Paper D33

Effect of pH on the phosphorous components of tetra-hydroxymethyl phosphonium chloride solution

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Abstract

At present, tetra-hydroxymethyl phosphonium chloride (THPC) is widely used in textile flame retardant finishing, industrial water treatment and leather manufacture industry etc., and its decomposition caused by pH changes will influence on the actual application and the quality of final products. Therefore, acid-alkali decompositions of THPC under different pH were studied by ^{31}P Nuclear Magnetic Resonance (^{31}P NMR), spectrophotometry and titration respectively. The results reveal that THPC solution is stable when pH<5.0, containing THPC, tri-hydroxymethyl phosphine (TrHP), and tri-hydroxymethyl phosphine oxide (TrHPO). THPC starts to decompose at pH5.0 and yields an unstable substance tetra-hydroxymethyl phosphonium hydroxide (THPH), whose chemical shifts is 36ppm. At pH8.0, THPC converts to TrHP and TrHPO completely. When pH>9.0, all of the phosphorus compounds converts to TrHPO. Consequently, THPC content decreases when pH of the THPC solution rising, meanwhile, which could give a favorable guide in THPC application.

Keywords: tetra-hydroxymethyl phosphonium chloride; phosphorous compound; ^{31}P NMR; acid-alkali decomposition

1. Introduction

Tetra-hydroxymethyl phosphonium chloride (THPC) was firstly reported by Hoffman [1] in 1921. 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 fields, such as flame retardant finishing [3], industrial water treatment [4], intermediate producing [5], and leather manufacture industry [6] and so on. In THPC applying processes, it will convert to different phosphorous compound because of environmental pH changing. At the same time, free formaldehyde will be generated, which may influence on the actual application and products quality [7, 8]. In order to make clear with the effects of pH on phosphorous components of THPC solution, the reaction of acid-alkali decomposition were studied by THPC content titration, free formaldehyde content determination, ^{31}P NMR analysis, etc. The results obtained will give a favorable guide to industrial practice.

2. Materials and method

2.1 Materials and instruments

Main materials and instruments used in the experiments are listed in Table1.

Table 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 Co. Ltd., China
ammonium acetate (AR)	Wuxi Unisen Chemical Product Co. Ltd., China
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

2.2 Preparation of THPC solution with different pH

16 THPC samples (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, and 11.0 by solid sodium hydroxide. The solutions were kept 24h at room temperature for later use.

2.3 Acid-base reversible reaction of THPC

2 THPC samples (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 24h, THPC and free formaldehyde contents were determined by followed methods. Then the pH of THPC solutions was adjusted to original pH3.0 by hydrochloric acid. After keeping 24h, 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 (V_1, 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. The peak areas were calculated to determine the contents of each phosphorous compound.

3. Results and discussion

3.1 Formaldehyde standard curve

Figure1 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.

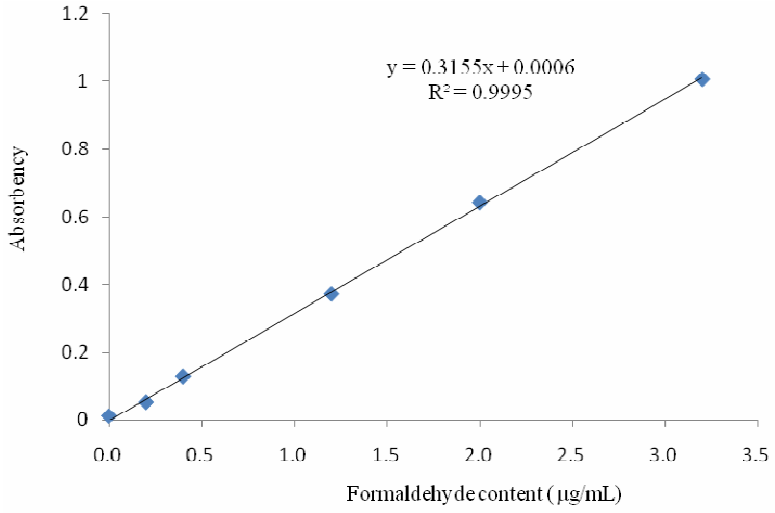

Figure 1. Free formaldehyde content standard curve

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

Figure 2 and 3 are the THPC and formaldehyde content curves at different pH. 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.

Furthermore, obvious trend of content change could be obtained from Figure 2 and 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%.

