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Synthesis of mono(1-chloride 2-hydroxy propyl) phosphate and antimony mono(1-chloride 2-hydroxy propyl) phosphate^①

LIU Your nian(刘又年), SHU Wan gen(舒万良), ZENG Dong ming(曾冬铭), HUANG Ke-long(黄可龙)
(Institute of Chemistry and Chemical Engineering, Central South University of Technology,
Changsha 410083, P. R. China)

[Abstract] The synthesis, properties and flame retardation of two kinds of flame retardants, mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate were reported. Mono(1-chloride-2-hydroxy propyl) phosphate was synthesized from epichlorohydrin and phosphoric acid at molar ratio of 1:1.2 in the solvent of methyl benzene with AlCl_3 catalyst under the conditions of reaction temperature of 90 °C and reaction time of 2 h, its total yield is 82.5 %. Antimony mono(1-chloride-2-hydroxy propyl) phosphate was synthesized from mono(1-chloride-2-hydroxy propyl) phosphate and antimony trioxide in the solvent of dimethyl sulfoxide with oxalic acid catalyst under the conditions of reaction temperature of 92 °C and reaction time of 4 h, the total yield is 85.6 %. The physical-chemical properties of the products were determined. When adding 15 % of mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate in polyethylene respectively, the oxygen indexes (OI) are 31.4 and 33.7 respectively.

[Key words] antimony; phosphate; flame retardants; synthesis

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1 INTRODUCTION

Many alternative materials can be used as flame retardants. The main flame retardants currently used in plastics fall into several classes: 1) alumina trihydrate; 2) halogenated compounds, usually used in combustion with Sb_2O_3 ; 3) borax and boric acid; 4) the phosphorous, phosphorous-nitrogen, and phosphorous-halogen compounds. The cost performance often dictates their interaction or interference with one of the three required components of a fire: 1) a combustible substance or fuel; 2) heat, supplied either externally or from the combustion process itself; 3) an oxidizing gas, primarily oxygen^[1,2].

Antimony trioxide (commonly referred to as antimony oxide) is used to impart flame retardance to variety of plastics, and can act synergistically with certain bominated or phosphorus flame retardants; but will make the transparence of plastics loss. When Sb_2O_3 was added to plastics, much smoke may be raised in the processes of combustion of plastics. The above two major shortages limited the use of Sb_2O_3 as flame retardant. Some organic compounds of antimony have good compatibility with plastics, thus, the transparence and physical properties of plastics will not be varied too much when adding these type of flame retardants^[3,4].

Phosphites are also main flame retardants, and they have got great development recently, but the curing time will increases when adding phosphorous

compounds into some coatings (i.e. polyurethane and alkydresin varnish)^[5,6]. Some Alkal phosphate esters have been synthesized as flame retardants and other uses by Hironaka^[7], Hirose^[8] and TANG^[9]. We have also synthesized phosphate esters and antimony phosphate esters^[10-12]. The oxygen index was 26.8 when adding 15 % antimony mono(2-hydroxypropyl) phosphate epoxy resin^[10].

2 EXPERIMENTAL

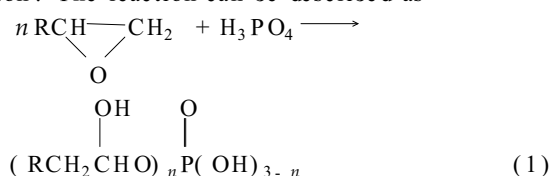
2.1 Main reagents and apparatus

Main reagents include antimony oxide, phosphoric acid, methyl benzene, epichlorohydrin, aluminum chloride, dimethyl sulfoxide, oxalic acid, polyethylene, etc. All reagents are of chemical pure and without furth treatment.

Main apparatus are FT-740 Infrared spectrograph, WC-1 Micro melting point apparatus, and HC-2 Oxygen Index Tester.

