SYNTHESIS OF LEAD TETRAACETATE BY ELECTROCHEMICAL OXIDATION OF LEAD DIACETATE AT THE ANODE

M. Ia. Fioshin and L. I. Kazakova

Lead tetraacetate is a strong oxidizing agent with a wide range of oxidizing action [1]. The chemical method of synthesis of lead tetraacetate consists of treatment of red lead with glacial acetic acid [2]. The method has the drawback that only one third of the lead entering into the make-up of the red lead is utilized, and two thirds goes into the discard as lead diacetate. It is possible to increase the utilization of lead by simultaneous treatment of the red lead with acetic acid and chlorine [3]. However, in this case one third of the lead is lost as chloride, purification from which is a rather difficult operation involving unavoidable losses of lead tetraacetate. The presence of the slightest contamination of the lead tetraacetate with the chloride is undesirable, since chlorination of organic compounds may occur along with oxidation. As a result of all the purification and separation operations the yield of lead tetraacetate totals 40-50%.

Attempts at electrochemical synthesis of lead tetraacetate until recently had little success. Of all the not very numerous investigations we can take note only of the work [4] in which by electrochemical oxidation of lead diacetate at a platinum anode in acetic acid containing sodium acetate an 80% yield of lead tetraacetate based on the current was obtained. A necessary condition for the formation of the lead tetraacetate was the presence of 1-2% of water in the acetic acid. However, the yield of lead tetraacetate attained was maintained only for the first minutes of the electrolysis, falling after 30 minutes to 26%, and after somewhat more time, practically to zero. The reason for this phenomenon had been established previously; it consisted of the formation on the anode of a film of lead tetraacetate that shielded its surface and prevented the further oxidation of the lead diacetate. Schall and Melzer [4] worked with the electrolyte cooled to 35° and the surface of the anode cooled to 8°. At a higher temperature decomposition of the lead tetraacetate by the water present in the acetic acid occurred.

In the publication [5] the electrolysis was carried out in anhydrous acetic acid containing potassium acetate at 85°, which facilitated solution of the film of lead tetraacetate and maintenance of the high yields of it for a long time. However, in this work only the basic possiblity of accomplishing the electrooxidation of lead diacetate to the tetraacetate was established and the fundamental parameters of the process found.

In the present work a preparative method for the synthesis of lead tetraacetate has been developed on the basis of the data previously obtained.

EXPERIMENTAL

1. Preparation of solutions. An electrolyte of the composition previously found [5] was used: 2.1 N $Pb(CH_3COO)_2$, 0.6 N CH_3COOK, and anhydrous acetic acid. The direction of the process and the yield of lead tetraacetate depend on careful dehydration of the acetic acid and the lead and potassium acetates. The acetic acid was dehydrated with copper sulfate, boiled with an excess of acetic anhydride for 1.5-2 hours, and distilled, whereupon a fraction was collected that distilled at 117-118°. The lead diacetate and potassium acetate were dissolved in the acetic acid thus prepared. The solution obtained was boiled with excess acetic anhydride for 5 hours, then allowed to stand for 2 days.

2. Arrangement of electrolyzer. The electrolyzer was a glass jar equipped with a coil. In the jar a ceramic diaphragm was placed across that served as a cathode area. Inside the diaphragm was another coil. It was necessary to cool because of the weak electric conductivity of the electrolyte and the considerable amounts of heat

developed when the current was passed. A nickel wire served as the cathode and a platinum mesh cylinder as the anode. The volume of the anode space was 200 ml.

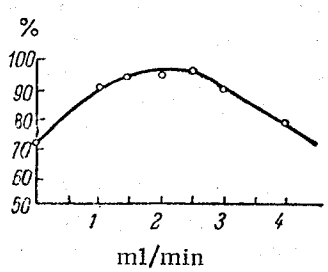
3. Separation of lead tetraacetate. The solubility of lead tetraacetate depends greatly on the temperature. On cooling to 17° more than 80% of the product precipitated from the solution. Part of the lead tetraacetate precipitated in the electrolyzer and another portion in the flask into which the electrolyte was admitted after the electrolysis. The product dried with filter paper contained 97.5% $Pb(CH_3COO)_4$. The finished product was best kept under glacial acetic acid.

