# Decomposition Reaction of Tetra-hydroxymethyl Phosphonium Chloride

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**Abstract:** At present, tetra-hydroxymethyl phosphonium chloride (THPC) is widely used in flame retardant finishing, industrial water treatment and leather manufacture industry *etc.*, and its decomposition will affect the actual application. So the thermal decomposition and acid-alkali decomposition of THPC were studied by $^{31}$P nuclear magnetism resomance ($^{31}$P NMR), thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) respectively. The results showed that THPC solution was stable when pH<5.0, containing THPC, tri-hydroxymethyl phosphine (TrHP), and tri-hydroxymethyl phosphine oxide (TrHPO). THPC began to decompose at pH5.0 and yielded an unstable substance tetra-hydroxymethyl phosphonium hydroxide (THPH), whose chemical shifts was 36ppm. At pH8.0, THPC converted to TrHP and TrHPO completely. When pH>9.0, all of the phosphorus compounds converted to TrHPO. Consequently, THPC content decreased when pH of the THPC solution rose. Thermal decomposition experiment was also carried out. The structure of THPC began to change when heated to 152.4℃ and lose weight at 184.41℃. Therefore, application temperature should be below 152℃, which could give a favorable guide in THPC application.

**Key words:** tetra-hydroxymethyl phosphonium chloride (THPC); acid-alkali decomposition; thermal decomposition

## 1 Introduction

Tetra-hydroxymethyl phosphonium chloride (THPC) was first reported in 1921 by Hoffman[1]. It is a rather unusual and little-investigated organic phosphorus compound that undergoes many interesting reactions[2]. At present, it is widely used in chemical engineering field, such as flame retardant finishing[3], industrial water treatment[4], intermediate producing [5], leather manufacture industry[6] and so on. In THPC applying process, THPC will decompose because of heating or neutralizing. At the same time, free formaldehyde and phosphine compounds will be generated, which may influence on the actual application and products quality [7, 8]. In order to make clear with the THPC decomposition rule, the reaction of thermal decomposition and acid-alkali decomposition were studied by THPC content determination, free formaldehyde content determination, $^{31}$P NMR analysis, etc.

## 2 Experimental

### *2.1 Materials and instruments*

Main materials and instruments used in the experiments are listed in Tab. 1.

**Tab.1 Main materials and instruments used in experiments**

| Main materials and instruments | Supplier |
|---|---|
| iodine standard solution (0.0999mol/L) | Guangdong Xilong Chemistry Co. Ltd., China |
| sodium thiosulfate standard solution | Ningbo Aobo Scientific Instrument Co. Ltd., China |
| ammonium acetate (AR) | Wuxi Unisen Chemical Product Co. Ltd., China |

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| | |
|---|---|
| THPC sample (pH 3.48, purity of 70.51%) | Zhejiang Zengxin Chemistry Co. Ltd., China |
| acetylacetone (purity of 99.50%) | Shanghai Reagent Co. Ltd., China |
| BS110S analytical balance | Sartorius, Germany |
| 2000 Spectrophotometer | Shanghai Unico Co. Ltd., China |
| PHS-25 pH meter | Shanghai Liancun Co. Ltd., China |
| AVANCE 300 | Bruker, Germany |
| Pyris 1 TGA | Perkin Elmer, America |
| DSC 200/1/H PHOXC520L | Netzsch, Germany |

### *2.2 Preparation of THPC solution with different pH*

16 pieces of THPC sample (about 3.000g) were added into 100mL volumetric flasks, respectively. Then the volume was determined at 100mL and put to flask. Each pH of THPC solutions was adjusted to 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0 by solid sodium hydroxide. The solutions were kept overnight at room temperature for later use.

### *2.3 Acid-base reversible reaction of THPC*

2 pieces of THPC sample (about 3.000g) were added into 100mL volumetric flasks. Then the volume was determined at 100mL and put to flask. The pH of THPC solutions were adjusted to 7.0 and 9.5 respectively by sodium hydroxide. After standing overnight, THPC and free formaldehyde contents were determined by followed method. Then the pH of THPC solutions was adjusted to original pH3.0 by hydrochloric acid. After keeping overnight, THPC and free formaldehyde contents were determined once again.