2.2 Synthesis principle

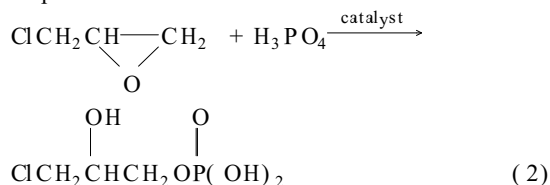
The chemical properties of epoxide compounds are very active, and it is inclined to proceed ring-open reaction. The reaction can be described as



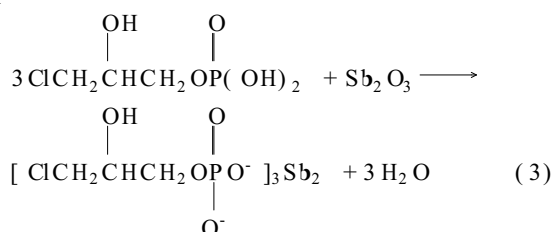
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where R is hydrogen or alkyl; n is an integer number from 1 to 3. The rather high yield of monoester can be obtained by controlling reaction condition. Thus, mono(1-chloride-2-hydroxy propyl) phosphate can be prepared from the reaction of epichlorohydrin and phosphoric acid with certain conditions



And, antimony mono(1-chloride-2-hydroxy propyl) phosphate is synthesized by reacting of antimony oxide and mono(1-chloride-2-hydroxy propyl) phosphate as



2.2.1 Synthesis method of mono(1-chloride-2-hydroxy propyl) phosphate

Place 40 g H_3PO_4 , 100 mL toluene solvent and a small amount of aluminum chloride catalyst into a dry 250 mL three necked flask equipped with cooler, temperature controller, magnetic stirrer and water knockout trap. Then, add 35 mL epichlorohydrin into this reactor slowly. After 2 h, distill the product at 87 °C, 2 kPa to remove solvent, then mono(1-chloride-2-hydroxy propyl) phosphate is obtained, with the yield of 82.5 %.

2.2.2 Synthesis method of antimony mono(1-chloride-2-hydroxy propyl) phosphate

Place 30 g suspension of 10 % Sb_2O_3 , 42 mL mono(1-chloride-2-hydroxy propyl) phosphate, 150 mL dimethyl sulfoxide solvent and 1 g catalyst oxalic acid into a 1 000 mL three necked flask equipped with heater, temperature controller, magnetic stirrer and water knockout trap. The reactants are heated and refluxed for about 4 h. Then, add 100 mL 50 % (volume fraction) ethanol-water solution into the reaction system, and cool to room temperature, then the white crystal is obtained. Filtrate the resultant, wash with pure water, and dry the crystal product. The yield of antimony mono(1-chloride-2-hydroxy propyl) phosphate is about 85.6 %.

2.3 Methods of analysis

The antimony content is determined by the method of oxidimetry with potassium bromate^[13]. The content of chlorine and phosphorus is determined by the routine methods. Infrared spectra is recorded in KBr on a Model Nicolet FT-IR740 spectrophotometer in the range of $4\,000\text{ cm}^{-1} \sim 400\text{ cm}^{-1}$. The

melting point of antimony mono(1-chloride-2-hydroxy propyl) phosphate is tested by using WC-1 micromelting point meter. The oxygen index is tested in HC-2 Oxygen Index Tester.

3 RESULTS AND DISCUSSION

3.1 Synthesis conditions of mono(1-chloride-2-hydroxy propyl) phosphate

The conditions of synthesis have been studied by the method of orthogonal test. The influence factors on yield of mono(1-chloride-2-hydroxy propyl) phosphate, which comprise of temperature, the amount of solvent, the molar ratio of acid and epichlorohydrin, the amount of catalyst and reaction time, were studied. The experimental results showed that the reaction temperature is the most remarkable factor affecting the yield of the product, the rate of adding epichlorohydrin is the next. The other factors are not obvious.

The reaction can not proceed until the temperature reaches above 50 °C. Because this is an exothermal reaction, the temperature raises rapidly as reaction goes on, and if the temperature is higher than 90 °C the color of the product changes to yellow. The optimum synthesis conditions are as follows: while the temperature of reactants rises to 50 °C, epichlorohydrin is added into the reactor; meanwhile, controlling the adding rate of epichlorohydrin, so as to keep the temperature of the reaction system to about 90 °C. Because the chemical property of epichlorohydrin is very active, and it is tended to react with oxygen to form alcohol ether and ketone in the present of acid, epichlorohydrin is added into phosphoric acid to keep the low level of acid in reaction system. Thus, the degree of side reaction can decrease to minimum. The molar ratio of epichlorohydrin and phosphoric acid is 1:1.2.