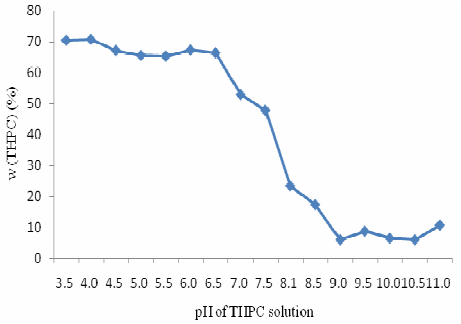

Figure 2. THPC content Vs pH

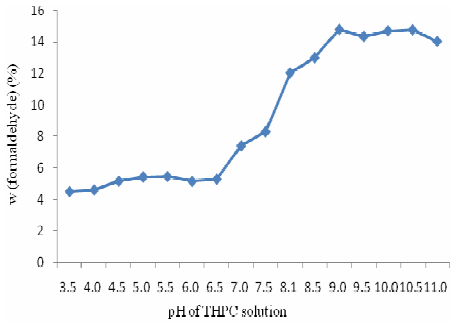

Figure 3. Formaldehyde content changes with pH

3.3 Acid-base reversible reaction of THPC

Table 2 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.

Table 2. 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

Figure 4 are the structures of phosphorous compounds in THPC solution.

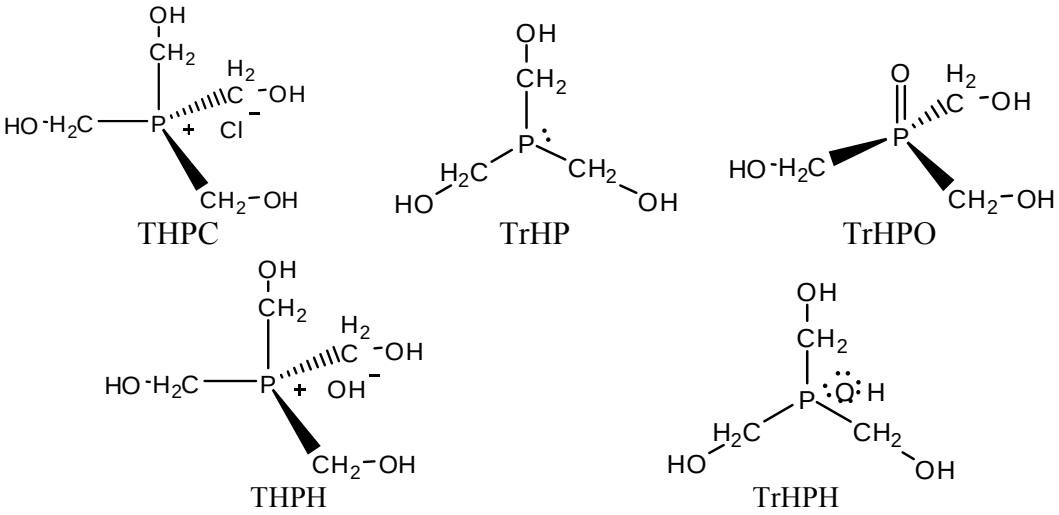

Figure 4.Structures of phosphorous compounds

Figure 5 shows the different phosphorous compounds in THPC solution at pH3-pH11. At pH 3.32, THPC solution mainly contains THPC (δ, +26ppm). It also has a small quantity of tri-hydroxymethyl phosphine (TrHP; δ, -24ppm) and tri-hydroxymethyl phosphine oxide (TrHPO; δ, +49ppm). THPC begins to decompose at pH5.0 and yields an unstable substance tetra-hydroxymethyl phosphonium hydroxide (THPH; δ, +36ppm). At pH6-pH7, tri-hydroxymethyl phosphine hydroxide (TrHPH; δ, +18ppm) was formed temporarily with very small amount. At pH8.0, THPC converts to TrHP and TrHPO completely. When pH>9.0, all the phosphorus compound converts to TrHPO.

