree of fluorescence intensity attenuation can indicate the degree of borane hydrolysis. The fluorescence intensity of the solutions containing varying amounts of $n$-$B_{18}H_{22}$ was measured. Fig. 1(a) shows the spectral characteristics of $n$-$B_{18}H_{22}$ solution with different concentration. As can be seen from the figure, a blue fluorescent exhibiting maximum fluorescence intensity at 422 nm after excitation at 360 nm was produced. In this paper, all measurements of this study were carried out at 422 nm after excitation at 360 nm. The maximum fluorescence intensity-concentration curve was shown in Fig. 1(b), and the calibration plot of fluorescence intensity versus the concentrations of $n$-$B_{18}H_{22}$ was established, the correlation coefficient was 0.998.

Figure 1(a). Fluorescence intensity of aqueous solutions versus concentration of ($n$-$B_{18}H_{22}$) ; (b).
Fitting curve of fluorescence and intensity-concentration (298.15K)

3.1.2 Reaction order. The order of the hydrolysis reaction was determined by studying the reaction at different concentrations of \( n-\text{B}_{18}\text{H}_{22} \) (1.5, 2.0, 3.0 \( \times 10^{-2} \) mol/L) and the fluorescence intensity-time curves were generated. The results indicated that the fluorescence intensity was concentration dependent (Fig. 2). The three solutions have similar hydrolysis behavior, the fluorescence intensity decreased rapidly with increasing hydrolysis time. After 9 hours, the fluorescence intensity changed little, indicating that \( n-\text{B}_{18}\text{H}_{22} \) hydrolysis is nearly complete.

It can be seen from Fig.2 that the maximum emission peak moved slightly after reacting for 4 hours. In this paper, the range of time was limited to 4 hours.

Figure 2. Curves of fluorescence intensity with time in aqueous solutions of different concentrations of \( n-\text{B}_{18}\text{H}_{22} \)

The hydrolysis reaction occurs with relative excess amount of water which can be considered as constant. Therefore, the hydrolysis was obeyed the following equation

\[
-\frac{dc}{dt} = kc^n
\]  

Where: \( c \) is the molar concentration of \( n-\text{B}_{18}\text{H}_{22} \), \( k \) is the rate constant, \( t \) is the measuring time, and \( n \) is the order of the reaction. To second-order reaction, plot of \((1/c-1/c_0)\) versus time is linear. In the experiment, \((1/c-1/c_0)\) was plotted versus time, the results were shown in Fig.3. It can be seen from Fig.3, in three cases, straight lines with nearly the same slopes and passing through the origins were obtained, all of plots are linear, indicating second-order hydrolysis kinetics. Correlation coefficients \((R^2)\) from 0.994 to 0.999 indicated that the second-order kinetics model simulated the hydrolysis of \( n-\text{B}_{18}\text{H}_{22} \) well. The second-order rate constants, \( k \) are calculated from the slopes of these straight line plots, the rate constants of the three different initial concentrations of \( n-\text{B}_{18}\text{H}_{22} \) are almost identical, no obvious dependence of the second-order rate constants on the initial concentration of \( n-\text{B}_{18}\text{H}_{22} \) is observed. Calculated values of \( k \) are independent of the concentration of \([n-\text{B}_{18}\text{H}_{22}]\), confirming second-order kinetics. Half-live \((t_{1/2})\) can be calculated from the equation:

\[
t_{1/2} = \frac{1}{2ka}
\]  

The results are shown in table.1.
3.2 The Effect of pH

For investigating the effect of pH, the hydrolysis reaction was performed at different pH values (2.91-11.34). The results indicated that the rate constant was pH dependent (Fig. 4). Similarly, the second-order equation was used to fit a curve to estimate rate constants of \( n\)-\( \text{B}_{18}\text{H}_{22} \) in different pH solutions, and correlation coefficients (\( R^2 \)) from 0.983 to 0.997 indicated that the second-order kinetics model accorded well with the experimental data. The half-lives (\( t_{1/2} \)), rate constant (\( k \)), and correlation coefficient (\( R^2 \)) are presented in Table 2.