### *2.4 THPC content determination*

The iodimetric method was employed to determine the THPC content in the samples at different pH [9]. Firstly, 5mL THPC solution was added to a flask. Then 1mL starch-iodide indicator (1%) was added into the flask and shaken up. After that, Titration with iodine standard solution ($c_1$=0.0999mol/L) was carried out. The end point of titration was obtained through the solution became blue. Write down the consumption volume of iodine standard solution (V1, mL) and calculate the THPC content (w (THPC), %) by followed formula, in which m(THPC) is mass of THPC sample.

$$w(THPC) = \frac{V_1 \times c_1 \times 190.56}{1000 \times m(THPC)} \times 100\%$$

### *2.5 Free formaldehyde content determination*

#### *2.5.1 Collection of free formaldehyde from THPC solution*

THPC solution should be distilled at 90℃ under $N_2$ flow 200mL/min for 1h. Most free formaldehyde would be transferred into the collection flask with certain amount of water. Then free formaldehyde content of collected solution was determined by actylacetone method.

#### *2.5.2 Acetylacetone method*

The acetylacetone method was adopted to determine the free formaldehyde content in the free formaldehyde solutions [10]. 2.8mL 37% formalin was added into 1000mL volumetric flask and the volume was completed with distilled water. The free formaldehyde content of the standard solution was approximate 1mg/mL. Then the standard solution was diluted to 10μg/mL. 0.00, 0.50, 1.00, 3.00, 5.00, 8.00mL diluted solution were added to 25mL volumetric flasks and the volumes were completed with distilled water after the addition of 2.5mL acetylacetone chromogenic agent, respectively. The treated

solution was then heated in 60±5℃ water bath for 30min and the colored solution was obtained. The absorbency at 414nm was determined when it was cool. Draw the standard curve with the above absorbency data. The free formaldehyde content of the collected solution was determined through the absorbency after treated like above.

### *2.6 $^{31}P$ NMR Analysis*

$^{31}P$ NMR was employed to describe the different structure of phosphorus compounds of the samples at different pH. $D_2O$ was used as solvent, and $H_3PO_4$ was used as the internal standard.

### *2.7 TGA analysis*

5mg THPC sample was used to make TGA analysis. The temperature range was 50-700℃, the heating rate was 20℃/min.

### *2.8 DSC analysis*

3mg THPC sample was employed for DSC analysis. The temperature range was 50-180℃. The heating rate was 20℃/min, under the protecting gas at $N_2$ 60mL/min and the purge gas at $N_2$ 20mL/min.

## 3 Results and discussion

### *3.1 Formaldehyde standard curve*

Fig. 1 demonstrates the standard curve of formaldehyde content. The correlation coefficient is 0.9995. The equation was obtained for further free formaldehyde content of THPC solution calculation.

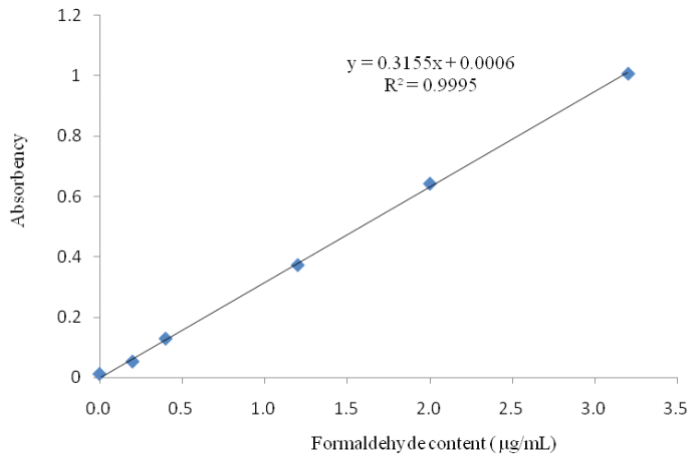


**Fig. 1 Free formaldehyde content standard curve**

### *3.2 THPC and formaldehyde contents in acid-alkali decomposition of THPC*

Tab. 2 lists the THPC and free formaldehyde contents change with different pH of THPC solutions. With the pH rises, the THPC will react with alkali, and decomposition will be taken place. So the content of THPC decreases from 70.51% to less than 10%, while the yielded free formaldehyde increases from 4.49% to about 14%. Therefore, it is concluded that the increased formaldehyde is related to acid-base decomposition of THPC.