The high yield of product was obtained when the reaction performs for about 2 h. It was observed in the experiment that if the reaction time is more than 2 h, the yield decreased instead. This is probably because the side reactions will increase with time. If AlCl_3 catalyst was not added into reaction system, H_3PO_4 acted as self-catalyzed reaction, the reaction products were mixture of mono(1-chloride-2-hydroxy propyl) phosphate, di(1-chloride-2-hydroxy propyl) phosphate, tri(1-chloride-2-hydroxy propyl) phosphate. Although the major product was mono(1-chloride-2-hydroxy propyl) phosphate, the content of other two esters was rather high also. Adding AlCl_3 catalyst could make the reaction to form mono(1-chloride-2-hydroxy propyl) phosphate.

3.2 Synthesis conditions of antimony mono(1-chloride-2-hydroxy propyl) phosphate

Similarly, the conditions of synthesis were stud-

ied by the method of orthogonal test. The influence factors on the yield of antimony mono(1-chloride-2-hydroxy propyl) phosphate, which comprise of temperature, the amount of solvent and reaction time, were studied. The experimental results show that the amount of solvent is the most remarkable factor affecting the yield of the product, the reaction time is the next, the other factors were not obvious. The optimum conditions are: mono(1-chloride-2-hydroxy propyl) phosphate and antimony oxide reacting at stoichiometric ratio in the solvent of dimethyl sulfoxide with catalyst dicarboxyl, and reaction time of 4 h.

3.3 Physical-chemical properties of products

Mono(1-chloride-2-hydroxy propyl) phosphate is a colorless liquid with special smell, its density is 1.340 kg/m^3 , boiling-point is 142°C (at 2 kPa), viscosity is 2.000 mPa . It changed to yellow liquid when heated to 210°C at atmosphere pressure, and can be solved in alcohol and amine, while can not be solved in benzene, chloroform and water. Its chemical composition ($w, \%$) is P 16.74, Cl 18.23, with reference to theoretical composition of P 16.27, Cl 18.63.

Antimony mono(1-chloride-2-hydroxy propyl) phosphate is white powder at room temperature. It is not solved in benzene, acetone, ethanol and chloroform; but, can be solved in dimethyl sulfoxide. The melting-point is 147°C . The chemical composition by analysis ($w, \%$) is P 11.0, Cl 12.9, Sb 32.4, with reference to theoretical composition of P 11.5, Cl 13.2, Sb 30.1.

3.4 Infrared spectra

The infrared spectra are measured on a FT-IR740 Fourier Transform Infrared Spectrograph. The infrared spectra of mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate are shown in Fig.1 and Fig.2, respectively.

In Fig.1, the stretching vibration of —OH lies in 3260 cm^{-1} , 3045 cm^{-1} is absorption peak of $(\text{P})\text{—OH}$, 1201 cm^{-1} is absorption peak of P=O ,