Under the condition of 300.15K, the calculated half-lives of \( n\)-\( \text{B}_{18}\text{H}_{22} \) hydrolysis in the solutions of pH 2.91, 4.92, 8.73 and 11.34 were 1.4, 1.6, 1.1 and 4.9 hours, respectively. \( n\)-\( \text{B}_{18}\text{H}_{22} \) hydrolyzed more rapidly in an acidic solution than in a strongly alkaline solution demonstrating the influence of the solution pH to \( n\)-\( \text{B}_{18}\text{H}_{22} \) hydrolysis in water. There is no noticeable difference between pH = 2.91 and 8.73. Hydrolysis at higher rates under strong alkaline conditions may suggest that the reaction was effectively inhibited by hydroxide ions.

3.3 The Effect of Temperature

To obtain information about the activation energy of \( n\)-\( \text{B}_{18}\text{H}_{22} \) hydrolysis, the temperature dependence of the rate constant was determined. The effect of temperature on \( k \) was studied at different temperatures (300.15–318.15 K) in order to obtain the thermodynamic parameters for the hydrolysis reaction.

The results were shown in Fig. 5, and indicated that the hydrolysis rate increased with the increased temperature (Table 3), indicating the significance of the temperature to \( n\)-\( \text{B}_{18}\text{H}_{22} \) hydrolysis in water. The half-life of \( n\)-\( \text{B}_{18}\text{H}_{22} \) was shortened by approximately 70% when the temperature rose from 300.15K to 318.15K (Table 3). Similar to the hydrolysis reaction of organic molecules, the hydrolytic reaction of...
n-B18H22 was thermal reactions, and the activation energy mainly comes from n-B18H22 molecular collision, as the temperature increases, the hydrolysis of n-B18H22 increases.

Table 3. Kinetic parameters of hydrolysis of n-B18H22 at different temperatures

| T/K  | Reaction rate constant (k/(h⁻¹)) | Correlation coefficient (R²) | Half life (t₁/₂/h) |
|------|----------------------------------|-----------------------------|-------------------|
| 300.15 | 60.9                             | 0.996                       | 0.82              |
| 308.15 | 105.5                            | 0.989                       | 0.47              |
| 318.15 | 200.3                            | 0.998                       | 0.256             |

3.4 Calculation of Activation Energy

The activation energy, the minimum kinetic energy a molecule must possess in order to undergo the reaction, can be determined from Arrhenius equation

\[ k = Ae^{-\frac{E_a}{RT}} \]  

where \( k \) is the rate constant for a reaction, \( A \) is a pre-exponential factor, \( E_a \) is the energy of activation, \( R \) is the gas constant, and \( T \) is the absolute temperature.

The logarithmic form of the above equation is written as follow:

\[ \ln k = \ln A - \frac{E_a}{RT} \]  

Equation (6) should yield a straight line of slope \(-E_a/R\) and intercept of \( \ln A \).

The activation energy of the hydrolysis reaction of n-B18H22 was determined by studying the reaction at different temperatures; 300.15K, 305.15K, and 318.15K using fixed concentrations of n-B18H22. Plots of \((1/c-1/c₀)\) versus time at these temperatures were constructed to determine the rate constant [Fig.5], then plotting \(1/T\) against \(\ln k\) to determine the slope of the line [Fig.5]. The slope \((-E_a/2.303R\) was -6299.07, the activation energy (52.37kJ mol⁻¹) can be calculated. This low activation energy indicated the instability of n-B18H22 in water.

The intercept \(\ln A\) was 25.1, so the pre-exponential factor \(A\) was 7.9x10¹⁰.

The hydrolysis kinetic equation of n-B18H22 can be expressed as:

\[ \ln k = 25.1 - \frac{6.299}{T} \]  

Figure 5. Relationship between \(\ln k\) and \(1/T\)

4. Conclusion

The results indicated that the hydrolysis of n-B18H22 in different pH solution can be fitted by second-order reaction kinetics very well. The solution pH and temperature influenced n-B18H22 hydrolysis significantly, with high pH inhibiting and low pH and temperature favoring the reaction. The calculated half-life of n-B18H22 hydrolysis in the solutions of 300.15, 308.15, 318.15K were 0.82, 0.47 and 0.256 hours in the pH = 7 solution, respectively. The activation energy for n-B18H22 hydrolysis was 52.37kJ/mol (300.15K-318.15K) and the pre-exponential factor \(A\) was 7.9x10¹⁰.

The results of this study lay a good foundation for the in-depth study of chemical reaction
performance of $n$-B$_{18}$H$_{22}$.

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