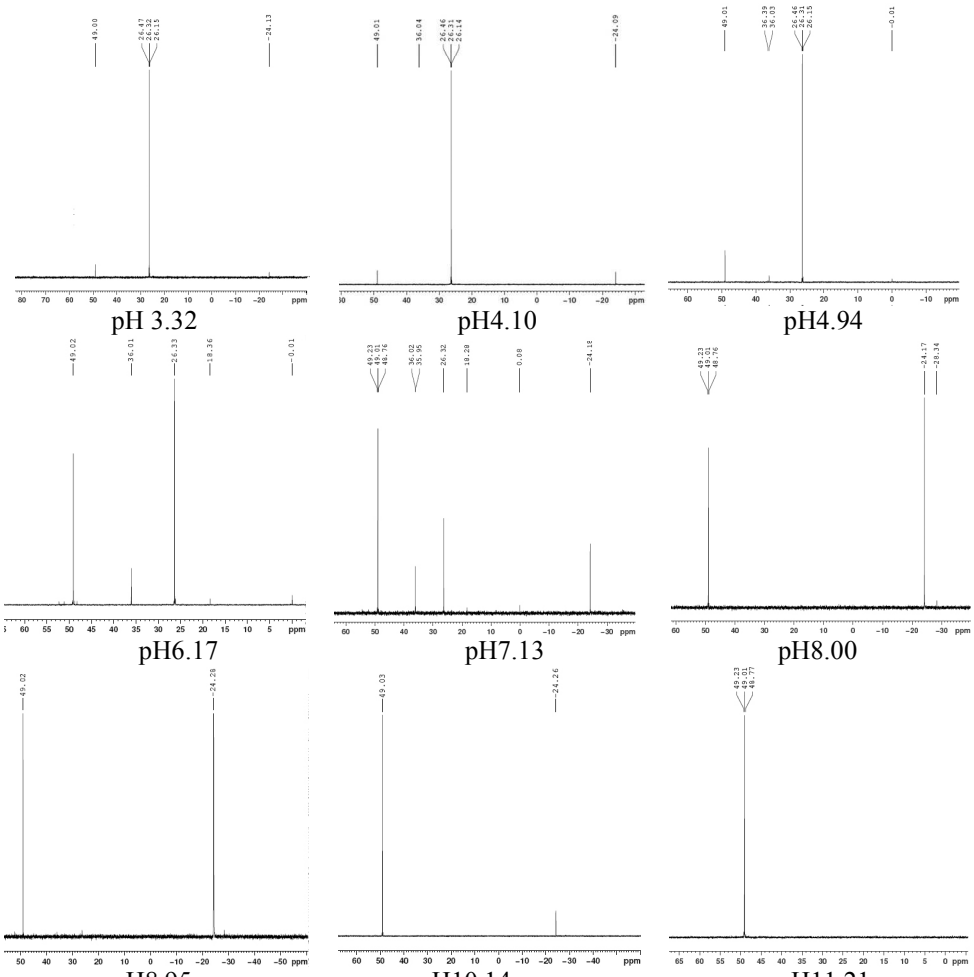

Figure 5. ^{31}P NMR spectra of THPC at different pH

The contents of phosphorous compounds in THPC solution at different pH were obtained by the peak area integration basing on ^{31}P NMR results. Figure 6 indicates the contents changes of phosphorous compounds at different pH. From pH3-pH11, THPC content decreases from 92.84% to 0% with THPC solution pH increasing. When pH6, TrHP starts to increase sharply and reaches the peak 88.51% when pH9. When pH>9, TrHPO content increases greatly from 11.49% to 100%, which means TrHP will be oxidized to TrHPO easily. Between pH6-pH8, there are two peaks. One of them is THPH and the other is TrHPH, which are intermediate products during pH increasing process.

Higher eletrophilicity of hydroxyl ion and lone pair electrons of P in tetra-hydroxymethyl phosphonium cation (THP^+) and TrHP make the TrHPH and THPH forming possible. But THPH and TrHPH are unstable and difficult to be separated from the solution.

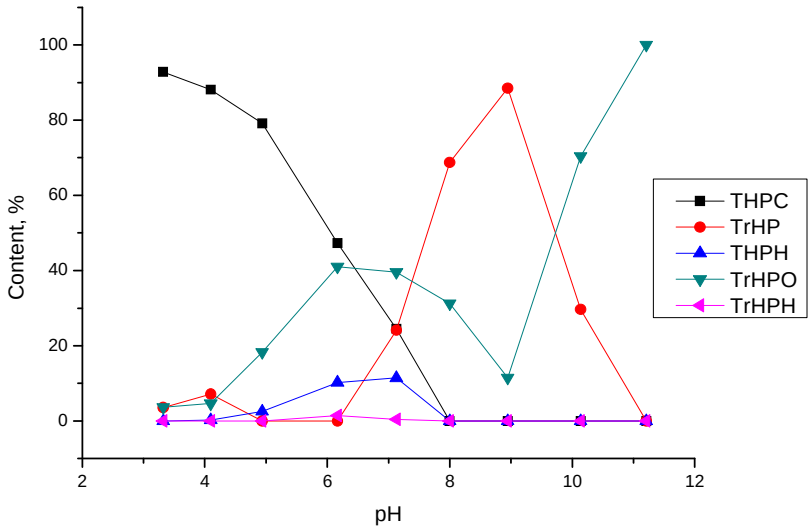

Figure 6. Contents of phosphorous compounds at different pH

4. Conclusions

With pH of THPC solution increasing from 3-11, THPC acid-base decomposition reaction will take place irreversibly. THPC will convert to TrHP and further will be oxidized to TrHPO. Simultaneously, formaldehyde content will increase in THPC solution. Between pH6-pH8, there are two intermediate products, TrHPH and THPH, which would accelerate the TrHP and TrHPO forming.

5. References

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6. Acknowledgements

This work was supported by the National Natural Science Funds (21076109), Scientific Research Fund of Zhejiang Provincial Education Department (ZD2007008). Thanks the National Natural Science Foundation of China and Department of Education of Zhejiang Province for this programme grant.