**Tab.2 The contents of THPC and formaldehyde content of THPC solution with different pH**

| No. | m(THPC) ( g) | pH | Absorbency | w(HCHO) ( %) | w(THPC) (%) |
|---|---|---|---|---|---|
| 1 | 3.0055 | 3.48 | 0.262 | 4.49 | 70.51 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 3.0130 | 3.98 | 0.269 | 4.60 | 70.82 |
| 3 | 3.0216 | 4.48 | 0.303 | 5.16 | 67.22 |
| 4 | 3.0341 | 5.00 | 0.319 | 5.42 | 65.62 |
| 5 | 3.0060 | 5.50 | 0.318 | 5.45 | 65.41 |
| 6 | 3.0238 | 6.00 | 0.302 | 5.14 | 67.35 |
| 7 | 3.0142 | 6.50 | 0.309 | 5.28 | 66.48 |
| 8 | 3.0282 | 7.00 | 0.435 | 7.40 | 53.01 |
| 9 | 2.9980 | 7.50 | 0.477 | 8.29 | 47.95 |
| 10 | 3.0107 | 8.06 | 0.703 | 12.03 | 23.58 |
| 11 | 3.0117 | 8.46 | 0.759 | 12.99 | 17.51 |
| 12 | 3.0142 | 9.03 | 0.864 | 14.78 | 6.17 |
| 13 | 3.0272 | 9.50 | 0.842 | 14.34 | 8.95 |
| 14 | 3.0309 | 10.02 | 0.864 | 14.70 | 6.68 |
| 15 | 3.0043 | 10.48 | 0.861 | 14.76 | 6.18 |
| 16 | 3.0339 | 11.00 | 0.826 | 14.03 | 10.89 |

Fig. 2 and Fig. 3 are the THPC and formaldehyde content curves at different pH. Obvious trend of content change could be obtained from Fig.2 and Fig.3, which illustrates that THPC begins to decompose at pH 6.5. From this point, formaldehyde content starts to rise. It can also draw a conclusion that THPC would stop decomposition at pH9.0. At same time, formaldehyde content reaches to about14%.

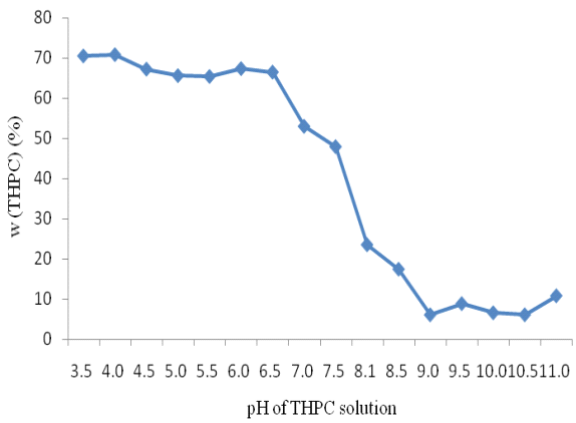


**Fig. 2 THPC content change with pH**

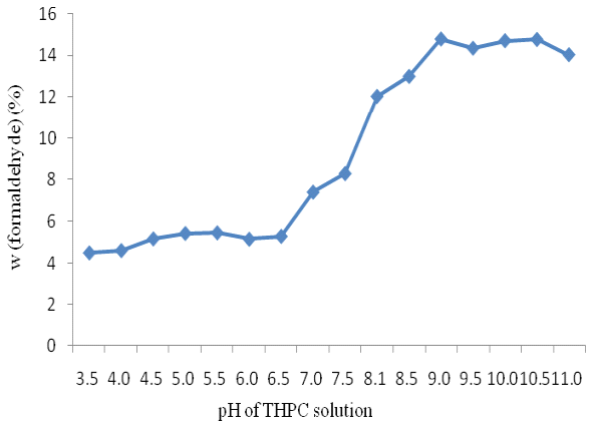


**Fig.3 Formaldehyde content change with pH**

### *3.3 Acid-base reversible reaction of THPC*

Tab.3 demonstrates THPC content change in acid-base reversible reaction. When pH of THPC solution rise to 7.00 and 9.48 respectively, THPC contents decrease to 57.56% and 10.87%. Then the pH reduces to original pH, THPC content does not increase. Therefore, THPC acid-base decomposition reaction is irreversible.

