



Obtaining of Trialkylphosphates in Anodic Dissolution of Copper Phosphide

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ABSTRACT

Due to obtain trialkylphosphate is suggested to use anodic solution of copper phosphide in alcohol solutions. At this, it can use copper phosphide, obtained at the processing of wastes of phosphorus production. Moreover, it is presented ways of obtaining of tri-*n*-butylphosphate and tri-*izo*-butylphosphate.

Key words: trialkylphosphate, tri-*n*-butylphosphate, tri-*izo*- butylphosphate, Copper phosphide, electrosyntheses, sacrificial anodes.

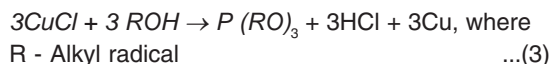
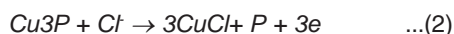
INTRODUCTION

In the research^{1,2} are shown the possibilities of obtaining of trialkylphosphate by the electrolysis of suspensions of red phosphorus. The authors of work³ used dialkylphosphoric acid as the initial phosphorus containing compounds for synthesis of trialkylphosphate. Next authors⁴ studied the process of synthesis of tryalkyl phosphates, i.e., derivatives of methanol, butanol, and diethylene glycol, by anodic oxidation of dimethyl phosphite in the corresponding alcohol. It

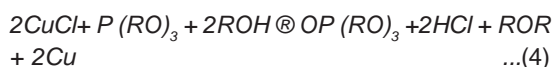
was found that three alkyl phosphates corresponding to the three possible combinations of substituents bound to phosphorus in phosphate are formed.

In this regard, it was interesting to investigate the possibilities of obtaining of trialkylphosphates by the using of sacrificial copper-phosphorus anode as a donor of phosphorus. The copper-phosphorus alloys are produced by industries, in addition, these alloys are formed at the processing of phosphorus sludge⁵.

Mechanism of anodic dissolution of copper-phosphorus alloys in the alcohol solutions of hydrogen chloride can be represented by the following equations:



The formed phosphides are subjected to further oxidation. This process may proceed on the anode or in solution with the participation of oxygen or copper compounds. In the latter case, the reaction may be in the form



Trialkylphosphates are the efficient complex forming reagents. Particularly, in this regard the valuable substances are tri-*n*-butylphosphate and tri-*izo*-butylphosphate, which are used for selective extractions of uranium, thorium⁶. Currently, these reagents are used in nuclear fuel engineering, therefore the development of new methods of the obtaining of trialkylphosphate presents practical interest.

MATERIAL AND METHODS

Electrosynthesis of tri-*n*-butylphosphate

In glass electrolyzer, equipped by water jacket and return refrigerator 200 cm³ of *n*-butane alcohol was loaded. Previous of electrolyzing the alcohol was saturated by dry gaseous hydrogen chloride. In this purpose it is very convenient to obtain the dry hydrogen chloride by the action of concentrated sulfuric acids on concentrated hydrochloric acid with the followed passing of hydrogen chloride through a flask with concentrated H₂SO₄.

A plate of copper – phosphorus alloys (phosphorus content is 10 mass %) weighing 112 g with the total area 3.5·10⁻³ m², and working surface 2.5·10⁻³ m², the copper plates cathodes with analogous size were used in electrolysis.

Electrolysis was performed at current density of 0.25-0.30 A/m²·10⁻⁴ during 5 hours. Temperature of an electrolyte was 65-70°C. The voltage on the bath was not exceeding 20-22 W. The passed current, which was measured by copper coulometer, was 35 ampere hour (A·h). At this, in the results the electrolysis was dissolved 29.6 g of copper phosphide anode. 25.2 g of copper powder was isolated on the cathode, the part of which fell to the bottom of the electrolysis.