The mother liquor after the electrolysis could be saturated with lead diacetate and again subjected to electrolysis. However, it must be kept in mind that the solution cannot be saturated with moist lead diacetate, since decomposition of the lead tetraacetate remaining in the mother liquor then occurs. Therefore the lead diacetate must first be dried at 50-55° for 4-6 hours and the solution should stand for 1-2 days with an excess of acetic anhydride before the electrolysis.

The amount of lead tetraacetate contained in the solution was determined iodometrically.

4. Experimental results. The electrolysis was carried out in the electrolyte for which the composition is given above. At the anode the current density was 3 amp/dm^2 and the temperature was kept at 80-85° by cooling. The current strength was 2 amp. The voltage in the electrolyzer was about 100 v.

The main effort was directed toward establishment of a process procedure that guaranteed the possibility of carrying it out continously, i.e., with a circulating electrolyte. For this purpose a series of experiments was set up with different rates of circulation of the electrolyte. The relation of the yield of tetraacetate based on the current to the rate of circulation of the electrolyte is presented in the figure, from which it is apparent that the change in the yield on the basis of the current with the rate of circulation passes through a maximum at 2.5 ml/min and reaches 95.5% under these conditions. With a load in the electrolyzer at 2 amps for 1 hour, 16 g of lead tetraacetate was produced, which amounts to 8 g per amp-hour. The expenditure of electrical energy was approximately 12 kw-hr per kg of lead tetraacetate.



Relation of yield of lead tetraacetate based on current to rate of circulation of electrolyte.

Very interesting results were obtained in attempts to replace the platinum serving as the anode material with lead peroxide prepared by a method [6] consisting of the following.

The lead peroxide reagent was built up on a foundation of perchlorovinyl fabric. Then the fabric thus treated was immersed in a saturated solution of lead nitrate. The supply of current from the positive pole of the current source was carried by means of a nickel wire woven into the fabric. A lead rod served as the cathode.

Electrolysis was carried out at room temperature and an anode current density of 0.25 (for the first four hours) – 1.0 amp/dm^2. To avoid depleting the electrolyte of lead ions too rapidly as a result of their discharge at the cathode, cupric nitrate (50-80 g/l) was added to the solution. Unfortunately, when lead peroxide was used as the anode we did not succeed in solving the problem of supplying current to it. In the place of contact of the nickel wire with the lead peroxide, evolution of heat occurred which resulted in burning of the fabric. But we succeeded in carrying out some experiments nevertheless. It was ascertained that the yield of lead tetraacetate based on the current at an anode of PbO_2 was the same as at a platinum anode. However, we did not succeed in solving the problem of the duration of service of a lead peroxide anode or the supplying of current to it, which appears to be a subject for further investigations.

SUMMARY

1. A preparative method has been developed for the first time for the synthesis of lead tetraacetate by electrochemical oxidation of lead diacetate at a platinum anode.

2. The possibility has been established of carrying out this process at an anode of lead peroxide.

LITERATURE CITED

[1] R. Krigge, Coll. "New Methods of Preparative Organic Chemistry." IL, 139 (1950).*

[2] A. Colson, C. r. 136, 575 (1903); O. Dimroth and R. Schweizer, Ber. 56, 1375 (1923).

[3] A. Colson, C. r. 136, 1664 (1903); R. Oesper and C. Deasy, J. Am. Chem. Soc. 61, 927 (1939).

[4] C. Schall and W. Melzer, Z. Electroch. 28, 474 (1922).

[5] M. Ia. Fioshin and V. A. Gus'kov, Proc. Acad. Sci. USSR, 112, 303 (1957).

[6] N. F. Razina, Diss. "Electrode Processes at a Lead Anode and Its Corrosion in the Electrolysis of Sulfuric Acid Solutions." (1955).

Received July 6, 1957

D. I. Mendeleev Moscow Chemico-Technological Institute.

*Russian translation.