**Tab. 3 THPC content change in acid-base reversible reaction**

| No. | m(THPC, g) | pH change | w(TPHC, %) |
|---|---|---|---|
| 1 | 3.0425 | 2.91 →7.00 | 57.56 |
| 2 | 3.0425 | 2.91→7.00→2.90 | 56.19 |
| 3 | 3.0478 | 2.97 →9.48 | 10.87 |
| 4 | 3.0478 | 2.97→9.48→2.66 | 9.06 |

### *3.4 $^{31}$P NMR Analysis of THPC solution with different pH*

Fig.4 shows the different phosphorus compounds in THPC solution at pH3-pH11. At pH 3.32, THPC solution mainly contains THPC ($\delta$, +26ppm). It also has a small quantity of tri-hydroxymethyl phosphine (TrHP; $\delta$, -24ppm) and tri-hydroxymethyl phosphine oxide (TrHPO; $\delta$, +49ppm). THPC begins to decompose at pH5.0 and yields an unstable substance tetra-hydroxymethyl phosphonium hydroxide (THPH; $\delta$, +36ppm). At pH8.0, THPC converts to TrHP and TrHPO completely. When pH>9.0, all the phosphorus compound converts to TrHPO.

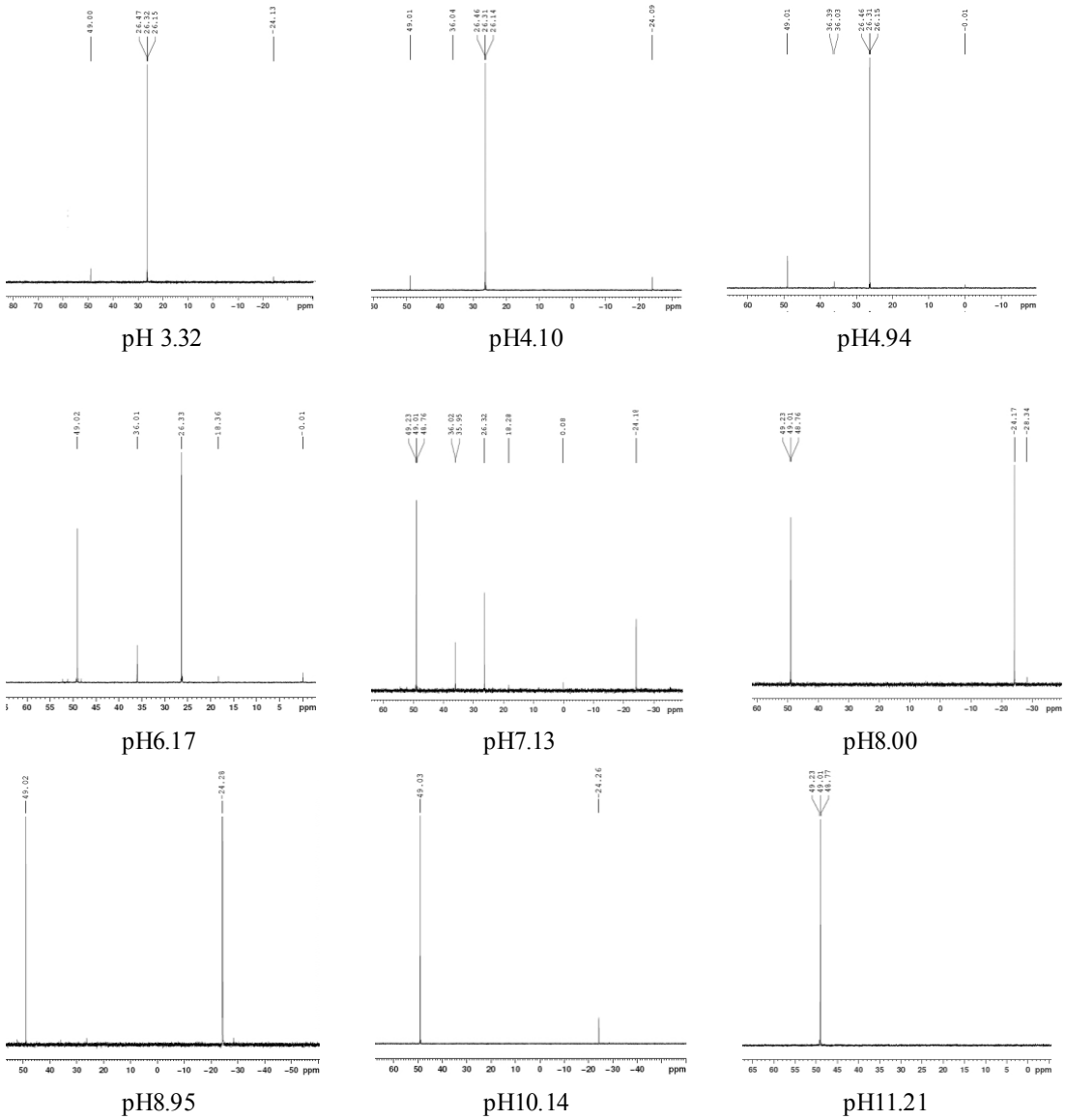