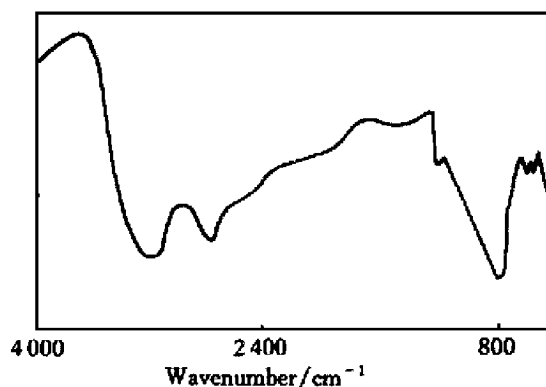


Fig.1 IR spectrum of mono(1-chloride-2-hydroxy propyl) phosphate

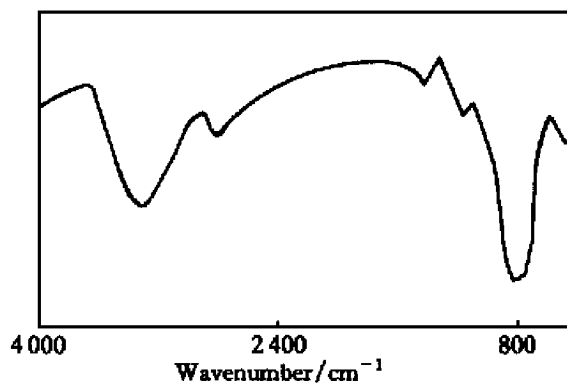


Fig.2 IR spectrum of antimony mono(1-chloride-2-hydroxy propyl) phosphate

and 1087 cm^{-1} is absorption peak of $(\text{P})\text{—O—C}$. Comparing Fig.2 with Fig.1, the absorption peak of $(\text{P})\text{—OH}$ in 3045 cm^{-1} disappears. It indicates that antimony atom has replaced hydrogen of $(\text{P})\text{—OH}$ and formed Sb—O bond in antimony mono(1-chloride-2-hydroxy propyl) phosphate. The stretching vibration of —OH lies in 3405 cm^{-1} , 1018 cm^{-1} is absorption peak of P=O .

On the basis of results of chemical analysis and IR analysis, it can be verified that the products are mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate.

3.5 Flame retardation of products

Add different usage level of mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate into polyethylene resin, mix, mill and press into slice, then carry out oxygen index test. The results are shown in Fig.3. When adding 15% mono(1-chloride-2-hydroxy propyl) phosphate (i.e. P 2.51%, Cl 2.73%) and antimony mono(1-chloride-2-hydroxy propyl) phosphate (i.e. P 1.65%, Sb 4.86%, Cl 1.93%) into polyethylene respectively, the oxygen index of polyethylene are 31.4 and 33.7. This indicates that antimony can act synergistically with phosphites flame retardants.

4 CONCLUSIONS

1) Mono(1-chloride-2-hydroxy propyl) phosphate can be synthesized from epichlorohydrin and H_3PO_4 with molar ratio of 1:1.2, and with AlCl_3 as catalyst. The reaction lasts for about 2 h at 90°C with the yield of 82.5%.

2) Antimony mono(1-chloride-2-hydroxy propyl) phosphate can be prepared by reacting mono(1-chloride-2-hydroxy propyl) phosphate and antimony oxide at stoichiometric with dicarboxyl catalyst in solvent dimethyl sulfoxide for about 4 h. The yield of

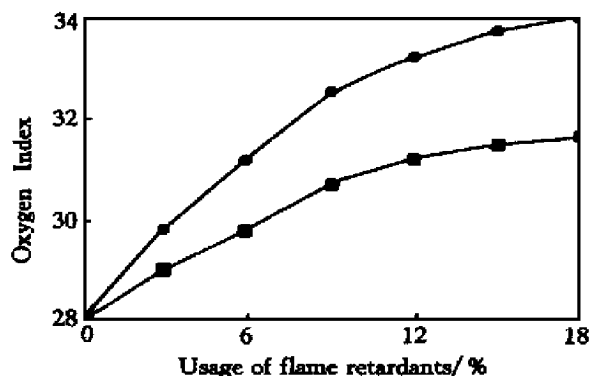


Fig.3 Flame retardancy of mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate
 ● — Antimony mono(1-chloride-2-hydroxy propyl) phosphate;
 ■ — Mono(1-chloride-2-hydroxy propyl) phosphate

antimony mono(1-chloride-2-hydroxy propyl) phosphate is 85.6%.

3) The flame retardation test indicates that the oxygen indexes of polyethylene are 31.4 and 33.7 when adding 15% of mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate respectively into polyethylene resin. It demonstrates that mono(1-chloride-2-hydroxy propyl) phosphate and antimony mono(1-chloride-2-hydroxy propyl) phosphate possess excellent flame retardation, and antimony and phosphate have synergistic flame retardation.

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