The Formation and Solubility of Various Lead(II) Compounds Prepared by the Hydrolysis of Lead(II) Nitrate

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(Received January 10, 1983)

Synopsis. Lead(II) nitrate was hydrolyzed by mixing with sodium hydroxide solutions at 25 and 50 °C. Four kinds of lead(II) hydroxide nitrates and two kinds of lead(II) oxides (massicot and litharge) were formed, depending on the pH, temperature, lead(II) nitrate concentration, and aging time of the suspension. The solubility of the products was also measured.

It is generally known that the kind of product obtained by the hydrolysis of lead(II) salts strongly affected by coexisting anions in the resulting suspension,[1,2] and that various basic lead(II) compounds are formed according to the formation conditions.[3–11] Among these studies, the hydrolysis of lead(II) chloride[3] and lead(II) acetate[4] have been investigated in detail. On the hydrolysis of lead(II) nitrate, the formation of various lead(II) hydroxide nitrates has been reported by earlier workers.[5–9] However, some of them have been thought to be ambiguous. Although recent results on the chemical composition of the products were reported by Kwestroo *et al.*[10] and Brusset *et al.*,[11] both results were partially different. Therefore, reliable information about the kind of the product from the hydrolysis of lead(II) ion in the presence of nitrate ion is needed, together with data about these particle characteristics and solubilities. This study will deal with the hydrolysis of lead(II) nitrate, especially with the effects of changes in pH, temperature, concentration of lead(II) nitrate and aging time on the kind, particle characteristic and solubility of the products.

Experimental

A 300 cm^3 acrylic resin cylindrical reactor was equipped with a reflux condenser, a dropping funnel, a nitrogen gas inlet tube, a glass electrode of a pH meter, a thermometer, and a magnetic stirrer. A 50 cm^3 portion of NaOH solutions was transferred to the reactor and maintained at 25±0.2 or 50±0.2 °C. Then, a 200 cm^3 portion of $Pb(NO_3)_2$ solution in the dropping funnel was added to the stirred NaOH solution. Total lead concentration in the suspension obtained after the mixing was set to be 0.05 and 0.5 M (1 M=1 mol dm^{-3}). Unless otherwise stated, the resulting suspension was stirred for a further 1 h. All procedures were carried out under nitrogen atmosphere. After measuring the pH of the suspension, the product was filtered off, washed with distilled water, and then dried at room temperature under reduced pressure. The identification of the product and the quantitative analysis of binary mixtures were made by X-ray diffractometry using a Rigaku Denki Geigerflex 2013 with Ni filtered Cu *Kα* radiation, with 30 kV and 10 mA. The observation of the product was performed using a Hitachi-Akashi Scanning Electron Microscope MSM 4C-102. The solubility of the product was determined by analyzing the filtrate for lead ion with atomic absorption spectroscopy.

Results and Discussion

The kind and solubility of the products at various pH values of the suspension are shown in Fig. 1. On the hydrolysis of 0.5 M $Pb(NO_3)_2$ at 25 °C (A in Fig. 1), the basicity in the chemical composition of the precipitated lead(II) hydroxide nitrates increased with increasing pH of the suspension, namely $Pb(NO_3)_2 \cdot Pb(OH)_2$ (phase **a**, white), $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$ (phase **b**, white), and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ (phase **d**, white), or a binary mixture of these three at pH range of 6—13. The pH range of the formation of binary mixtures was negligible. This tendency was the same as the results reported by earlier workers.[10,11] The X-ray diffraction patterns of these lead(II) hydroxide nitrates were identical with those reported by Kwestroo *et al.*[10] However, the formation of $Pb(NO_3)_2 \cdot 2Pb(OH)_2$ and $3Pb(NO_3)_2 \cdot 7Pb(OH)_2$ identified as an intermediate by Brusset *et al.*[11] from potentiometric and conductimetric measurements was not observed here after aging of 1 h, because of the unstability of these compounds. If the resulting suspension contains no anions, for example, in the case of the hydrolysis of lead(II) alkoxide,[12,13] massicot (orthorhombic), litharge (tetragonal), or hydrous lead(II) oxide ($3PbO \cdot H_2O$, tetragonal) should be formed over the same pH range. It was also found that the solubility of lead(II) hydroxide nitrates decreased with increasing basicity of products and was minimized at the pH range of 10—11. At the pH values higher than 11, the solubility gradually increased, and massicot (phase **M**, yellow) and litharge (phase **L**, red) were formed. Figure 2 shows the scanning electron micrographs of typical lead(II) hydroxide nitrates obtained here. The particle sizes were considerably smaller than those of massicot (10—20 μm) and litharge (5—10 μm).

On the hydrolysis of 0.05 M $Pb(NO_3)_2$ at 25 °C (B in Fig. 1), the pH range of the formation of these lead(II) hydroxide nitrates was shifted, on the whole, to the pH side lower than that of A in Fig. 1. It was also found that the pH range of the formation of massicot was broadened. This means that the stable phase is easily formed by decreasing the concentration of $Pb(NO_3)_2$. The particle sizes of these precipitates became progressively greater as the concentration of $Pb(NO_3)_2$ became lower, as shown in Fig. 2(e), whereas no changes in the particle shape were observed.