**Fig.4 $^{31}$P NMR spectra of THPC at different pH**

### *3.5 TGA analysis*

From Fig.5, THPC sample begins to decompose and lose weight when temperature reaches 184.41℃.

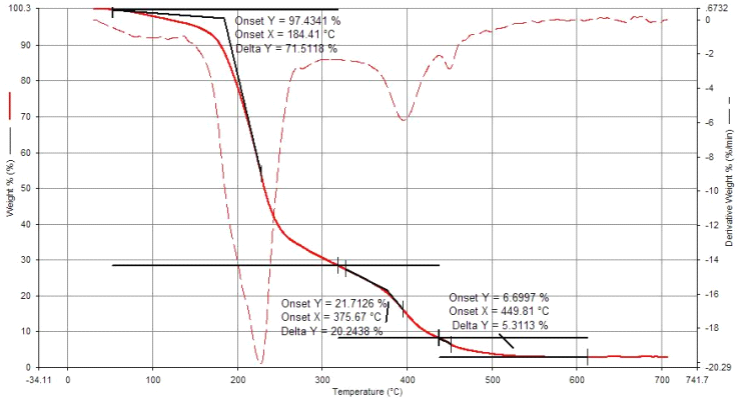


**Fig. 5 TGA result of THPC sample**

### *3.6 DSC analysis*

Fig.6 is the DSC result of THPC sample. The endothermic peak at 101℃ is due to water evaporation. And the peaks at 158.6℃,167.8℃,173.7℃ may due to the structure change of THPC when heating. Therefore, it is suggested that THPC sample should be apply under 152℃, because the onset temperature is152.4℃.

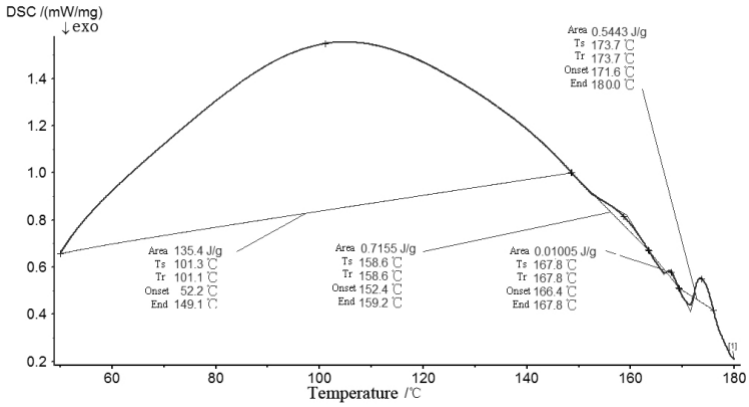


**Fig. 6 DSC result of THPC sample**

## 4 Conclusions

THPC begins to decompose at pH5.0 and yields formaldehyde and other phosphorus compounds. Its decomposition reaction is irreversible. When heating, the structure of THPC start to change at152.4℃. Therefore, THPC is suggested to be used at pH<5.0 and temperature<152℃.

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