After filtration, the solution was subjected to vacuum distillation. The unreacted butyl alcohol was distilled off at the temperature 32-35°C and the pressure 2.66·10³ Pa. The white deposit of copper monochlorides was precipitated in the remains, which it was filtered off. Weight of precipitate after drying was 3.1 g. The volume of filtrate was 30 cm³. Moreover, to this filtrate 60 cm³ of benzene were added and were mixed for 5-6 minutes, after that the solution was poured into the separating funnel and washed out with 40 cm³ of distilled water until the disappearances of blue color of copper ions in the aqueous layer. The benzene layer was filtered through anhydrous sodium sulfate. After distillation of benzene from liquid leavings by the vacuum distillation at a temperature of 159-165°C (1.60·10³ Pa) 20 cm³ of liquid containing phosphorus was obtained.

Electrosyntheses of tri-*izo*-butylphosphate.

Electrolysis with 300 cm³ of isobutyl alcohol (2-methyl-3-propanol), also previously saturated by hydrogen chloride was performed on the above presented procedure, the electrolysis performed at the current density of $i_a = (0.2-0.25) \cdot 10^{-4}$ A/m² and U = 20 -24 W. At these conditions 60 A/hours of electricity was passed through the electrolyte. The loss of anode mass was 46.1 g.

Further processing of electrolyte was conducted same ways, as tri-*n*-butylphosphate. After distillation of benzene, 35 cm³ of tri-*izo*-butylphosphate was remained, which has been subjected to vacuum distillation⁵

RESULTS AND DISCUSSION

Electrosyntheses of tri-*n*-butylphosphate

The density of tri-*n*-butylphosphate was

determined by State standard 18995.1-73 p.2⁷. The analysis of phosphorus in trialkylphosphate was conducted by Kjeldahl⁸. Determination of the refractive index was implemented according to State standard 18955.6-73⁹.

The boiling point of tri-*n*-butylphosphate was determined according to State standard 18995.6-73, p.1. IR-specters are taken by the «SPEKORD-IR», of Germany Company "Carl Seis, lena".

Quantitative analysis indicated, that the liquid contains about 11.09 % of phosphorus. Determination the boiling point, density, refractive index and take IR-spectra are gave the following results:

Boiling point – 289.6 °C (at 9,806.10⁴);

Density, g/cm³ - 0.9720

Refractive index – 1.4261

Character absorptions in the IR-specter

-1000 - 1100 cm⁻¹ P-O-C (valent)

- 1274 cm⁻¹ P=O (valent)

- 730 cm⁻¹ P-O (sym.valent).

These data allowed us to identify the product as tri-*n*-butylphosphate.

We conducted the calculation the yield of tri-*n*-butylphosphate containing phosphorus, as well as other trialkylphosphates by the following. In each experiment the amount of phosphorus, which passed into the solution, was analytically determined. In general, this value was about 9.8% of the total amount of copper - phosphorus alloys. Then, on the basis of reaction of formation, we determined the theoretical amounts of

trialkylphosphate.

Thus, 29.6 g of copper-phosphorus alloy was dissolved at the electrolysis, and $26.9 \times 0.098 = 2.90$ g of phosphorus passed into the solution. Theoretical amount of tri-*n*-butylphosphate was $266 \times 2.90 / 31 = 24.88$ g

The measured weight of 20 cm³ of tri-*n*-butylphosphate was equal to 19.40 g, i.e., the output of tri-*n*-butylphosphate was 77.9%.

Electrosyntheses of tri-*izo*-butylphosphate

In the result of distillation under pressure of 1.064×10^2 Pa, at the corresponding temperatures (T) were obtained the following (G) substances.

1) T = 86-87 °C, G-10 g

2) T = 110-112 °C, G-7 g

3) T = 120-130 °C, G-12 g

In each of these fractions were determined the content of phosphorus (P) and refractive index (n^{20}).

1) P = 10.3 %, $n^{20} = 1.4198$

2) P = 10.6 %, $n^{20} = 1.41983$

3) P = 12.1 %, $n^{20} = 1.4222$

As it is evident from the cited data, that first and second fractions have similar values by the contents of phosphorus and same refractive indexes. The third fraction is different by phosphorus content. However, all three fractions gave exactly the same IR-spectra, identical IR-specters of tri-*izo*-butylphosphate¹⁰.

On the basis of these data, we got product, which was identified as tri-*izo*-butylphosphat. Output of the amount of phosphorus was 71.11%.

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