At a higher temperature (50 °C, C in Fig. 1), the pH range of the formation of these lead(II) hydroxide nitrates was further shifted to the lower pH side and the particle sizes of these precipitates further increased, as shown in Fig. 2(f).

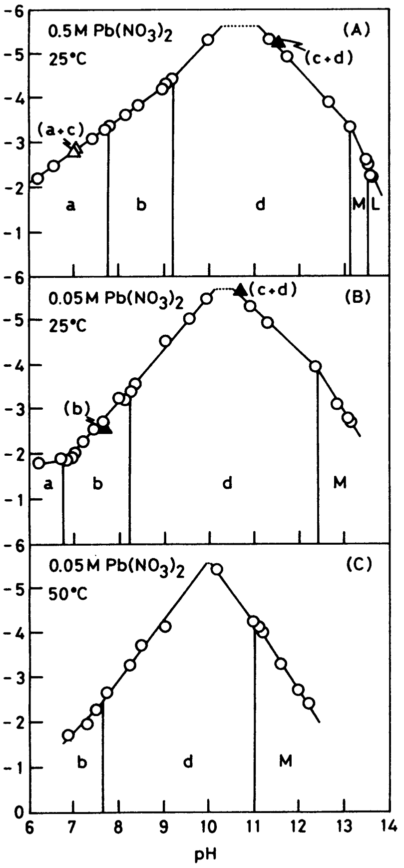

Fig. 1. Solubilities of lead(II) compounds at various pH values of the suspensions.
(a): $Pb(NO_3)_2 \cdot Pb(OH)_2$, (b): $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$, (c): $Pb(NO_3)_2 \cdot 3Pb(OH)_2$, (d): $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, (M): massicot, (L): litharge.
Aging time(h): ○ 1, △ 8, ▲ 24.

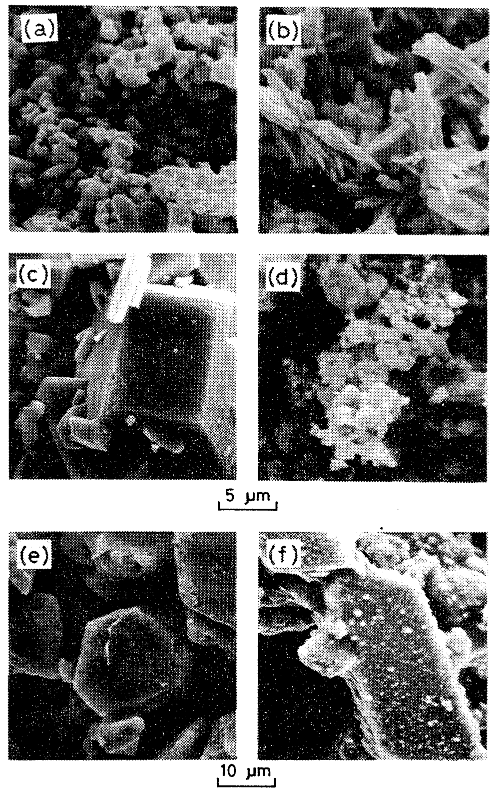

Fig. 2. Scanning electron micrographs of lead(II) hydroxide nitrates prepared by hydrolysis of lead(II) nitrate.
(a)—(d): samples in Fig. 1(A), (e): sample in Fig. 1(B), (f): sample in Fig. 1(C).
(a),(e): $Pb(NO_3)_2 \cdot Pb(OH)_2$, (b),(f): $2Pb(NO_3)_2 \cdot 5Pb(OH)_2$, (c): $Pb(NO_3)_2 \cdot 3Pb(OH)_2$, (d): $Pb(NO_3)_2 \cdot 5Pb(OH)_2$.

When the aging time was prolonged, the initial pH of the suspension of only 8—9 was occasionally changed; one of the reasons for this phenomenon is thought to be the occurrence of another phase during the aging. The kind and solubility of the products were changed with variation of pH. However, the solubility was found to change along with the solubility curves shown in Fig. 1 and there was no difference with the solubility values measured after 1 h. One other phase, $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ (Phase **c**, white) was formed together with $Pb(NO_3)_2 \cdot 5Pb(OH)_2$, the formation ratio of **c**/**d** being as about 4 after 24 h. This phase was also formed together with $Pb(NO_3)_2 \cdot Pb(OH)_2$, the formation ratio of **c**/**a** being as about 6 after 8 h. Kwestroo *et al.*(10) identified it only in diluted reaction mixtures. In this experiment it was obtained by aging the resulting mixtures for a while. As can be seen in Fig. 2(c), the particle size of $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ was larger than those of the coprecipitated $Pb(NO_3)_2 \cdot Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$.

The authors wish to thank Prof. Taijiro Okabe of the Department of Applied Chemistry, Tohoku University, for his helpful discussion.

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